

Determination of Platinum, Palladium, Ruthenium and Iridium in Geological Samples by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry Using a Sodium Peroxide Fusion and Tellurium Coprecipitation*

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A method was developed for the determination of Ru, Pd, Ir and Pt in geological samples by isotope dilution inductively coupled plasma mass spectrometry. After fusion of the sample with sodium peroxide, the platinum group elements were preconcentrated by Te coprecipitation. Results obtained for the reference materials WGB-1, TDB-1, UMT-1, WPR-1, WMG-1 and SARM-7 are in excellent agreement with the recommended values for elements above the detection limit level of 0.3–2.0 ng g⁻¹ (whole rock). Although the method used only 0.5 g of sample, no errors were found that could be associated with sample inhomogeneity effects in the analysis of the above reference materials. Further measurements indicated that the technique could be extended to the determination of Rh and Au by external calibration.

Keywords: *Platinum group element determination; geological sample; sodium peroxide fusion; isotope dilution; inductively coupled plasma mass spectrometry*

Introduction

The development of methods for the determination of the platinum group elements (PGEs; Ru, Rh, Pd, Os, Ir and Pt) in geological samples has attracted considerable interest in recent years for several reasons. The economic importance of these elements has stimulated the development of analytical techniques appropriate for geochemical exploration and ore processing.¹ However, there is also increasing academic interest in the geochemistry of these elements in studies of, for example, mantle and metallogenetic processes^{2,3} and the Cretaceous–Tertiary boundary layer with its associated Ir anomaly.⁴ This resurgence of interest has been further stimulated by the recent development of isotopic techniques for Os/Re geochronometry studies.^{5,6}

The low concentration of PGEs in geological samples (with typical background levels of a few ng g⁻¹) makes the

determination of PGEs a challenge. Appropriate analytical procedures generally have three steps: chemical decomposition of the sample, separation of the PGEs from the matrix (*i.e.*, preconcentration) and finally elemental determination. One of the most successful methods for both decomposing the sample and concentrating the PGEs is the nickel sulfide fire assay procedure coupled to the high sensitivity of inductively coupled plasma mass spectrometry (ICP-MS) instrumentation for the determination stage,^{7,8} later improved by an intermediate Te coprecipitation step.^{9–12} The nickel sulfide fire assay method offers the advantage of accepting large sample aliquots (routinely 20–50 g), which is essential in the analysis of any sample that might contain discrete PGE minerals. In such circumstances, serious sampling errors are likely to occur (caused by the ‘nugget effect’) if techniques that employ smaller sample masses (*e.g.*, <1 g) are used. However, the nickel sulfide procedure has some disadvantages. One is the relatively large amounts of reagents used and the contribution they may make to the analytical blank unless very high purity reagents are used. Another potential difficulty is that judgement is required to optimize flux composition in the analysis of some sample types (*e.g.*, chromite and sulfide-bearing samples or kimberlites).^{13–15} A third potential difficulty is that some investigations have indicated that PGE recoveries by nickel sulfide fire assay may not always be quantitative, with losses occurring during the fusion procedure itself¹⁶ and during subsequent crushing¹⁷ and dissolution of the nickel sulfide button.⁹ Alternative procedures are often used for the analysis of mantle rocks, in Os/Re isotope studies for example, where geochemical and thermodynamic constraints would indicate that discrete PGE grains are unlikely to be present. In these circumstances, a low blank decomposition procedure is more important than the capability to analyse 50 g sample aliquots and indeed, many studies have been undertaken successfully using techniques requiring less than 1 g of sample.^{18–20}

In the analysis of mantle rocks, several approaches have been used to dissolve the sample. Some of the most common are those based on acid attack (total or partial)^{21,22} and fusion procedures.^{23,24} The digestion with *aqua regia* in sealed tubes^{25,26} is also being used because of its effectiveness in dissolving PGE-bearing phases and the low blank levels, the latter being crucial in Re/Os geochemistry. The fusion of powdered samples with oxidizing fluxes such as sodium

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peroxide has been widely used both to decompose resistant minerals after a preliminary acid attack²⁷ and to decompose the entire sample in radiochemical neutron activation analysis methods.²⁰ Indeed, fusions with oxidizing fluxes have the advantage that they are very effective in dissolving both resistant and sulfide mineral phases.²⁸ However, such procedures must normally be restricted to small samples, usually 1 g or less, in applications such as those referred to above where sampling errors are not likely to occur.

In this work, a method has been developed for the determination of Ru, Pd, Ir and Pt using a fusion with sodium peroxide to decompose the sample in glassy carbon crucibles. After dissolution of the fused cake, the sample solution was spiked and the PGEs were separated by Te coprecipitation prior to determination of the PGEs by isotope dilution ICP-MS. The method was applied to five Canada Centre for Mineral and Energy Technology (CANMET) PGE reference materials: WGB-1 (gabbro rock), TDB-1 (diabase rock), UMT-1 (ultramafic ore tailings), WPR-1 (altered peridotite) and WMG-1 (mineralized gabbro), and to the mineralized ore of the South African Bureau of Standards (SARM)-7. Additional studies were carried out to evaluate the determination of the mono-isotopic elements Rh and Au by conventional external calibration. The fusion and Te coprecipitation procedure described here is similar to that used in the radiochemical neutron activation method of Stone and Crockett.²⁰ The over-all method is similar to the isotope dilution ICP-MS procedure described by Sen Gupta and Gregoire.²⁹ However, instead of using a two-stage sample dissolution procedure based on an initial acid attack, followed by fusion of any residue with sodium peroxide, we have adopted a single-stage digestion based on a sodium peroxide fusion and have included Pt in the list of analysed elements.

Experimental

Reagents

Quartz-distilled HCl and sub-boiling distilled HNO₃ were used in the analytical procedure. De-ionized water was used and all other reagents were of analytical-reagent grade. Poly(tetrafluoroethylene) (PTFE), glassware and glassy carbon crucibles were cleaned by soaking in freshly prepared *aqua regia* and then repeatedly soaking and rinsing with de-ionized water.

A standard solution of the PGE (100 µg g⁻¹, Spex Industries Edison, NJ, USA) was used to check natural isotope ratios and to prepare a mixed solution (monitor) with the spike solutions to correct the measured ratios of the samples for instrumental mass bias.³⁰ Isotope dilution was undertaken using enriched stable spike solutions of ¹⁰¹Ru, ¹⁰⁵Pd, ¹⁹³Ir and ¹⁹⁴Pt (US Services, Summit, NJ, USA, courtesy of Dr. D. C. Gregoire, Geological Survey of Canada, Ottawa, Canada). Spike solution concentrations were determined against the standard by isotope dilution ICP-MS.

Spike solutions were always weighed instead of only measuring the required volume. The same procedure was carried out with the standard solution used to prepare the monitor solution.

Tellurium solution (1 mg ml⁻¹). Tellurium (0.1 g) was dissolved in 5 ml of *aqua regia* and the solution evaporated to dryness. The residue was converted into TeCl₄ by evaporating to dryness three times with 2 ml portions of HCl (6 mol l⁻¹). The residue was dissolved in 2 mol l⁻¹ HCl, diluted to 100 ml with the same acid and stored in a PTFE bottle.

Tin(II) chloride solution (1 mol l⁻¹). Small amounts of this solution were prepared before use to ensure that it was fresh. The required amount (4.5 g) of tin(II) chloride was dissolved

by heating gently in 6 ml of 6 mol l⁻¹ HCl. De-ionized water was added to dilute the solution to a final volume of 20 ml.

Sample Decomposition

Samples were dried at 105 °C overnight and cooled in a desiccator before weighing. Conical crucibles made of glassy carbon with a capacity of 60 ml (Sigri, Meitingen, Germany) were used in the sample fusion procedure. In order to protect the crucible from attack by the sodium peroxide flux, a layer of sodium carbonate (3.5 g) was used to line the bottom and walls of the crucible before each fusion. Sodium peroxide (0.5 g), sample (0.5000 g) and then more sodium peroxide (1.5 g) were weighed into the crucible onto the sodium carbonate lining. The sample and sodium peroxide were carefully mixed using a nickel spatula. The crucible was covered with a lid and transferred into a cold furnace. The temperature of the furnace was raised to 200 °C and left for 15 min and then raised to 490 °C and left for 1 h. The crucible was then removed from the furnace and allowed to cool. With the crucible transferred into a 400 ml beaker (covered with a watch-glass) the cake was dissolved in 50 ml of warm de-ionized water, swirling the contents periodically. After dissolution, the spike solution containing Pt, Pd, Ir and Ru was added to the alkaline sample solution. The crucible was removed from the beaker using a PTFE tweezer and rinsed repeatedly with small volumes of de-ionized water and 6 mol l⁻¹ HCl to ensure quantitative transfer of the contents into the beaker. More acid was added (total 45 ml) to dissolve completely the hydroxides and to acidify the solution. The solution was then gently boiled for a few minutes to destroy peroxides. Any precipitated silica was removed by filtration using a Millipore filtration apparatus (with Whatman No. 4 filter-paper) and the filtrate collected in a 250 ml Pyrex filter-flask. The original beaker and the precipitate were washed with hot 1 mol l⁻¹ HCl (20 ml), which was added to the filtrate.

The filter-flask containing the solution was then heated to boiling and 2 ml of Te solution were added. The solution was brought back to boiling and tin(II) chloride solution (10 ml) was slowly added. The solution was boiled for a few minutes until the black precipitate was thoroughly coagulated. At this point, more Te solution (1 ml) was added. The solution was boiled again for 5–10 min to coagulate the precipitate. The flask was removed from the hot-plate and allowed to cool for a while to settle the precipitate. The mixture was filtered using a Millipore membrane filter (Type HA, 0.45 µm) using suction provided by a water-pump. The precipitate was rinsed with hot 1 mol l⁻¹ HCl (approximately 100 ml). The filter membrane was transferred into a 30 ml PTFE flask (Savillex) using small plastic tweezers and while holding it bent inside the flask, the precipitate was dissolved by dropping concentrated HNO₃ onto the membrane. In this way, the precipitate could be dissolved, avoiding the necessity to dissolve the membrane. In order to ensure quantitative dissolution, the membrane, and any precipitate adhering to the filtering apparatus, was rinsed with a few more drops of HNO₃. The resulting solution was evaporated to dryness by placing the beaker in a PTFE vessel, through which filtered air was passed, and heating with an infrared lamp. The residue was dissolved in 1 ml of dilute *aqua regia* (6 mol l⁻¹ HCl–concentrated HNO₃, 6 + 1) by re-heating the PTFE flask with its screw cap lid in place. This reagent was used in a slightly diluted form because 6 mol l⁻¹ HCl was the highest concentration that could be purified by sub-boiling distillation. The resulting solution was stored awaiting analysis and diluted with de-ionized water just before the ICP-MS measurements. Blank samples were prepared using the same procedure but omitting the addition of the spike solution.

During the development of this procedure, some difficulties were encountered in achieving quantitative recoveries of the Te precipitate. Attempts to use centrifugation to separate the precipitate as suggested by Sun *et al.*¹¹ were not successful because when the supernatant was decanted, a small amount of the loosely settled precipitate was lost because it was found to float on the surface of the supernatant solution. The procedure described above was found to give reliable quantitative recoveries, which although not necessary for a method based on isotope dilution, was important in extending the technique to elements (such as Au and Rh) that must be determined by external calibration.

ICP-MS Measurements

The sample solutions were analysed by ICP-MS using the upgraded prototype instrument at the NERC ICP-MS Facility, Centre for Analytical Research in the Environment (CARE), Imperial College at Silwood Park. A summary of the operating parameters used is given in Table 1. Ten runs were obtained for each isotope.

Several potential isobaric interferences with the isotopes measured here have been mentioned in the literature, mainly from Y, rare earth elements and hafnium oxides formed during ionization. It has been suggested that the addition of HF to the solution before the Te precipitation inhibits the coprecipitation of Hf.²⁰ However, this precaution was not found to be necessary in this work because no significant interferences were found.

Isotope Dilution Calculations

As the reference materials analysed in this work have a wide range of PGE concentrations, care had to be taken to optimize isotope dilution measurements. According to Heumann,³¹ the highest precision in an isotope ratio measurement can usually be achieved when the ratio A/B is approximately unity (where A and B are the abundances of the heavier and lighter isotope selected for analysis). However, in isotope dilution applications, to minimize the uncertainty introduced by the propagation of errors through the isotope dilution equation (see below), this isotope ratio (A/B) should be close to the geometric mean of its value in the spike and sample. The

amount of spike added to each sample in this work was chosen so that the spiked sample had an isotopic ratio of between 1 and the geometric mean value (Heumann³¹). The target ratios were approximately as follows: $^{108}\text{Pd}/^{105}\text{Pd} = 0.5$, $^{195}\text{Pt}/^{194}\text{Pt} = 0.6$, $^{101}\text{Ru}/^{99}\text{Ru} = 12$ and $^{193}\text{Ir}/^{191}\text{Ir} = 8$. The high values for the Ru and Ir ratios arose from the unusual isotope concentration of the spike available in this work, that is, for these two elements, the more abundant naturally occurring isotope was the isotope that was enriched in the spike.

The concentration (ng g^{-1}) of the element in the sample $[\text{E}]_{(\text{sample})}$ was calculated from the standard isotope dilution equation listed by Heumann³¹ [eqn. (3), p. 304], rearranged to make calculations simpler, as follows:

$$[\text{E}]_{(\text{sample})} = \frac{\text{spike mass (ng)}}{\text{sample mass (g)}} \times \frac{A_{\text{W}(\text{natural})}}{A_{\text{W}(\text{spike})}} \times \frac{A_{(\text{spike})} - [R \times B_{(\text{spike})}]}{[R \times B_{(\text{natural})}] - A_{(\text{natural})}}$$

where $A_{\text{W}(\text{natural})}$ and $A_{\text{W}(\text{spike})}$ are the relative atomic masses of the natural element and spike, A and B are the abundances (%) of the heavier and lighter isotopes, respectively, and R is the measured ratio A/B . Data in Table 2 show the isotopes selected for analysis and their natural and spike compositions. These isotopes were selected to avoid mass interferences in ICP-MS. Thus, although $^{102}\text{Ru}/^{101}\text{Ru}$ might be a better choice for Ru than $^{101}\text{Ru}/^{99}\text{Ru}$, the former was avoided because of ^{102}Pd interference. The measured ratios of the samples were corrected for instrumental mass bias using a spiked standard solution with isotopic ratios similar to those of the spiked samples.³⁰ Non-spiked procedural blanks were analysed and the blank count rate was subtracted from those of the samples before isotope ratios were calculated.

Results and Discussion

Detection Limits

In order to evaluate the detection limits, count rates of ^{99}Ru , ^{108}Pd , ^{191}Ir and ^{195}Pt were measured on the procedural blank sample. These isotopes were chosen because they are the less abundant in the spiked samples and therefore define a more realistic detection limit signal. The signal corresponding to three standard deviations ($+3s$) on the average of ten count rate measurements of these isotopes was taken and compared with the average count rate from a standard solution of known composition. The resulting detection limit values are listed in Table 3. These data are representative of the entire sample preconcentration procedure and include an allowance for small day-to-day variations in instrument response. Detection limit values for the elements Ru, Pd, Ir and Pt all lie in the range 0.3–2 ng g^{-1} (whole rock), based on the analysis of a 0.5 g sample.

Results for Certified Reference Materials

Concentrations for Ru, Pd, Ir and Pt obtained from an analysis of selected reference materials are listed in Table 4. In general, two sample aliquots were analysed, but for some samples none, one or three results are shown for some of the

Table 1 ICP-MS operating conditions

| | |
|-----------------------------------|---------------------------------------|
| Instrument | Surrey research instrument |
| Plasma gas | Ar |
| Plasma power | 1300 W |
| Reflected power | <5 W |
| Nebulizer | Cross flow |
| Outer gas flow rate | 14 l min ⁻¹ |
| Intermediate gas flow rate | 0.5 l min ⁻¹ |
| Nebulizer gas flow rate | 0.75 l min ⁻¹ |
| Sample uptake rate | 0.5 ml min ⁻¹ |
| Spray chamber coolant temperature | 5°C |
| Scan regions | 93.6–200.4 u, skip region 114.4–186.6 |
| Run time per sample | 30 s |
| Run mode | Scanning |

Table 2 Abundances of isotopes (%) and relative atomic masses (A_r) of the natural and spike elements used in isotope ratio measurements

| | Ru | | | Pd | | | Ir | | | Pt | | |
|---------|------|------|--------|-------|-------|--------|------|-------|--------|-------|------|--------|
| | 99 | 101 | A_r | 105 | 108 | A_r | 191 | 193 | A_r | 194 | 195 | A_r |
| Natural | 12.7 | 17.1 | 101.07 | 22.34 | 26.46 | 106.42 | 37.3 | 62.7 | 192.22 | 32.9 | 33.8 | 195.08 |
| Spike | 0.24 | 96.3 | 101.15 | 96.58 | 0.46 | 105.06 | 0.67 | 99.33 | 192.99 | 95.06 | 3.78 | 194.10 |

elements and the reasons for this are as follows: (i) in samples WGB-1 and TBB-1, Ir could not be determined because the count rates were below the detection limit; (ii) for the same samples, there is only one result for Ru because in only one set of measurements on duplicate test portions were the count rates sufficiently above the procedural blank to obtain meaningful data; (iii) in sample UMT-1 three values are shown for Ru, Pd and Ir and only two for Pt because the procedure was repeated an additional time for this sample, to provide more data for the low Pt results (see below) and (iv) only one set of results for SARM-7 is presented in Table 4 because this sample was only used for the first trials in developing the procedure. In any event, this reference sample is not fully representative of the type of rock for which the procedure was developed, because of its high concentration of PGEs.

The results for Ru, Pd and Ir shown in Table 4 are in excellent agreement with the recommended values and the excellent precision between the duplicate determinations shows that the method is very effective for determining these elements, provided that concentrations are above the detection limit level. The results for Pt for samples WGB-1, TDB-1 and SARM-7 are in excellent agreement with the certified values but for samples UMT-1, WPR-1 and WMG-1, lower results than the expected values were found. It is suggested that the reason for this discrepancy in Pt is related to difficulties in ensuring equilibration between spike and sample solution. In fact, the way in which the spike solution was added to the sample mixture was found to be the critical step. When the spike solution was weighed directly into a clean glassy carbon crucible and evaporated to dryness before the addition of sample and flux, good results were found for Ru

and Pt, but not for Ir and Pd, indicating that some physical or chemical reaction may occur between these elements and the crucible material. When the spike solutions were added to an acidified solution of the sample obtained after dissolution of the fused cake, good agreement was found for Ru, Pd and Ir, while Pt gave very low values. Only when the spike was added to the strongly alkaline sample solution obtained after dissolution of the cake were good results obtained for all elements. For Pt, these findings appear to be related to the aqueous chemistry of this element. Previous work in our laboratory (Enzweiler and Potts³²) showed that when alkaline solutions containing Pt salts are acidified with HCl, the Pt appears to be only partially converted into soluble chloro-complexes. We surmise, therefore, that the addition of a chloroplatinate spike solution to the sample solution after acidification with HCl prevents complete equilibration between the spike solution and the (apparently) unreactive Pt species present, so causing low recoveries. By comparison, better equilibration occurs when the spike is added to the strongly alkaline solution. Thus, it was observed that in three trial analyses of sample UMT-1, the results for Pt obtained when the acidified sample solution was spiked were in good agreement among themselves, but still had an average value of only 64% of the recommended value. These discrepancies did not affect simultaneous determinations of Ru, Pd and Ir, nor determinations of Pt at lower abundance in other reference samples (Table 4). It is possible that these low Pt values in UTM-1 may have arisen because insufficient time was allowed for equilibration in view of the higher concentrations of Pt in UTM-1, although a full explanation is still not possible.

Precision of the technique cannot be adequately judged from the small number of replicate results listed in Table 4. However, estimates of precision were made from the standard deviation data derived from the ten runs made for each isotope ratio measurement by ICP-MS (see under Experimental). Assuming no other contribution to the precision of the final analysis, typical values for the relative standard deviation (%) were calculated as follows: Pt in WMG-1: 2.7% (for Pt at the 631 ng g⁻¹ level); Pd in WGB-1: 5.1% (for Pd at the 14 ng g⁻¹ level); Ir in UMT-1: 3.4% (for Ir at the 8 ng g⁻¹ level); Ru in WPR-1: 7.7% (for Ru at the 21 ng g⁻¹ level).

Table 3 Detection limits (3s) for ⁹⁹Ru, ¹⁰⁵Pd, ¹⁹¹Ir and ¹⁹⁴Pt based on measurements from procedural blanks. Values (ng g⁻¹) were recalculated to whole rock assuming that 0.5 g of sample was taken for analysis

| | Ru | Pd | Ir | Pt |
|--|-----|-----|-----|-----|
| | 0.4 | 1.0 | 0.3 | 2.0 |

Table 4 Determination of Ru, Pd, Ir and Pt in reference materials by sodium peroxide fusion, isotope dilution, Te coprecipitation and measurement by ICP-MS. All values are in ng g⁻¹. Values marked with an asterisk are provisional or information values. All others are certified values. ± means 95% confidence limits

| | | Ru | Pd | Ir | Pt |
|--------------------|-------------|----------------|---------------|---------------|-----------|
| Reference material | WGB-1 | | | | |
| | This work | 0.28 | 14.1; 14.0 | — | 5.9; 5.4 |
| | Average | | 14.1 | | 5.7 |
| | Recommended | 0.3* | 13.9 ± 2.1 | 0.33* | 6.1 ± 1.6 |
| TDB-1 | This work | 0.37 | 23.0; 21.9 | — | 5.9; 5.5 |
| | Average | | 22.4 | | 5.7 |
| | Recommended | 0.3* | 22.4 ± 1.4 | 0.15* | 5.8 ± 1.1 |
| UMT-1 | This work | 9.5; 9.7; 10.4 | 108; 107; 105 | 8.2; 8.5; 8.6 | 109; 91 |
| | Average | 9.9 | 107 | 8.4 | 100 |
| | Recommended | 10.9 ± 1.5 | 106 ± 3 | 8.8 ± 0.6 | 129 ± 5 |
| WPR-1 | This work | 20.4; 21.8 | 233; 240 | 14.4; 14.7 | 263; 261 |
| | Average | 21.1 | 236 | 14.6 | 262 |
| | Recommended | 22 ± 4 | 235 ± 9 | 13.5 ± 1.8 | 285 ± 12 |
| WMG-1 | This work | 31; 32 | 370; 390 | 45; 39 | 662; 600 |
| | Average | 32 | 380 | 42 | 631 |
| | Recommended | 35 ± 5 | 382 ± 13 | 46 ± 4 | 731 ± 35 |
| SARM-7 | This work | 412 | 1506 | 70 | 3792 |
| | Recommended | 430 ± 57 | 1530 ± 32 | 74 ± 12 | 3740 ± 45 |

One limitation of the procedure described here is the relatively small amount of sample (0.5 g) taken for analysis, in comparison with fire assay procedures, for example. The only precaution taken in selecting this test portion was to mix the sample in the bottle before weighing, as recommended by the certified reference material suppliers. However, examination of duplicate or triplicate determinations on independent test portions listed in Table 4 shows excellent agreement between the measurements, indicating the absence of sample inhomogeneity effects in the samples studied here. The main disadvantage of the small amount of sample taken for analysis was the impossibility of determining routinely Ru and Ir in low-level samples. This problem might be overcome if the final volume (8–10 ml) prepared for ICP-MS analysis in the scheme described above were further reduced to obtain a higher preconcentration factor.

From the results obtained, it is possible to conclude that the fusion procedure was very efficient in attacking the PGEs and relatively rapid if compared with other procedures in which an initial acid attack is followed by fusion of any remaining insoluble residue.²⁷ The temperature selected for fusion (490 °C) was a compromise between the minimum temperature required to fuse the sodium peroxide flux and the maximum temperature to ensure the thermal stability of the glassy carbon crucibles.

The modified procedure used in this work to dissolve the Te precipitate from the filtration membrane (without having to dissolve the entire membrane) was much easier and more rapid than the alternative in which the membrane and contents are decomposed by acid attack,²⁷ and was shown to be quantitative.

In order to investigate the extension of the procedure to the determination of Au and Rh (elements that are monoisotopic and cannot, therefore, be determined by isotope dilution), previously prepared sample solutions of WPR-1 and WMG-1 were re-analysed using the appropriate external calibration. The results for these measurements are shown in Table 5. Good agreement was obtained for Rh in the two analysed samples and this indicates that the procedure can probably be extended to the determination of all PGE (except for Os, which is lost as the tetroxide when the acidified sample solution is boiled). For Au, good agreement was obtained for sample WPR-1, but low results in comparison with the expected value were obtained for sample WMG-1. It was not possible to identify the reasons for these poor results and further studies may be necessary to evaluate whether Au can be included in the list of analysed elements.

Conclusions

A method has been developed for the determination of Ru, Pd, Ir and Pt at ng g⁻¹ levels in geochemical samples by

Table 5 Determination of Rh and Au by ICP-MS after sodium peroxide fusion and Te coprecipitation, using an external calibration. All values are in ng g⁻¹

| Reference material | | Rh | Au |
|--------------------|-----------|-------------|-----------|
| WPR-1 | This work | 14.3; 16.2 | 45; 39 |
| | Average | 15.3 | 42 |
| | Certified | 13.4 ± 0.9* | 42 ± 3* |
| WMG-1 | This work | 28; 27 | 53; 72 |
| | Average | 28 | 63 |
| | Certified | 26 ± 2* | 110 ± 11* |

* ± Means 95% confidence limits.

isotope dilution ICP-MS after fusion of the sample with sodium peroxide and a Te coprecipitation procedure. Results from the analysis of selected reference materials show that good to excellent agreement can be obtained when the spike solution is added to the strongly alkaline solution obtained by dissolution of the fusion cake. Low values for Ir and Pd were observed if the spike solution was evaporated directly into the glassy carbon crucible and of Pt if the spike was added after acidifying the solution obtained from the fusion cake. Detection limits were of the order of 0.3–2 ng g⁻¹ (recalculated to whole rock). Further studies showed that the technique could be extended to the determination of Rh and possibly Au by external calibration. Sample inhomogeneity effects were not observed with the samples studied here, although as only 0.5 g was taken for analysis, this factor is likely to restrict application of the technique to mineralized samples that contain discrete PGE mineral grains.

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