Determination of Platinum, Palladium, Iridium and Gold in Selected Geological Reference Materials by Radiochemical Neutron Activation Analysis: Comparison of Procedures Based on *Aqua Regia* Leaching and Sodium Peroxide Sintering*

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A rapid and sensitive neutron activation method for the determination of platinum, palladium, iridium and gold in rocks is described. The procedure consists of thermal neutron irradiation of about 250 mg of sample, followed by chemical treatment of the rock, precipitation of gold and the platinum group elements with tellurium and high-resolution gamma-ray spectrometry with a hyper-pure Ge detector. Two different methods were used for the chemical treatment of the rock: *aqua regia* leaching and sintering with sodium peroxide. The procedures were evaluated by analysis of the certified reference material SARM-7 and the reference material CHR-Pt+. Sintering with sodium peroxide and precipitation with tellurium were more appropriate for the determination of Pd, Pt and Ir, giving results in good agreement (within ±10%) with literature values. For gold, *aqua regia* leaching gave more accurate results (relative errors from 0 to 6%). The detection limits for the analytical conditions employed were 0.1 µg kg^{-1} Au, 10 µg kg^{-1} Pd, 20 µg kg^{-1} Pt and 0.2 µg kg^{-1} Ir. The procedure employing fusion with sodium peroxide was applied to the analysis of the reference material CHR-Bkg and the concentrations of Au, Pt, Pd and Ir obtained are presented.

Keywords: Platinum, palladium, iridium and gold determination; geological sample; neutron activation analysis; aqua regia *leaching; sintering with sodium peroxide*

Introduction

In recent years, the development of sensitive and reliable techniques for the determination of the platinum group elements (PGEs) and gold in terrestrial materials has attracted great interest. This is due not only to the growing economic interest in PGEs and gold as mineral resources, but also to the information that these elements can provide on metal geochemistry. The determination of very low amounts of iridium is particularly important on account of some anomalies in iridium distribution in sedimentary rock samples, related to catastrophic events.[1]

The concentration of PGEs in many geological samples is in the ng g^{-1} or even sub-ng g^{-1} range, so sensitive and accurate techniques must be used to achieve reliable results. Neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS) are the most widely used

techniques for PGE determination in rocks.[2,3] NAA is one of the preferred methods of analysis because of its sensitivity, accuracy and freedom from contamination. Nevertheless, even when sensitive techniques are employed, it is necessary to separate the PGEs from matrix elements and concentrate them before analysis. Classical fire assay with lead collection and cupellation remains the most widely used technique for the preconcentration of PGEs, making possible the quantitative recovery of Au, Pt, Pd and Rh.[4] When analysing samples containing elements approaching detection limit concentrations, Ag must be added to the charge if Au, Pt and Pd are to be determined and Au if Rh is to be determined. For Ru, Os and Ir, the composition of the flux and the fusion conditions must be carefully controlled to avoid losses of these elements.[5] Nickel fire assay with radiochemical NAA has been used in recent years,[6,7] offering sensitivities at the ng g^{-1} level. However, this procedure requires reagents of high purity and the processing time may make difficult the determination of short-lived isotopes such as ^{109}Pd ($t_{1/2}$ = 13.5 h). Alternative procedures using alkali fusion and acid dissolution with PGE concentration by Te precipitation and NAA gave good results for Au, Pt, Pd, Ir, As, Se.[8] *Aqua regia* sample decomposition followed by tellurium precipitation with electrothermal atomic absorption spectrometry has also been used,[9] giving accurate results for Au, Pt, Pd and Rh, but not for Ir.

This paper describes a simple and rapid radiochemical NAA method for the determination of Pt, Pd, Ir and Au in small geological samples (<500 mg). The procedure represents a modification of the procedure described by Stockman,[10] and consists of sample irradiation in a nuclear reactor, chemical treatment of the sample, precipitation with tellurium and high-resolution gamma-ray spectrometry. Two different methods were used for chemical treatment of the rock: *aqua regia* leaching and sintering with sodium peroxide at 480 °C. The accuracy of the procedures and detection limits were verified by analysis of the reference material SARM-7 (platinum ore) distributed by the South Africa Bureau of Standards, representative of silicate materials, which has certified values for all the PGEs. The new reference materials of chromitite CHR-Pt+, which is enriched in the PGEs, and CHR-Bkg, which has much lower PGE concentrations, were also analysed. These were prepared and distributed by CRPG (Centre de Recherches Petrographiques et Geochimiques), and represent important reference materials to chromitite matrices, with which PGEs are frequently associated. The results obtained by the two procedures employed are compared and discussed. Since the first compilation data about the proposed chromitite reference materials CHR-Pt+ and CHR-

Bkg were reported recently,[11] this paper is also a contribution to Pt, Pd, Ir and Au values.

Experimental

Chemical Standards

Standard solutions were prepared by dissolving accurately weighed amounts of the salts $PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$ (Merck) and $IrCl_4$ (Aldrich Chemical) in dilute nitric acid (1 + 9) and Au metal in *aqua regia* [HCl–HNO_3 (3 + 1)]. A convenient aliquot of each standard solution was pipetted onto a 1 cm^2 piece of Whatman No. 40 filter-paper, evaporated to dryness under an infrared lamp and packed in a polyethylene vial. Each individual standard contained 14.6 µg of Pd, 1.0 µg of Pt, 419 ng of Ir and 106 ng of Au. The chemical standards were irradiated together with the samples.

Carriers

Carrier solutions containing 0.5 mg ml^{-1} of Pt, Ir and Au and 1.0 mg ml^{-1} of Pd were prepared as described for the standard solutions. Aliquots of 0.100 ml for Au, Pd and Ir and of 0.250 ml for Pt were used as carriers in the radiochemical procedure.

Tellurium and Tin(II) Chloride Solutions

A solution containing 1 mg ml^{-1} of Te was prepared by dissolving Te metal in *aqua regia*. The nitrates were removed by repeated evaporations to dryness with concentrated hydrochloric acid, to ensure a non-oxidant medium. The tellurium chloride formed was taken up in dilute hydrochloric acid (1 + 9). A tin(II) chloride solution was prepared fresh just before use by dissolving 5.5 g of $Sn_2Cl_2 \cdot H_2O$ in 5 ml of concentrated HCl and diluting the resulting solution to 25 ml with distilled water.

Irradiation

Irradiation was carried out at the IEA-R1 nuclear reactors of the Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, SP. Aliquots of about 250 mg of the powdered samples were weighed in pre-cleaned Al foils and placed, with the chemical standards, inside aluminium irradiation vessels, specially developed for use in the IEA-R1 reactor. Samples and standards were irradiated for 8 h at a thermal flux of about 10^{16} nm^{-2} s^{-1}. The cooling period before the radiochemical procedure was about 48 h.

Table 1 Radioisotopes used and their nuclear data

Radioisotope	Production	Half-life	Energy/keV
[198]Au	[197]Au(n,γ)	2.7 d	411.8
[109]Pd	[108]Pd(n,γ)	13.5 h	88.0
[199]Au	[198]Pt(n,γ,β−)	3.15 d	158.3
[192]Ir	[191]Ir(n,γ)	74.4 d	316.5

Radiochemistry

Aqua regia *leaching*

The irradiated sample was transferred into a beaker with 6 ml of freshly prepared *aqua regia* and carriers. The resulting solution was heated to boiling, evaporated to dryness and a further 6 ml of *aqua regia* were added. This procedure was repeated three times. The resulting solution was filtered through Whatman No. 42 filter-paper (4 cm diameter). The filtrate was evaporated to dryness and the residue was dissolved in concentrated HCl, to eliminate nitrates, and finally was dissolved in 10 ml of dilute HCl (1 + 2).

Sintering with sodium peroxide

The procedure employed was described by Enzweiler[12] for the determination of Ti, Cr, Al, Fe and Mg in chromitites. The irradiated sample was transferred into a nickel crucible and was throughly mixed with 1.5 g of sodium peroxide. After this, 0.75 g of sodium peroxide was added to the mixture. The crucible was covered with a nickel lid and introduced into a cold furnace. The temperature was raised to 200 °C for 30 min and then to 480 °C for 90 min. After sintering had finished, the crucible was transferred into a 400 ml beaker, with the addition of about 60 ml of warm water (60 °C), 10 ml of dilute HCl (1 + 2) and carriers. The crucible was removed from the beaker and was rinsed with distilled water.

Tellurium coprecipitation

The resulting solutions from the two procedures described for the chemical attack of the rock were boiled and 2 ml of Te solution were added to the beaker. Then, 10 ml of tin(II) chloride solution were added to precipitate a black cloud of metallic Te. The solution was boiled to coagulate the precipitate and then 1 ml of tin(II) chloride solution was added and the solution was boiled for 5 min. The precipitate was filtered onto a 4 cm Millipore filter (RA) and was rinsed with dilute HCl (1 + 9). The precipitate was dried under an infrared lamp and sealed in a plastic envelope.

Counting and gamma spectrometry

The measurements of the induced gamma-ray activity were carried out in a GMX, hyper-pure Ge detector, connected to an ADCAM 100 Multichannel Buffer (EG & G Ortec) and to a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma ray of ^{60}Co. The gamma-ray spectra were processed by using the program VISPECT, developed at IPEN by Piccot,[13] from Saclay, France. This program locates peak positions and calculates gamma-ray energies and net areas. The counting times were about 10 h for the samples and 1 h for the chemical standards. The radioisotopes measured and their nuclear data are presented in Table 1. The determination of Pt was performed with the radioisotope ^{199}Au, produced by the nuclear reaction ^{198}Pt (n,γ,β−) ^{199}Pt. The interference of Au, by the reaction

Table 2 Concentrations (mg kg^{-1}) of gold, palladium, platinum and iridium in the reference materials SARM-7 and CHR-Pt$^+$. Number of measurements (n) = 5; results presented correspond to the mean ± standard deviation

	CHR-Pt$^+$			SARM-7		
Element	*Aqua regia* leaching	Sintering (Na_2O_2)	Proposed values[11]	*Aqua regia* leaching	Sintering (Na_2O_2)	Certified values[14]
Au	4.3 ± 0.3	3.8 ± 0.3	4.3	0.29 ± 0.02	0.26 ± 0.02	0.31 ± 0.015
Pd	63 ± 4	84 ± 4	80.8	1.40 ± 0.09	1.4 ± 0.1	1.53 ± 0.032
Pt	34 ± 3	55 ± 4	58	3.21 ± 0.09	3.41 ± 0.03	3.74 ± 0.045
Ir	0.13 ± 0.07	5.6 ± 0.5	6.2	0.032 ± 0.003	0.076 ± 0.009	0.074 ± 0.012

^{197}Au(2n,γ) ^{199}Au, was corrected for by the irradiation of a pure gold source, from which the production of ^{199}Au from Au could be evaluated. According to Crocket and Cabri,[5] only ultramafic rocks are matrices in which the (2n,γ) interference is negligible.

Results and Discussion

The results obtained for the reference materials SARM-7 and CHR-Pt+, and also certified and proposed values,[11,14] are presented in Table 2. The reproducibility of the method was tested by five replicate analyses of the sample, and the errors associated with the data represent one standard deviation.

It can be observed that for Au, *aqua regia* leaching gave more accurate results for the two reference materials analysed, showing relative errors between 0 and 6% and good precision (average relative standard deviation $s_r = 7\%$), confirming the efficiency of *aqua regia* to extract Au from geological samples.[2,9]

For Pd, both chemical treatments gave similar results for SARM-7 (relative errors less than 10% and $s_r \approx 7\%$), but for CHR-Pt+ much better results were obtained when sintering was used, the relative errors for recommended values falling from 22% to 4%.

For Ir and Pt, the improvement in the results was remarkable when sintering was applied, for both SARM-7 and CHR-Pt+. In the latter, almost no Ir was extracted from the rock by partial attack with *aqua regia*, whereas an almost quantitative yield (more than 90%) was achieved by using the sintering procedure. These data agree with results reported by Gowing and Potts[2] and may be explained by the fact that dominant minerals containing Pt and Ir in CHR-Pt+ are insoluble in *aqua regia*. These observations indicate that the solubility of some PGE minerals may be a limiting factor for the use of *aqua regia* for PGE determination. It must be noted that, in the analysis of CHR-Pt+ using *aqua regia* leaching and flame atomic absorption spectrometry, Potts *et al.*[11] reported a higher concentration for Pt (45.17 μg g^{-1}), indicating an improved leaching efficiency.

The experimental quantitative detection limits for the analytical conditions described, in the analysis of SARM-7 when sintering with sodium peroxide and Te precipitation were used, calculated considering the Currie criterion,[15] were 0.1 μg kg^{-1} of Au, 10 μg kg^{-1} of Pd, 20 μg kg^{-1} of Pt and 0.2 μg kg^{-1} of Ir. The detection limits (L_d) were calculated according to the equation

$$L_d = 2.71 + 4.65\sqrt{B}$$

where B is the measured background area of a specific energy range in the gamma-ray spectra.

It is concluded that sintering with sodium peroxide followed by coprecipitation with tellurium seems to be more appropriate for the determination of Pd, Pt and Ir. Gold was successfully determined by using *aqua regia* leaching.

The sintering procedure was applied to the analysis of chromitite CHR-Bkg, and the results obtained for four determinations are given in Table 3, together with proposed values. For Pt and Pd, substantial discrepancies are observed between replicate analyses, with outliers in relation to proposed values, mainly for Au and Pt. Potts *et al.*[11] also reported 'gross' outliers for Au and Pd in CHR-Bkg, probably owing to minerological effects, and recommended the analysis of 10 g sub-samples, in duplicate, for the determination of Au and PGEs. For Ir, however, the results obtained showed good agreement with proposed values and relative standard deviations between replicate analyses of about 3%, which may indicate smaller differences in mineralogical behaviour for this element.

Compared with fire assay-based techniques, the procedure has the advantage of avoiding contamination, with strict control of reagent purity, being a relatively simple and rapid analytical procedure. The time consumed from the beginning of the rock attack until the recording of the gamma-ray spectra is about 20 h and several samples may be treated at the same time if gamma-ray spectrometers are available. Nevertheless, the milligram-sized samples (250 mg) may cause errors, mainly in the determination of gold, owing to the heterogeneous distribution in PGE minerals. The proposed method may be used in the determination of iridium anomalies in studies to associate the impact of an extra-terrestrial object with extinctions at the Cretaceous–Tertiary boundary, as typical iridium anomalies lie in the range 1–100 μg kg^{-1}.[16] For the particular case of Ir, owing to its relatively long half-life, detection limits may be improved by taking a larger amount of sample for analysis and applying the radiochemical procedure some days after irradiation, to avoid activity from short-lived radioisotopes.

The whole procedure is simple and rapid, giving accurate and precise results, and can be applied to different matrices in which minerals of PGEs are associated. Results obtained for Au, Pt, Pd and Ir in the proposed geostandards CHR-Pt+ and CHR-Bkg are a contribution to concentration values.

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Table 3 Concentrations (μg kg^{-1}) of gold, palladium, platinum and iridium in the reference material CHR-Bkg. Number of measurements (n) = 4; results presented correspond to the mean ± standard deviation

Element	Sintering (Na$_2$O$_2$)	Proposed values[11]
Au	6.6 ± 0.9	28
Pd	43 ± 16	70
Pt	77 ± 12	50
Ir	31.0 ± 0.9	28