

Determination of iridium at sub $\text{ng}\cdot\text{g}^{-1}$ levels in geological materials by RNAA

C. P. R. Morcelli, A. M. G. Figueiredo*

Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN/SP Caixa Postal 11049, 05422-970, São Paulo, SP, Brasil

(Received November 22, 1999)

Radiochemical neutron activation method is presented for the determination of iridium in geological materials. The procedure consisted of thermal neutron irradiation of an 500 mg sample followed by sinterization with sodium peroxide, precipitation with tellurium and high resolution gamma-spectrometry with a hyper-pure Ge-detector. The procedure was evaluated by the analysis of the certified reference materials SARM-7 and W-1. The detection limit for the analytical conditions employed was $0.004 \text{ ng}\cdot\text{g}^{-1}$ Ir. The procedure was applied to the reference materials TDB-1 and WGB-1, which present provisional values for Ir concentration, and GXR-3, GXR-5 and GXR-6, which do not present any reported data for Ir contents.

Introduction

The concentration of platinum group elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt) in geological materials is typically in the range of $\text{ng}\cdot\text{g}^{-1}$ ($0.1\text{--}10 \text{ ng}\cdot\text{g}^{-1}$),¹ therefore, sensitive and accurate techniques must be used to achieve reliable results. The determination of PGEs has attracted great interest due to the increasing utilization of these elements in modern industry. From the geochemical point of view, PGEs can provide relevant information on metal geochemistry, since they can be used as tracers of mantle processes. The determination of iridium, particularly, has played a important role in studies linking the impact of an extraterrestrial object to extinctions at the Cretaceous-Tertiary boundary.²

In the present paper, a radiochemical neutron activation method for the determination of iridium in geological materials, based on a previous work,³ is presented. The changes in the analytical procedure aimed a better sensitivity for the determination of Ir. The procedure consisted of thermal neutron irradiation of about 500 mg sample, followed by sinterization with sodium peroxide, precipitation with tellurium and high resolution gamma-ray spectrometry with a hyper-pure Ge detector. The accuracy and precision of the procedure were evaluated by the analysis of the certified reference materials, SARM-7, a platinum ore (South Africa Bureau of Standards) and W-1, a diabase rock (USGS). The detection limit for the analytical conditions employed was $0.004 \text{ ng}\cdot\text{g}^{-1}$. The procedure was applied to the reference materials TDB-1, diabase rock, and WGB-1, gabbro (CANMET), which have provisional values for Ir, and to the reference materials GXR-3, GXR-5 and GXR-6, soils (USGS), which do not present information values for Ir.

Experimental

Aliquots of about 500 mg of the powdered sample were weighted in Al foils and 200 μl of a Ir standard solution (SPEX Industries, $500 \text{ ng}\cdot\text{ml}^{-1}$) were pipetted in quartz ampoules. Samples and standards were placed inside aluminum irradiation vessels, specially developed for use in the IEA-R1m reactor of the IPEN-CNEN/SP, and were irradiated for 8 hours at a thermal flux of about $10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. The cooling period before the radiochemical procedure was about 20 days.

The irradiated sample was transferred into a Ni crucible containing aliquots of 100 μl of carrier solutions of Ir, Pt, Pd and Au (solutions prepared by dissolving convenient amounts of chloride salts of Ir, Pd and Pt in dilute nitric acid and Au metal in aqua regia, containing $1.0 \text{ mg}\cdot\text{ml}^{-1}$ of Ir, Pt and Au and $0.5 \text{ mg}\cdot\text{ml}^{-1}$ of Pt). The sample was thoroughly mixed with 4.5 g of sodium peroxide, the crucible was covered with a nickel lid and introduced into a cold furnace. The temperature of the furnace was raised to 200 °C for 30 minutes and then to 480 °C for 1.5 hours. The crucible was transferred into a 600 ml beaker with 50 ml of warm water (60 °C) and 45 ml of HCl 6M. The solution obtained was gently boiled and insoluble silicates were filtered in a Whatman 40 filter paper. The solution obtained was boiled and 2 ml of a 1M Te solution, prepared as described by STOCKMAN,⁴ were added to the beaker. Then, 10 ml of a Sn(II) chloride solution, freshly prepared, were added to precipitate the metallic Te. The solution was boiled to coagulate the precipitate, 1 ml of the Sn(II) chloride solution was added, and the solution was boiled for 5 minutes. This solution was then filtered onto a 4 cm Millipore filter (RA) and the precipitate was dried under an infrared lamp and sealed in a polyethylene envelope. Figure 1 presents a flow scheme of the radioanalytical procedure.

* E-mail: grafigue@curiango.ipen.br

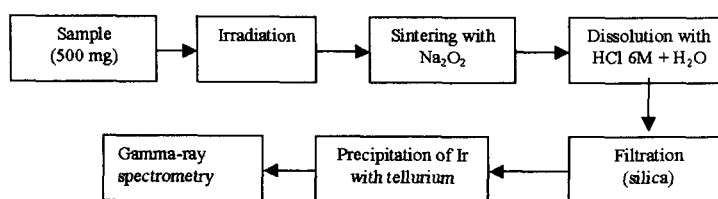


Fig. 1. Flow scheme of the radiochemical procedure

The measurements of the induced gamma-ray activity were carried out in a GMX20190 hyperpure Ge-detector (Canberra). The multichannel analyser was a 8192 channel Canberra S-100 plugged-in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ⁶⁰Co. The gamma-ray spectra were processed by using the program VISPECT, developed by PICCOT,⁵ from Saclay, France. This program locates peak positions and calculates gamma-ray energies and net areas. The counting times were about 12 hours for the samples and 0.5 hour for the standard. The radioisotope measured was ¹⁹²Ir (half-life of 73.83 d and main gamma-ray energies of 316.5 keV and 468.7 keV).

Chemical yield

In order to determine the chemical yield of the procedure, a radioactive tracer of ¹⁹²Ir (50 µl of the irradiated Ir standard solution) was added to 500 mg of a non irradiated sample of the analysed reference materials and the sample was submitted to the radiochemical procedure. The measured gamma activity of the precipitate of Te obtained was compared to the activity corresponding to the radioactive tracer added.

The chemical yield (Fig. 2) ranged between 38% (for GXR-6) to 58% (for SARM-7), which was similar to the chemical yield reported by STOCKMAN⁴ (60%) in the determination of Ir in the reference materials PCC-1 and W-1, by using a radiochemical procedure that included the precipitation of the PGEs with Te. It was observed that a better chemical yield could be achieved if a mixture of carries of Ir, Pt, Pd and Au was used in the radiochemical procedure, instead of using only Ir as carrier. This fact indicates that the presence of the PGEs Pt, Pd and Au may improve the coprecipitation of Ir with Te. Since a significant variation in the chemical yield was verified as the matrix changed, the chemical yield was determined for each experiment, processing simultaneously the irradiated sample and the same sample (not irradiated), to which a radioactive tracer of

¹⁹²Ir was added. The concentration of Ir was obtained by comparing the activities of the precipitates of Te obtained at the end of both chemical procedures and the chemical yield was calculated in relation to the activity of ¹⁹²Ir added.

Results and discussion

The results obtained for the reference materials analyzed, as well as certified and provisional values, are presented in Table 1. The reproducibility of the method was tested by replicate analysis and the errors associated with the data represent one standard deviation.

The data obtained for the reference materials SARM-7 and W-1 were in good agreement with certified values, with relative errors of 5% and 2%, respectively, showing the accuracy of the method. For the reference materials TDB-1 and WGB-1, relative errors for literature values were 25% and 40%, respectively. It must be noted that the concentration of Ir in these materials is very low (0.15 and 0.33 ng·g⁻¹) and that the reported values are provisional values. The coefficient of variation was of 14.3% for the analysis of SARM-7 and of about 30% for the other reference materials.

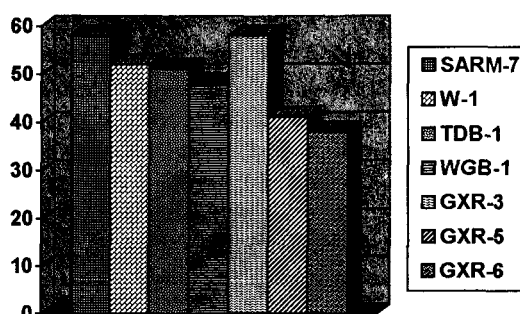


Fig. 2. Chemical yield (in %) obtained for the analyzed reference materials

Table 1. Concentration (in $\text{ng}\cdot\text{g}^{-1}$) of iridium in the reference materials SARM-7, W-1, WGB-1, TDB-1, GXR-3, GXR-5 and GXR-6

Geological Reference Material	Concentration of Ir	Certified and provisional values
SARM-7 ($n=5$)	70 ± 10	74 ± 12^6
W-1 ($n=7$)	0.275 ± 0.059	0.28^7
WGB-1 ($n=5$)	0.200 ± 0.059	0.33^8
TDB-1 ($n=5$)	0.187 ± 0.054	0.15^9
GXR-3 ($n=9$)	0.066 ± 0.024	–
GXR-5 ($n=5$)	0.051 ± 0.009	–
GXR-6 ($n=4$)	0.032 ± 0.009	–

n – number of measurements; results correspond to the mean \pm standard deviation.

The method presented a good precision, considering the very low range of concentration of Ir in the analyzed samples (sub $\text{ng}\cdot\text{g}^{-1}$). A discussion about the problems of discrepancies between replicates in PGEs analysis and in the subsequent interpretation of data in PGEs geochemistry was recently presented by MCDONALD.¹⁰ Data reported in this article show that, in the analysis of PGEs in different geological materials, the coefficient of variation (determined from replicate analysis) may range from 1 to 100%, depending on the mass of the sample and on the concentration of PGEs, indicating the necessity of replicate analysis to overcome this problem.

The experimental quantitative detection limit for the analytical conditions described, according to the CURRIE¹¹ criterion, was $0.004 \text{ ng}\cdot\text{g}^{-1}$.

The method proposed provides accurate and precise results for the determination of Ir at sub $\text{ng}\cdot\text{g}^{-1}$ levels, in different matrices. The method is a relatively simple analytical procedure, and can be applied to the determination of anomalies in iridium distribution in sedimentary rock samples related to catastrophic events. Results obtained for Ir in WGB-1, TDB-1, GXR-3, GXR-5, and GXR-6 are a contribution to concentration values.

*

C. P. R. M. thanks the Brazilian agency CNPq for financial support.

References

1. S. J. BARNES, A. J. NALDRETT, M. P. GORTEN, *Chem. Geol.*, 53 (1985) 303.
2. L. W. ALVAREZ, W. ALVAREZ, F. ASARO, H. V. MICHEL, *Science*, 208 (1980) 1095.
3. C. A. NOGUEIRA, A. M. G. FIGUEIREDO, *Analyst*, 120 (1995) 1441.
4. H. W. STOCKMAN, *J. Radioanal. Chem.*, 78 (1983) 307.
5. D. PICCOT, personal communication, 1989.
6. T. W. STEEL, J. LEVIN, I. COPELOWITZ, *Nat. Inst. Metall. Repub. S. Afr. Rep.*, 1696 (1975).
7. S. ABBEY, *Geostand. Newsl.*, 4 (1980), 163.
8. CCRMP 96, WGB-1: Additional Certified Elements, 1996.
9. CCRMP 94-1E, TDB-1: A certified PGE geochemical reference material, 1994.
10. I. MCDONALD, *Geostand. Newsl.*, 22 (1998) 85.
11. L. A. CURRIE, *Anal. Chem.*, 40 (1968) 586.