I Brazilian PGE Meeting, 1993

STUDIES FOR THE DETERMINATION OF PLATINUM GROUP ELEMENTS BY NEUTRON ACTIVATION ANALYSIS AT THE INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES - IPEN-CNEN/SP

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Introduction In recent years, considerable interest has been shown in the development of analytical techniques for the determination of platinum group elements (PGE) in geological samples. This is due not only to the important role the PGE play in world's economy and in the production of various industrial products, such as high-octane gasoline, pharmaceuticals, antibiotics, laser crystals, jewellery and eletronic components, but also because the PGE represent a coherent group of siderophile elements from which it may be possible to deduce aspects of the history of a rock (Gupta & Gregoire 1989, Oddone et al. 1990).

Great attention has recently been payed by the scientific community to reliable determination of very low amounts of PGE in terrestrial materials, mainly on account of some anomalies in iridium distribution in sedimentary rock samples, related to catastrophic events (Alvarez et al. 1980).

Neutron activation analysis has been used to determine PGE in several kinds of rocks (Stockman 1983, Cocherie et al. 1987). Many reasons make this technique a powerful tool for the determination of PGE, like high sensitivity, the possibility of determining all the elements of the group, the accuracy and reliability of results.

Despite the low detection limits of neutron activation analysis, this technique, such as other analytical techniques, requires a preconcentration step, so that the parts per billion (ppb) level, essential in geological applications, can be achieved. In the Radiochemistry Division of IPEN,, a method for the determination of iridium by neutron activation analysis was developed. The preconcentration step was accomplished by an acid attack and separation of iridium by ionic exchange. The method was applied to the USGS standard rock peridotite PCC-1 and to samples of sedimentary rocks collected at different depths in the Campos basin - RJ, Brazil (Armelin et al. 1989).

Several papers present the use of a partial attack of the rock with acqua regia in the preconcentration of the PGE (Gowing & Potts 1991, Sighinolfi et al. 1984).This is due to the fact that the noble metals are contained in the rocks in a metal form or in mineral phases (sulphides, tellurites etc) that are easily dissolved by the mixture HNO_3-HCl. The acqua regia attack has been used currently for the determination of gold in geological samples (Kontas et al. 1990) and has been applied successfully in the Radiochemistry Division (Nogueira et al. 1992). This method does not require specialized personnel and needs only usual laboratory equipments.

A method for the determination of PGE by neutron activation analysis is being developed, based on the partial attack of the irradiated rock with acqua regia and precipitation of the PGE with tellurium. The procedure was applied to the geological standard SARM-7 and presented good results to Au, Pd and Pt.

In the present work, the results obtained up to now for the determination of PGE by neutron activation analysis at the Radiochemistry Division of IPEN are presented.

Determination of Iridium

- Experimental Procedure About 1 g of the sediments and 200 mg of the PCC-1 standard were irradiated with thermal neutrons in a fux of 5.10^{12}n.cm^{-2}s^{-1}, for 8 hours, at the IPEN reactor IEA- R1, with a standard solution of iridium.

After 10-15 days following the irradiation, the rock was treated with a HF-HNO_3-HCl mixture in a teflon coup inserted in a stainless steel bomb, for 5 hours at about 100°C. After total dissolution of the rock, the mixture was evaporated to dryness. The residue was taken up in HCl 0,03M in the presence of H_2O_2 (120 vol). The resulting solution was passed through a chromatographic column containing a cationic resin (50W X-8), previously conditioned with HCl 0,03M and H_2O_2. The complex (IrCl6-2) present in the solution was not sorbed by the resin, while the interfering elements were sorbed. The effluent solution was measured, as well as the standard solution of iridium, in a gamma spectrometer, consisting of an hyperpure Ge detector coupled to a multichannel analyser and associated eletronic. The radioisotope used for the iridium determination was 192Ir, with a half life of 74 days and a gamma ray energy of 467,8 keV.

- **Results** The accuracy of the method was evaluated by means of analysis of the geological satandard PCC-1.

Table 1 shows the result obtained for the iridium concentration , relative to 14 determinations, as well as some literature values. It can be seen that the result obtained is in good agreement with the consensus value. The practical detection limit was 0,5 ppb of Ir.

The results obtained for the 16 sedimentary rocks didn't present the iridium anomaly mentioned by Alvarez et al.(1980). The deviations in iridium concentration were related to normal sedimentation processes.

Determination of Au, Pd and Pt

- **Experimental Procedure** About 250 mg of the standard SARM-7 and convenient aliquots of standard solutions of Pd, Pt and Au, prepared respectively from the salts PdCl2, PtCl6 and metallic gold, were irradiated with thermal neutrons in a flux of about 1012n.cm-2s-1, for 8 hours.

The irradiated rock was treated with 6 ml of hot acqua regia. The resultant solution was concentrated and more 6 ml of acqua regia was added. This procedure was repeated 3 times. The residue was separated by filtration and stored for further measurement. The filtrate was evaporated to dryness and was taken up in concentrated HCl several times, to eliminate the nitrate, and taken up in 10 ml of diluted HCl (2:1). The procedure of coprecipitation of the PGE with tellurium was described by Stockman (1983).

The precipitate of tellurium and the standard solutions were measured in a gamma spectrometer. The radioisotopes used in the analysis and their nuclear characteristics are in Table 2.

- **Results** The concentration of the analysed elements was calculated by comparing the spectra obtained from the tellurium precipitate and from the standard solutions measurements. The results obtained, relative to 4 determinations, are in Table 3, as well as certified values.

It can be seen that the method presented accurate results, with good precision. In order to verify the possibilities to other kinds of samples, the method will be applied to other reference materials.

Acknowledgments - To Fundação de Amparo à Pesquisa do Estado de São Paulo - FAPESP - for research fundings.

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Table 1. Concentration of iridium (ppb) in the geological standard PCC-1

This work	Gladney et al. (1983)	Govindaraju (1987)
5,37+/-1,38	4,8+/-1,9	4,8

Table 2. Radioisotopes used in the analysis and their nuclear characteristics

Radioisotope	Formation	Half-Life	Energy (keV)
^{198}Au	^{197}Au(n,g)	2,7d	411,8
^{109}Pd	^{108}Pd(n,g)	13,5h	88,0
^{199}Au	^{198}Pt(n,g,b^{-})	13,1d	158,3

Table 3. Concentration of Au, Pd and Pt in the geological standard SARM-7 (ppb)

Element	This work	Steele et al.(1975)
Au	0,29+/-0,01	0,31+/-0,015
Pd	1,40+/-0,09	1,53+/-0,032
Pt	3,21+/-0,09	3,74+/-0,045