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DETERMINATION OF IRIDIUM CONCENTRATIONS IN  
SEDIMENTARY ROCKS AND IN THE GEOLOGICAL  
PCC-1 BY RADIOCHEMICAL NEUTRON ACTIVATION  
ANALYSIS

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RESUMO - NOTAS / ABSTRACT - NOTES

A radiochemical neutron activation analysis procedure is described for the determination of concentration levels of iridium in sedimentary rocks and in the geological standard PCC-1. After irradiation, the powdered rock samples and standard are dissolved with a mixture of HF, HNO<sub>3</sub> and HClO<sub>4</sub> in a teflon pump. The final solution obtained, in diluted HCl, is percolated through a column containing the cationic resin Bio AG 50W-X8. The interfering radionuclides are sorbed by the resin. The effluent solution containing iridium is concentrated for counting by evaporation. Experiments with radioactive tracer for checking radiochemical separation yield are carried out. The accuracy of the method is evaluated by means of analysis of the USGS standard rock peridotite, PCC-1. The method is used for the determination of iridium in 16 samples of sedimentary rocks collected at different depths in the "Campos" basin-RJ (BRAZIL).

OBSERVAÇÕES / REMARKS

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DETERMINATION OF IRIIDIUM CONCENTRATIONS IN SEDIMENTARY ROCKS AND  
IN THE GEOLOGICAL STANDARD PCC-1 BY RADIOCHEMICAL  
NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

A radiochemical neutron activation analysis procedure is described for the de<sup>u</sup>termination of concentration levels of iridium in sedimentary rocks and in the ge<sup>o</sup>logical standard PCC-1. After irradiation, the powdered rock samples and standard are dissolved with a mixture of HF, HNO<sub>3</sub> and HClO<sub>4</sub> in a teflon pump. The final so<sup>l</sup>ution obtained, in diluted HCl, is percolated through a column containing the cationic resin Bio Rad AG 50W-X8. The interfering radionuclides are sorbed by the resin. The effluent solution containing iridium is concentrated for counting by evaporation. Experiments with radioactive tracer for checking radiochemical separation yield are carried out. The accuracy of the method is evaluated by means of analysis of the USGS standard rock peridotite, PCC-1. The method is used for the determination of iridium in 16 samples of sedimentary rocks collected at different depths in the "Campos" basin-RJ (BRAZIL).

INTRODUCTION

The discovery in 1980 by Alvarez et al<sup>(1)</sup> of a clay layer marking the Cretaceous/Tertiary (65 My) boundary enriched relative to crustal abundances of noble metals such as iridium and other platinum group elements has lead to a vast amount of publications concerning hypothesis on extinction mechanisms that occurred at the geological time. The iridium enriched layer which marks this event, appears to be global in extent and was attributed by Alvarez and collaborators to the impact of a large extraterrestrial object with the Earth.



While most of these publications deal with the interpretations of reported data, only scarce references are made to new improved measurement techniques. At the ppb level of Ir, neutron activation analysis is one of the most reliable techniques, applicable to iridium determination, due to the high thermal neutron activation cross section exhibited by this element. However, in some cases, it is necessary to carry out radiochemical separation procedures to cut off spectral interferences and to improve sensitivity, before applying this technique.

Some works have been published in which several radiochemical separation procedures were used for removal of interfering radionuclides, in the iridium determination by neutron activation analysis. Oddone et al<sup>(2)</sup> studied a method for noble metals sorption on an anionic resin. Stockman<sup>(3)</sup> used the noble metals coprecipitation as a group with Te, using  $\text{Sn}^{2+}$  as a reducing agent. Several works<sup>(4,5)</sup> used selective sorption of the noble metal group on Srafion NMRR ion exchange resin. The fire assay technique, which concentrates the noble metals into a nickel sulfide button was employed by Borthick et al<sup>(6)</sup>.

This paper presents the development of a radiochemical separation procedure for elimination of some interfering radionuclides in the iridium determination by neutron activation analysis. The accuracy of the procedure was confirmed through the use of the method for the determination of iridium in the USGS standard rock peridotite - PCC-1. The method was used for preliminary determination of iridium in 16 samples of marine sediment cores, collected at different depths in the "Campos" basin-RJ (BRAZIL) by the local state oil company (Petrobrás). These sediment cores correspond to the Cretaceous/Tertiary age but may not contain the gradational interface.

## EXPERIMENTAL

### Treatment of the Sedimentary Rocks

The rock samples were first broken in smaller fragments by using a hammer. About 100 g of rock were then ground in a manual agate mortar, until all the powder passed through a 150 mesh sieve.

### Preparation of Stock and Standard Solutions

A stock solution containing  $2.13 \text{ mg Ir.mL}^{-1}$  was prepared by dissolution of iridium tetra-chloride (Pfaltz and Bauer, Inc) in 2M HCl. The standard solution, containing  $4.26 \text{ } \mu\text{g Ir.mL}^{-1}$  was prepared by dilution of the stock solution. From this solution an aliquot of 100  $\mu\text{L}$  was pipetted on analytical filter paper for irradiation.

## Irradiation and Counting

Sample (about 1 g) and standard solution were irradiated together in aluminium tubes, at a neutron flux of approximately  $5.10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  for a period of 8 hours.

Radiochemical processing of the sample started after a delay time of about 10 to 15 days after irradiation.

Countings were carried out using a high resolution solid state ORTEC Ge(Li) detector, with a resolution of 2.8 keV for the 1332 keV peak of  $^{60}\text{Co}$ . The detector was coupled to a 4096 - channel analyser. The 468 keV gamma-ray emitted by  $^{192}\text{Ir}$  ( $t_{1/2} = 74.4 \text{ d}$ ) was used for analysis. Data reduction was carried out using mini-computers and one or both of the following software for spectral analysis: Program FALA<sup>(7)</sup>, Program Ge(Li) Gam, from ORTEC.

## Radiochemical Separation Procedure

After the cooling period, the irradiated sample was transferred to a teflon beaker. An aliquot of stock solution was then added as carrier (2 mg Ir), followed by a mixture of concentrated acids ( $\text{HF}$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ ). This beaker was covered with a teflon disk and placed in a stainless steel dissolution pump. Finally, the pump was kept in a stove at  $100^\circ\text{C}$  for about 5 hours.

The dissolution pump was allowed to cool off and then the teflon beaker was removed from it. The solution was taken to almost dryness for elimination of acids.

The residue was taken up with 150 mL of 0.03M  $\text{HCl}$  and 3 mL of  $\text{H}_2\text{O}_2$  (120 vol) were added.

The resulting solution was percolated through a chromatographic column (1 cm diameter and 30 cm height) containing the cationic resin Bio-Rad AG 50W-X8, previously conditioned with 60 mL of a 0.03M  $\text{HCl}$  solution.

The complex ion ( $\text{IrCl}_6^{2-}$ ) present in solution was not sorbed by the resin, while the interfering elements (lanthanides, Se, Na, Fe, Co) were sorbed<sup>(8)</sup>.

The effluent solution containing iridium was concentrated by evaporation to  $25 \text{ cm}^3$  and transferred to penicillin type containers for counting.

The iridium standard was dissolved in an equal volume of 6M  $\text{HNO}_3$  and 2M  $\text{HCl}$  solution. The activities of both sample and standard were measured and compared.

## RESULTS AND DISCUSSION

### Determination of Radiochemical Separation Yield

The procedure was tested with non-irradiated marine sediments to which was



added an iridium radioactive tracer. A mixture of concentrated acids ( $\text{HF}$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ ) together with the radioactive tracer of  $^{192}\text{Ir}$  was added to the teflon beaker containing about 1 g of the marine sediment. The radiochemical separation yield was computed by comparing the added and recovered activities.

The average yield obtained with 10 determinations was  $(76 \pm 2)\%$ .

#### Accuracy of the Method

In order to check the accuracy of the method, 14 determinations of iridium were made in the USGS Standard rock: Peridotite - PCC-1.

Results obtained are shown in Table 1.

Table 1

The comparison of the obtained data to the existing values in the literature for PCC-1 showed that the accuracy and reproducibility of results for the iridium measured with the developed method is well suited for the purpose of determination of the iridium anomaly at the Cretaceous/Tertiary boundary and other geological studies employing iridium as a tracer.

#### Application of the Method to the Analysis of Ir in Marine Sediment Samples

The method was used for the determination of iridium in 16 samples of sedimentary borehole cores taken at several depths in the "Campos" basin in the continental platform off Rio de Janeiro, Brazil (Table 2).

Table 2

The samples were chosen from a suite of borehole cores belonging to the Brazilian State Oil Company (Petrobrás). It was selected the borehole nº 1-KJS-19 from 2834,8 to 2838,7 meters depth, which contains the geological interface between the Cretaceous and the Tertiary periods. This interface in Brazil has been subjected to erosional processes in all but a few uncertain cases. Reliable location and determination of the iridium anomaly is not always possible. The present study was useful to determine the background level of iridium in the sediments. The method will be applied later to samples containing confirmed gradational Cretaceous-Tertiary interfaces in Brazil.

The main interference found in the analysis of iridium in the marine sediment samples, came from the presence of lanthanide elements and scandium. The complexity of the  $\gamma$ -ray spectrum of the lanthanides and the high Sc content hindered the iridium determination by means of purely instrumental activation analysis.

Therefore the most important steps of the radiochemical separation procedure are the sorption of interfering elements by the Bio Rad AG 50W-X8 resin and the passing of the iridium (IV) species for the adequate recuperation of iridium to the effluent solution, because the  $\text{IrCl}_6^{3-}$  was found to be weakly sorbed by the resin(8).

## CONCLUSIONS

In this work an improved radiochemical method for the determination of iridium at ppb level in borehole sediment core samples was developed and applied to samples of Cretaceous-Tertiary geological interface in order to find the background level of iridium of this sedimentary basin. In order to verify the accuracy and reproducibility, the method was tested with an USGS standard rock, PCC-1.

The analytical method developed has shown to be adequate for the purpose of the present work, with a relative standard deviation of about 25%, which can be considered as good for determinations at the ppb level. The agreement with the values published by Flanagan<sup>(9)</sup> and Gladney<sup>(10)</sup>, for the PCC-1 standard are also good, as can be seen in Table 1.

Results obtained for the sediments (Figure 1) have shown wide excursions of iridium concentration for different depths. Since geological and paleontological studies of the "Campos" basin made by Petrobrás indicate that the Cretaceous/Tertiary is not gradational, the peaks of iridium in Figure 1 are probable not of an "anomalous" characteristic but are related to normal sedimentation processes. The method will now be applied to a more complete set of sediment core samples and normal samples from others regions of Brazil, for which the gradational interface is known, in order to proceed with the studies of the unsolved Cretaceous/Tertiary interface enigma.

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TABLE 1

Results of the Determination of Iridium in the USGS Standard Rock-PCC-1, Using Radiochemical Neutron Activation Analysis

Ir Concentration (ng/g)
(6.07 $\pm$ 1.20)
(5.14 $\pm$ 0.71)
(4.70 $\pm$ 1.49)
(3.42 $\pm$ 0.67)
(6.90 $\pm$ 0.96)
(7.18 $\pm$ 1.42)
(3.91 $\pm$ 0.69)
(4.38 $\pm$ 1.39)
(6.64 $\pm$ 1.76)
(7.32 $\pm$ 1.03)
(5.12 $\pm$ 0.71)
(4.05 $\pm$ 0.70)
(3.79 $\pm$ 0.75)
(6.54 $\pm$ 1.74)

Mean  $\pm$  Standard deviation = 5.37  $\pm$  1.38

Gladney (10) = 4.8  $\pm$  1.9

Flanagan (9) = 5.2

TABLE 2

Results for the Analysis of Iridium in Marine Sediments of "Campos" Basin-RJ  
(Brazil)

Depth (m)	Number of Determinations	Iridium Contents (ng/g) (Mean $\pm$ Standard Deviation)
2834.78	4	( 1.44 $\pm$ 0.63 )
2835.0	4	( 1.23 $\pm$ 0.56 )
2835.31	6	( 3.00 $\pm$ 1.75 )
2835.51	4	( 1.14 $\pm$ 0.32 )
2835.70	4	( 1.97 $\pm$ 1.03 )
2835.93	6	( 4.49 $\pm$ 0.68 )
2836.13	4	( 0.73 $\pm$ 0.19 )
2836.57	4	( 0.93 $\pm$ 0.17 )
2836.93	4	( 0.62 $\pm$ 0.10 )
2837.20	4	( 1.23 $\pm$ 0.23 )
2837.46	8	( 1.63 $\pm$ 0.67 )
2837.76	4	( 1.87 $\pm$ 0.06 )
2837.96	8	( 1.83 $\pm$ 0.29 )
2838.27	3	( 3.55 $\pm$ 1.37 )
2838.54	3	( 2.26 $\pm$ 0.09 )
2838.66	4	( 0.66 $\pm$ 0.28 )



CAPTION FOR FIGURE

Figure 1 - Profile of Iridium Obtained in the Region where the Samples were Collected.

