

USE OF NEUTRON ACTIVATION ANALYSIS IN THE STUDY OF THE COMPOSITION OF BRAZILIAN GEOLOGICAL SAMPLES

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Abstract

USE OF NEUTRON ACTIVATION ANALYSIS IN THE STUDY OF THE COMPOSITION OF BRAZILIAN GEOLOGICAL SAMPLES.

The Radiochemistry Division of the Instituto de Pesquisas Energéticas e Nucleares (IPEN), Comissão Nacional de Energia Nuclear, São Paulo, has for many years been applying nuclear techniques, mainly neutron activation analysis, to the study of the composition of Brazilian mineral resources. The main elements of interest were the rare earth elements (REEs), uranium and thorium. The contents of other elements at trace level, such as scandium, tantalum, hafnium, gold and iridium, were also determined for these geochemical studies. The contents of REEs were determined mainly by applying instrumental neutron activation analysis (INAA), using thermal and epithermal activation, followed by high resolution gamma ray spectrometry using Ge(Li) and Ge detectors. This procedure in general permits the determination of the contents of eight REEs: Ce, Eu, La, Lu, Nd, Sm, Tb and Yb. Radiochemical separations (radiochemical neutron activation analysis (RNAA)) led to the analysis of other REEs, such as Dy, Gd, Ho and Pr. The contents of REEs were determined by INAA and/or RNAA, mainly in alkaline rocks from the apatite mine at Jacupiranga, São Paulo, and in volcanic rocks from the Paraná Basin, for geochemical studies, and in geological samples, such as xenotime, tantalite and zircon, for exploration purposes. A delayed neutron counting system was assembled for analysis, mainly of uranium in geological materials and also thorium. Neutron counting was carried out by means of a group of six BF₃ detectors immersed in a paraffin moderator. The system was not totally automated, allowing analysis of approximately one hundred samples per day. The determination limit for uranium was 1 ppm and 85 ppm for thorium. The other elements mentioned (Sc, Ta and Hf) were determined generally by INAA. In the particular case of iridium, a radiochemical separation procedure based on ion exchange was developed for the analysis of marine sediments from the Campos Basin (Rio de Janeiro). Coal from the southern region of Brazil was analysed by INAA for 38 elements by using thermal and epithermal activation. Using RNAA, the contents of Se and Zn were also determined.

1. INTRODUCTION

The rate of industrial development in Brazil over the last three decades has led to an increase in mineral prospecting in order to (a) locate alternative energy sources, which can satisfy internal demand, and (b) explore for metallic ores for utilization in industry.

According to the literature [1], Brazil has uranium reserves estimated to be approximately 300 000 t of U_3O_8 , distributed across eight mines. There are also large deposits of monazite, which is the main source of rare earth elements (REEs) in Brazil. The measured reserves comprise approximately 20 000 t of rare earth oxides, located all along the Brazilian coast, but mainly in the States of Rio de Janeiro (69%) and Espírito Santo (22%). There is also a reserve of 300 000 t of REEs contained in iron ore from Poços de Caldas (Minas Gerais), which constitutes a new source of rare earths, uranium and thorium.

From an academic point of view, knowledge of the concentrations of REEs and other trace elements in rocks is of great interest in the geosciences. Trace elements, including Ba, Co, Cs, Hf, Rb, Sc, Ta, Th, U and REEs have been extensively used in petrogenetic studies of igneous rocks, since they facilitate the evaluation and estimation of the extent of the main processes involved in the generation and differentiation of melts.

Neutron activation analysis (NAA) has been widely used in the determination of these elements in rocks owing to its high sensitivity, as well as its good precision and accuracy [2, 3]. It is capable of the simultaneous determination of the contents of many elements at the parts per million (ppm) level and some at the parts per billion (ppb) ($1 \text{ billion} = 10^9$) level, often without destruction of the sample.

Many years have been devoted to academic research in the geosciences at the Radiochemistry Division of the Instituto de Pesquisas Energéticas e Nucleares (IPEN), of the Comissão Nacional de Energia Nuclear, São Paulo (CNEN/SP). Several methods of radiochemical separation for elements in geological samples have been developed and instrumental neutron activation analysis (INAA) has been optimized for many applications. The accuracy and precision of these methods have been verified by the analysis of international geological standards, such as G-2, GSP-1 (United States Geological Survey (USGS)) and GS-N (Association nationale de la recherche technique), and also standards that are being prepared in Brazil, such as basalt (BB-1) and granite (GB-1).

Much work has been performed in collaboration with other research institutions in the field of geosciences, such as the Instituto Astronomico e Geofisico of the University of São Paulo [4-6] and the National Institute of Space Research [7]. More recently, the Radiochemistry Division has been engaged in the analysis of REEs, uranium and thorium in such ores as xenotime, tantalite and zircon for purposes of mineral exploration. The analysis of uranium and thorium in granite and basalts has been carried out using the delayed neutron counting method [8], for

exploration purposes as well as for geochemical studies. Uranium-235/uranium-238 isotopic ratios were also determined by this method [9].

The aim of this work is to present the methods developed in the Radiochemistry Division of IPEN-CNEN/SP for the analysis of geological samples. Some results obtained for geological standards and samples are also reported.

2. NEUTRON ACTIVATION ANALYSIS FOLLOWED BY HIGH RESOLUTION GAMMA RAY SPECTROMETRY

2.1. Principle of the comparative NAA method

In this method, standards containing known quantities of the elements of interest are subjected, along with the samples, to a neutron flux and the activities induced are measured under the same conditions using Ge(Li) or high purity Ge detectors.

Since each radioisotope has its characteristic half-life and energy (or energies) of gamma radiation, it is possible, in general, to identify the isotope of the element. The quantity of this element in the sample is considered to be directly proportional to the counting rate of gamma radiation.

2.2. EXPERIMENTAL

2.2.1. General procedures

2.2.1.1. Sample preparation

Reference materials, such as standard rocks from the USGS, the IAEA and other institutions, were not subjected to any further treatment, since they were already received as fine powders. The rocks that arrived in coarser fragments were first broken with a hammer and then crushed into smaller fragments in a porcelain mortar until they were of a reasonable size for grinding in a mechanical agate mortar.

After grinding the rocks, the treatment was continued in a manual agate mortar until the powder could pass through a 150 mesh nylon sieve. This final treatment was considered necessary in order to ensure a reasonable degree of homogeneity of the material. Contact with metallic parts was avoided as much as possible, since the problem of contamination of the samples by foreign elements can be very serious at this level of granulometry.

2.2.1.2. Standards

Since the comparative method of activation analysis was always used in this work, the choice of standards is crucial. In cases where the quantities of a great number of elements had to be determined (for example, 20–30), reference materials, such as rocks BCR-1 (basalt), AGV-1 (andesite), GSP-1 (granodiorite) from the USGS and GS-N (granite) from ANRT, were used. Special attention was paid to the choice of tabulated values from the literature [10, 11]; only those that were classified in the categories of "recommended" or "consensus values" were selected. When the content of one element at a time, or a small group of elements, was determined, such as in the case of the analysis of uranium and/or thorium, iridium or the group of REEs, synthetic standards were prepared at the laboratory.

2.2.1.3. Irradiation

Aliquots of approximately 50–500 mg of the powdered rock sample were weighed in pre-cleaned aluminium foils or polyethylene capsules and placed inside aluminium irradiation vessels specially developed for use in the nuclear reactor IEA-R1. The samples and standards were subjected to a reactor neutron flux for periods of time ranging generally from 8 to 72 h, depending on the concentration of the elements to be analysed. The geological materials can be subjected to 'thermal' or 'epithermal' irradiation.

In the first case, the samples and standards were subjected to a thermal neutron flux of the order of 10^{12} to 10^{13} neutrons \cdot cm $^{-2}$ \cdot s $^{-1}$. In the case of epithermal irradiation, the thermal, or slow neutron, component of the flux was suppressed by using cadmium foil as a shield. Epithermal irradiation suppressed the activation of some strong interfering elements in the analysis of REEs, uranium, thorium and other elements.

2.2.1.4. Gamma spectrometry measurements

Two main counting systems were used in this work: (1) the ENERTEC high purity Ge detector coupled to an ORTEC 4096 channel Model 7450 analyser, which was connected to a Monydata PC-200 Plus microcomputer. The resolution (full width at half-maximum (FWHM)) of this system was 2.5 keV for the 1332 keV gamma ray of ^{60}Co and 1.4 keV for the 122 keV gamma ray of ^{57}Co . The gamma ray spectra were processed by using a modified version of the FALA program written in Pascal language. This program locates peak positions and calculates gamma ray energies and net areas. (2) An ORTEC hyperpure Ge detector (LEPD) was coupled to an ORTEC 4096 channel Model 6240B analyser, which was connected to a PDP 11/04 minicomputer. The resolution (FWHM) of the system was 0.58 keV for the 122 keV peak of ^{57}Co .

2.2.2. *Multielement analysis of Brazilian coal samples*

Coal samples from several regions of Brazil were analysed using INAA [12]. The objective of these analyses was to check for possible polluting elements and also to detect elements of economic importance that could be extracted from the coal ash. Knowledge of the concentration of several elements, such as uranium, thorium and the lanthanides, can also yield valuable information on the origins of mines.

A combination of thermal and epithermal irradiation and different irradiation times (10 min, 8 h and 16 h with thermal neutrons) and 72 h with epithermal neutrons permitted determination of the presence of: Al, As, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Dy, Eu, Fe, Ga, Hf, In, K, La, Lu, Mg, Mn, Mo, Nd, Ni, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Ti, U, V, W and Yb, in different coal samples. The contents of Se and Zn were determined after radiochemical separation. The quantities of most elements were determined at the ppm level, except Au (ppb) and K, Fe, Al, Ca, Mg, Ti (%).

2.2.3. *Analysis of REEs, uranium, thorium and other trace elements*

Neutron activation analysis, followed by high resolution gamma ray spectrometry, is widely used for the determination of REE content, as well as uranium, thorium and other trace element content, in geological samples. The results obtained are characterized generally by good precision and accuracy; INAA can be used for the determination of the content of most REEs in geological materials.

A useful alternative that avoids some types of interference in the gamma ray spectra of REEs is the low energy photon detector. Better results are sometimes obtained for Ce, Gd, Nd, Sm, Yb [13], elements which are the origins of radioisotopes that emit X rays or low energy gamma rays.

There are some cases, however, where instrumental analysis does not result in satisfactory results, thereby requiring chemical separation before or after irradiation. Techniques applied for the separation of interfering elements are, in general, based on the use of ion exchange resins, solvent extraction and co-precipitation.

At the IPEN Radiochemistry Division, both INAA, with thermal and epithermal neutrons, and radiochemical neutron activation analysis (RNAA), or chemical separation before irradiation, have been used, permitting the determination of the content of most of the REEs, Ba, Co, Cs, Hf, Rb, Sc, Ta, Th, U [2-5, 13-16].

2.2.4. *Analysis of iridium*

Knowledge of the concentration of iridium and other noble metals in geological materials is very important for geochemical studies and geological prospecting. At the Radiochemistry Division, a radiochemical procedure was developed for the

determination of iridium in the USGS standard PCC-1, in peridotite and in marine sediments from the Campos Basin (Rio de Janeiro State) [7].

The determination of iridium in the materials is related to a study carried out of the possible occurrence of iridium anomalies in this region of the Atlantic coast, which was conducted in collaboration with the Brazilian Institute of Spatial Research (INPE, São José dos Campos). In other regions of the Earth, noble metals were found to be enriched, relative to average crustal abundances, in layers marking the Cretaceous/Tertiary (65 million years) boundary. The anomaly, first found by Alvarez et al. [17], was attributed to the impact of a large extraterrestrial object on the Earth. This was the beginning of a new theory about mass extinction that has given rise to a great deal of controversy in the scientific community.

The method of radiochemical separation that was developed, based on the retention of interferents, such as REEs and scandium in a cation exchange resin, was applied to the determination of iridium in PCC-1 standard rock and in samples of sedimentary borehole cores taken at several depths in the Campos Basin, in the continental platform of Rio de Janeiro, Brazil.

3. NEUTRON ACTIVATION ANALYSIS FOLLOWED BY DELAYED NEUTRON COUNTING

3.1. Principles of the method

The principle involved in the delayed fission neutron technique is that fissionable materials (restricted in practice to U and Th) can fission upon neutron capture and yield some fission products that decay by neutron emission following β^- decay. These delayed neutron emitters can be categorized conveniently into six groups, with half-lives ranging from approximately 0.17 s to 56 s. Thus, the emission of delayed neutrons is specific for fissionable materials, with two exceptions: ^9Li ($T_{1/2} = 0.17$ s) and ^{17}N ($T_{1/2} = 4.2$ s) that decay to excited state neutron emitters.

The number of neutrons emitted by the element that undergoes fission is proportional to the mass of the element present in the sample; thus, measurement of these neutrons is a means of performing quantitative analysis. Using cadmium or boron carbide filters to shield thermal neutrons, it is possible to determine simultaneously uranium and thorium content and also to calculate $^{235}\text{U}/^{238}\text{U}$ isotopic ratios by the delayed neutron counting method [8, 9].

3.2. Experimental

Samples or standards were packed into polyethylene envelopes. Cadmium was used as a filter for uranium and thorium analysis when the quantities of both elements

were to be determined, while composite cadmium and boron carbide were chosen as filters in the determination of the $^{235}\text{U}/^{238}\text{U}$ ratios.

Irradiation was carried out at the IEA-R1 research reactor in a position where the neutron flux had the following intensities: thermal flux = 4.4×10^{11} neutrons $\cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, epithermal flux = 4.0×10^{10} neutrons $\cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, fast flux = 1.6×10^{11} neutrons $\cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. The delayed neutron emissions from the irradiated samples were measured by means of six BF_3 detectors, enriched to about 90% ^{10}B , connected in parallel and immersed in a paraffin cylinder, which acts as a neutron moderator. The detector assembly was coupled to an electronic counting system consisting of preamplifier, monochannel analyser, scaler and timers [8]. Irradiation, decay and counting times were always 60, 20 and 60 s, respectively.

4. RESULTS AND DISCUSSION

4.1. Analysis of REEs, uranium, thorium and other trace elements

The results obtained for G-2 and GS-N geological standard rocks are presented in Table I. They show good reproducibility for INAA and pre-separation methods [18]. The accuracy of the results was also good, with the relative error lower than 15% for the majority of REEs.

No significant differences were observed between the results obtained by the INAA method and by the chemical procedure. This may be explained by the low concentration of U in these rocks. The chemical procedure is particularly useful for the analysis of uraniferous rocks.

The results obtained for REEs and other trace elements in the Brazilian geological standards GB-1 and BB-1 also agreed well with literature values (relative errors lower than 13%) [4].

Analysis of REEs and other trace elements in 158 samples of volcanic rocks from Paraná Basin was carried out in the Radiochemistry Division. Table II shows, as an illustration, the results obtained for one acid rock (SiO_2 concentration < 55%) and one basic rock (SiO_2 concentration > 63%) from the Paraná Basin and also the results obtained by RNAA for a carbonatite from the apatite mine at Jacupiranga. It can be seen that the data were obtained with good precision, with standard deviations of less than 15%.

4.2. Analysis of iridium

In order to check the accuracy and precision of the method, 14 determinations of iridium were made in the PCC-1 standard rock. An average of 5.37 ± 1.38 ppb was obtained, which shows reasonable agreement with literature values (Govindaraju = 5.2 [11], Gladney et al. = 4.8 ± 1.9 [10]).

TABLE I. CONCENTRATIONS (IN ppm) OF REEs IN THE GEOLOGICAL STANDARDS G-2 (USGS) AND GS-N (ANRT)

Element	G-2 standard rock			GS-N standard rock		
	This work		Ref. [10]	This work		Ref. [11]
	a	b		a	b	
La	87 ± 5	85 ± 5	86.0 ± 5.0	72 ± 5	71 ± 5	75
Ce	168 ± 14	148 ± 12	159.0 ± 11.0	133 ± 7	133 ± 12	140
Nd	60 ± 8	55 ± 3	53.0 ± 8.0	49 ± 7	54 ± 6	50
Sm	7.1 ± 0.3	7.1 ± 0.4	7.2 ± 0.6	7.7 ± 0.7	7.8 ± 0.4	8.2
Eu	1.42 ± 0.03	1.44 ± 0.9	1.41 ± 0.12	1.6 ± 0.1	1.7 ± 0.2	1.7
Gd	4.7 ± 0.4	—	4.1 ± 0.8	5.5 ± 0.4	—	—
Tb	0.45 ± 0.01	0.44 ± 0.04	0.48 ± 0.07	0.65 ± 0.07	0.68 ± 0.04	0.6
Yb	0.7 ± 0.1	0.82 ± 0.11	0.78 ± 0.14	1.8 ± 0.3	1.8 ± 0.2	1.7
Lu	0.11 ± 0.01	0.083 ± 0.017	0.113 ± 0.024	0.22 ± 0.04	0.19 ± 0.03	0.2

a: Results obtained by INAA and RNAA (for Nd and Gd).

b: Results obtained using chemical separation before irradiation.

—: Analysis not carried out.

TABLE II. RESULTS (IN ppm) FOR REEs AND OTHER TRACE ELEMENTS IN BRAZILIAN GEOLOGICAL SAMPLES

Element	Volcanic rocks from the Paraná Basin		Carbonatite from the apatite mine from Jacupiranga	
	Acid	Basic	INAA	RNAA ^a
Sc	17 ± 2	39 ± 4	14.1 ± 0.8	14.8 ± 1.5
Co	4.61 ± 0.05	47 ± 2	15 ± 1	16.2 ± 0.6
Rb	197 ± 7	8.61 ± 0.03	—	—
Cs	9.7 ± 0.5	0.118 ± 0.004	—	—
Ba	677 ± 31	184 ± 2	963 ± 214	961 ± 62
La	50 ± 4	13 ± 1	134 ± 8	137 ± 7
Cl	95 ± 8	29 ± 2	370 ± 18	268 ± 7
Nd	41 ± 4	17 ± 3	93	156 ± 14
Sm	9.8 ± 0.4	4.0 ± 0.2	21.8 ± 1.4	22.9 ± 0.9
Eu	1.9 ± 0.1	1.20 ± 0.08	5.8 ± 0.4	5.2 ± 0.5
Tb	1.52 ± 0.03	0.77 ± 0.03	—	1.8 ± 0.2
Ho	—	—	—	1.3 ± 0.1
Yb	5.1 ± 0.6	2.8 ± 0.1	1.70 ± 0.17	2.20 ± 0.22
Lu	0.74 ± 0.07	0.36 ± 0.04	0.24 ± 0.02	0.27 ± 0.04
Hf	8.3 ± 0.4	2.9 ± 0.1	—	—
Ta	2.12 ± 0.02	0.46 ± 0.01	—	—
Th	17 ± 2	2.49 ± 0.03	—	—
U	5.2 ± 0.3	0.47 ± 0.04	—	—

^a Radiochemical neutron activation analysis.

—: Analysis not carried out.

TABLE III. SENSITIVITIES, LIMITS OF DETECTION AND LIMITS OF DETERMINATION FOR URANIUM AND THORIUM ANALYSIS

	Detection limits (ppm)	Determination limits (ppm)
Natural uranium	0.31	1.0
Thorium	25	85

Note: Detection limits and determination limits were calculated for a 1.5 g sample.

TABLE IV. RESULTS OF NON-DESTRUCTIVE AND SIMULTANEOUS ANALYSIS OF URANIUM AND THORIUM IN IAEA AND BRAZILIAN THORIUM ORES

Sample	U (ppm)	Relative error ^a (%)	Th (%)	Relative error (%)
S-14	(26 ± 2)	10.3	(0.067 ± 0.007)	9.8
S-15	(80 ± 2)	5.9	(0.372 ± 0.018)	2.5
S-16	(433 ± 5)	2.7	(1.71 ± 0.08)	1.8
Monazite	(1300 ± 24)	—	(5.0 ± 0.1)	—
Monazite with low Th content	(330 ± 10)	—	(1.11 ± 0.04)	—

^a Relative errors are compared with the certified values published by the IAEA.

Note: Means and standard deviations are for six determinations.

Sixteen samples of a sedimentary borehole core taken at several depths in the Campos Basin were analysed: the iridium concentrations ranged from (0.62 ± 0.10) ppb to (4.49 ± 0.68) ppb, which did not constitute anomalies.

4.3. Analysis of uranium and thorium by delayed neutron counting

4.3.1. Sensitivities, limits of detection and limits of determination for uranium and thorium analysis

The sensitivities, limits of detection (from Kaiser's criterion) and limits of determination (from Long and Winefordner's criterion) under conditions established for uranium and thorium analysis are shown in Table III.

4.3.1.1. Accuracy and precision of the method

The accuracy and the precision of the method were evaluated by analysing geological samples provided by the IAEA through an intercomparison programme for uranium and thorium analysis. The results obtained in this study for two Brazilian thorium ores are given in Table IV.

Once the delayed neutron counting system was assembled and the analytical parameters established, the method was applied for geochemical studies, as well as for geological prospecting, a few thousand samples in all being analysed. One of the studies conducted, part of an IAEA research contract entitled "Uranium Distribution in Brazilian Granitic Rocks — Identification of Uranium Provinces", was a collaboration with the Institute of Geosciences of the University of São Paulo.

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