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NEUTRON ACTIVATION ANALYSIS APPLIED TO THE STUDY OF THE COMPOSITION OF BRAZILIAN GEOLOGICAL SAMPLES

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ABSTRACT

The Radiochemistry Division of IPEN-CNEN/SP has been applying, for many years, 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. Other elements such as scandium, tantalum, hafnium, gold and iridium were also determined for geochemical studies. The REEs were determined mainly by instrumental neutron activation analysis (INAA), using thermal and epithermal activations followed by high resolution gamma-ray spectrometry using Ge(Li) and Ge detectors. This procedure allows, in general, the determination of eight REEs: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu. The application of radiochemical neutron activation analysis (RNAA) led to the analysis of the REEs like Pr, Gd, Dy and Ho. REEs were determined mainly in alkaline rocks from the apatite mine of 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 of uranium in geological materials and also thorium. The other elements mentioned (Sc, Ta, Hf) were determined generally by INAA. In the particular case of iridium, a radiochemical separation procedure was developed for the analysis of marine sediments from the Campos Basin (Rio de Janeiro). Coals from the Southern region of Brazil were analysed by INAA for 36 elements by using thermal and epithermal activations.

RESUMO

A Divisão de Radioquímica do IPEN-CNEN/SP vem, há muitos anos, aplicando técnicas nucleares, principalmente a análise por ativação com nêutrons, ao estudo da composição de recursos minerais brasileiros. Os principais elementos de interesse têm sido os elementos terras raras (ETR), urânio e tório. Outros elementos, como escândio, tântalo, háfnio, ouro e irídio também têm sido determinados, para estudos geoquímicos. Os ETR são determinados principalmente por análise por ativação com nêutrons, usando ativações térmicas e epitérmicas (AANI), seguidas de espectrometria de raios gama de alta resolução usando detectores de Ge(Li) e de Ge. Esse procedimento permite em geral a determinação de oito ETR: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu. A aplicação de análise por ativação com nêutrons com separação radioquímica (AANR) leva à determinação de outros ETR, como Pr, Gd, Dy e Ho. Os ETR têm sido determinados principalmente em rochas alcalinas da mina de apatita de Jacupiranga, São Paulo e em rochas vulcânicas da Bacia do Paraná, para estudos geoquímicos, e em amostras geológicas como xenotima, tantalita e zirconita, para fins de exploração mineral. Um sistema de contagem de nêutrons retardados de fissão foi montado para a análise de urânio e tório em materiais geológicos. Os outros elementos mencionados (Sc, Ta, Hf) são determinados geralmente por AANI e espectrometria de raios gama. No caso particular do irídio, um processo de separação radioquímica foi desenvolvido para a análise de sedimentos marinhos da Bacia de Campos (Rio de Janeiro). Carvões da região sul do Brasil foram analisados por AANI para 36 elementos, usando ativações térmicas e epitérmicas.

INTRODUCTION

The industrial development verified in Brazil, mainly in the last three decades, has incremented mineral prospection in order to find energetic alternative sources, to supply internal demand, and to explore metallic ores for utilization in industry.

On the other hand, from an academic point of view, the knowledge of the concentrations of rare earth elements (REEs) and other traces in rocks is of great interest in the field of Geosciences. Trace elements including U, Th, Ba, Sc, Rb, Ta, Cs, Co, Hf and REEs have been extensively used in petrogenetic studies of igneous rocks since they allow the evaluation and the extent of the main processes involved in the generation and differentiation of melts. They are also used in the study of igneous and metamorphic rocks to predict the nature of source materials, giving information about their chemical and mineralogical composition.

Neutron activation analysis has been widely used in the determination of these elements in rocks due to its high sensitivity as well as good precision and accuracy (Vasconcellos & Lima, 1978; Vasconcellos et al., 1986). It is readily capable of simultaneous determination of many elements at parts per million (ppm) and some at parts per billion (ppb) levels, often without destruction of the sample. Table 1 presents the sensitivities for REEs, U and Th by reactor neutron activation analysis both instrumental and with radiochemical separation (Erdtmann & Petri, 1986).

Instrumental neutron activation analysis may be applied for the determination of a wide range of elements in rocks, including most lanthanides. The application of radiochemical separation employing inorganic exchange, ion-exchange, solvent extraction and precipitation improves the detection limits of some elements of the lanthanide group and allows the analysis of other elements, such as iridium.

The Radiochemistry Division of IPEN-CNEN/SP has worked for many years devoted to academic research. Several methods of radiochemical separations for many elements in geological samples have been developed and instrumental neutron activation analysis has been optimized for many applications. The accuracy and precision of these methods have been verified analysing international geological standards like G-2, GSP-1 (USGS) and GS-N (ANRT - Association Nationale de la Recherche Technique) and also standards that are being prepared in our country, such as basalt BB-1 and granite GB-1.

Many works have been performed in collaboration with other research institutions in the Geoscience field, like the Instituto Astronômico e Geofísico da Universidade de São Paulo (Figueiredo & Marques, 1989; Atalla et al., 1985; Mantovani et al., 1985) and the Instituto de Pesquisas Espaciais (Armelin et al., 1989).

More recently, the Radiochemistry Division has been engaged in the analysis of rare earth elements, uranium and thorium in ores such as xenotime, tantalite and zircon for mineral exploration purposes. The analysis of uranium and thorium in granites and basalts has been performed using the delayed neutron counting method (Armelin & Vasconcellos, 1986), for exploration purposes, as well as for geochemical studies. $^{235}U/^{238}U$ isotopic ratios were also determined by this method (Vasconcellos et al., 1987).

Table 1 – Sensitivities of Reactor Neutron Activation Analysis for REEs, U and Th.

	Sensitivities (Erdtmann & Petri, 1986)	
Element	Instrumental Neutron Activation Analysis ($\mu g/g$)	Radiochemical Neutron Activation Analysis ($\mu g/g$)
La	4×10^{-3}	5×10^{-6}
Ce	2×10^{-1}	5×10^{-4}
Pr	7×10^{-2}	1×10^{-5}
Nd	3×10^{-2}	5×10^{-4}
Sm	5×10^{-4}	1×10^{-6}
Eu	2×10^{-5}	6×10^{-8}
Gd	9×10^{-2}	1×10^{-5}
Tb	7×10^{-2}	4×10^{-6}
Dy	1×10^{-4}	8×10^{-8}
Ho	2×10^{-3}	7×10^{-7}
Er	5×10^{-3}	2×10^{-6}
Tm	7×10^{-2}	2×10^{-6}
Yb	2×10^{-2}	2×10^{-6}
Lu	7×10^{-4}	5×10^{-7}
U	2×10^{-3}	2×10^{-5}
Th	1×10^{-1}	5×10^{-6}

Neutron flux assumed: 8×10^{10} n cm^{-2} s^{-1}
Irradiation time: 1 - 60 min.

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, reporting some results obtained for geological standards and for geological samples of economic importance.

NEUTRON ACTIVATION ANALYSIS FOLLOWED BY HIGH RESOLUTION GAMMA-RAY SPECTROMETRY

Principle of the Comparative Neutron Activation Analysis Method

In this method, standards containing known amounts of the elements of interest are submitted to a neutron flux along with the sample and the induced activities 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 element. The amount of this element in the sample is considered as directly proportional to the counting rate of gamma radiation.

Samples and standards being irradiated together at the same conditions of irradiation time and neutron flux, the concentration of a particular element of interest is obtained by comparing the counting rates of the sample and standard spectra. This concentration is calculated from the expression:

$$C^i_a = \frac{A^i_a \times m^i_p}{A^i_p \times M_a} e^{(ta-tp)\, 0.693/T_{1/2}}$$

where A^i_p and A^i_a are counting rates (areas of the peaks) of element *i* in the standard and in the sample, respectively; m^i_p is the mass of element *i* in the standard; M_a is total mass of the sample; $T_{1/2}$ is the half life of the radioisotope, ta and tp are decay times of sample and standard respectively.

Experimental Procedures

Sample preparation

Reference materials, such as standard rocks from the USGS (United States Geological Survey), IAEA (International Atomic Energy Agency) and other institutions, generally were not submitted to any further treatment, since they were already received as fine powders.

The rocks that arrived in coarser fragments were first broken and then crushed to smaller fragments in a porcelain mortar until a reasonable size for grinding in a mechanical agate mortar was obtained.

After grinding the rocks, the treatment was continued in a manual agate mortar, until the powder passed through a 150 mesh nylon sieve. This final treatment was considered necessary to assure a reasonable 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.

Standards

Since the comparative method of activation analysis was always applied in the present work, the problem of choice of standards is a crucial one.

In the case of determination of a great number of elements, about 20 to 30, reference materials such as rocks BCR-1 (basalt), AGV-1 (andesite), GSP-1 (granodiorite) from USGS, GSN (granite) from ANRT were utilized. Special attention was payed to choose among tabulated values from the literature (Gladney et al., 1983; Govindaraju, 1984) those that were classified in the categories of ''recommended values'' or ''consensus values''. values''.

When one element at a time or a small group of elements were determined, such as in the case of analysis of uranium and/or thorium, iridium or the group of the rare earth elements, synthetic standards were prepared at the laboratory.

Aliquots of about 50-100 microliters of the diluted solutions were pipetted onto 1 cm² pieces of Whatman No. 40 analytical filter paper, drying slowly under and infra-red lamp. In the case of determination of a group of elements, such as the REEs, sometimes mixed solutions containing several elements were prepared.

Irradiation

Aliquots of about 50-500 mg of the powdered rock sample were weighed in pre-cleaned Al foils or polyethylene capsules and placed inside aluminum irradiation vessels, specially developed for use in the nuclear reactor IEA-R1.

Samples and standards were submitted to the reactor neutron flux, for periods of time ranging generally from 8 to 72 h, depending on the concentration of the analysed elements.

The geological materials can be submitted to so-called thermal or epithermal irradiation.

In the first case, the samples and standards are submitted to a thermal neutron flux of the order to 10^{12} to 10^{13} n cm^{-2} s^{-1}. In the case of epithermal irradiation, the thermal or slow neutron component of the flux is suppressed by using cadmium foil as shield.

Epithermal irradiation suppresses activation of some strong interfering elements for analysis of the REEs, uranium, thorium and other elements.

Gamma Spectrometry Measurements

In this work two main counting

systems were used: (1) ENERTEC high purity Ge detector coupled to an ORTEC 4096 channel Model 7450 analyzer connected to a Monydata PC 200 Plus microcomputer. The resolution (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 the modified version of FALA program, written in Pascal language. This program locates peak positions and calculates gamma ray energies and net areas. (2) ORTEC hyperpure Ge detector (LEPD) coupled to an ORTEC 4096 channel Model 6240B analyzer connected to a PDP 11/04 minicomputer. The resolution (FWHM) of the system was of 0.58 keV for the 122 keV peak of ^{57}Co.

Multielemental Analysis of Brazilian Coal Samples

Coal samples from several regions of Brazil were analysed by instrumental neutron activation analysis (Atalla & Requejo, 1982).

The objective of these analysis was to check possible polluting elements and also to detect elements of economic importance that could be extracted from the coal ashes. The knowledge of the concentration of several elements, such as uranium, thorium and the lanthanides can also give valuable information about the genesis of mines.

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

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 REEs in gelogical samples, as well as uranium, thorium and other trace elements.

The results are generally obtained with good precision and accuracy, and instrumental neutron activation analysis (INAA) may be applied for the determination of most REEs in geological materials.

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

In the Radiochemistry Division of IPEN, both INAA, with thermal and epithermal neutrons and Radiochemical Neutron Activation Analysis (RNAA) or chemical separation before irradiation have been applied, allowing the determination of most of the group of REEs, U, Th, Ba, Rb, Ta, Hf, Cs, Co and Sc.

Instrumental neutron activation analysis (INAA)

In general, INAA with high-resolution gamma-ray spectrometry allows the simultaneous determination of about eight REEs: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and also U, Th and the other traces cited.

This is a great advantage, compared to other techniques that always require sample dissolution. Besides, INAA utilizes small amounts of material for analysis, which makes it very adequate for the study of separate mineral phases.

Thermal Neutron Activation (TNAA)

This type of activation, that uses as activation particles neutrons, with most probable energy of 0.026 eV, is specially favourable for the determination of Eu, Yb and Lu. The elements La, Ce, Nd, Sm can also be analysed, provided that the concentration of uranium is small compared with the REEs concentration, since the fission of ^{235}U gives origin to the radioisotopes ^{140}La, ^{141}Ce, ^{147}Nd and ^{153}Sm, which are the same utilized for the analysis.

Besides uranium, the elements Na, Fe and Sc can interfere with the NAA of the REEs, due to the high induced activities or to spectral interferences.

Also the elements Th and Ta, even in low concentrations can affect the analysis of Sm, Gd and Yb, also due to spectral interferences.

A good alternative to avoid some interferences in gamma-ray spectra of rare earth elements is the use of low energy photon detectors. Better results are sometimes obtained for Ce, Sm, Gd, Nd, Yb (Figueiredo, 1988), elements which give origin to radioisotopes that emit X-rays or low energy gamma-rays.

Epithermal Neutron Activation (ENAA)

Epithermal neutron activation can be very useful for analysis of REEs, due to the fact that interferences of radioisotopes such as ^{24}Na, ^{59}Fe and ^{46}Sc are considerably reduced.

To carry out this type of irradiation, samples are involved in cadmium shields, to filter low-energy neutrons.

Better results are obtained with ENAA, compared to TNAA, for the elements Sm, La, Ce and Tb.

ENAA is also successfully applied to analysis of REEs in geological materials that contain significant uranium concentrations, because with the filtering of thermal neutrons, the fission of ^{235}U is considerably suppressed and the elements La, Nd and Sm can be determined without interferences.

Using ENAA, generally the elements Sm, La, Ce, Nd, Eu and Tb are determined. In favourable conditions, it is possible also to analyse Gd and Yb.

ENAA is also employed for the analysis of U, Th, Ba, Rb, Ta, Hf, Cs, Co, Sc, since more interferences free gamma ray spectra are obtained, with respect to high activities of radioisotopes such as ^{24}Na and ^{56}Mn.

Analysis with Radiochemical Separation (RNAA)

Radiochemical separations or pre-irradiation separations are employed for the determination of REEs when purely instrumental analysis does not yield satisfactory results.

The most common cases are of spectral interferences, absorption of gamma-rays by the sample, saturation of equipments due to high induced activities and interferences due to uranium fission products.

Pre-irradiation separations are applied mainly in cases of analysis of geological materials containing relatively high (>30 ppm) uranium concentrations. Also for determination of Dy, Pr and Ho, that give rise to short-lived radioisotopes, separations before irradiation are sometimes employed (Saiki, 1989; Figueiredo et al., 1987a).

Radiochemical separations present the advantage that samples are not contaminated by chemical reagents introduced. On the other hand it is necessary to have adequate laboratories and skilled personnel to work with radioactive material.

Sample dissolution can be carried out by means of alkaline or acid digestion. This last approach has been more utilized, lately using extensively teflon bombs, with a mixture of concentrated acids, such as HF, HNO_3 and $HClO_4$.

The methods most commonly utilized for separation of the group of REEs from interferents are ion exchange and retention in inorganic exchangers (Atalla et al., 1985; Figueiredo et al., 1987a,b), precipitation and coprecipitation (Figueiredo & Marques, 1989), solvent extraction (Saiki, 1989).

In sum, the main advantages of employing chemical separation are the improvement in sensitivity of the method, and the possibility of determining all the group of REEs. Group radiochemical separations can also improve detection limits for other trace elements in geological materials.

Analysis of Iridium

The knowledge of the concentration of iridium and other noble metals in geological materials is also very important for geochemical studies as well as for geological prospection.

At the Radiochemistry Division of IPEN, a radiochemical procedure was developed for the determination of iridium in the USGS standard PCC-1 peridotite and in marine sediments from the Campos Basin (State of Rio de Janeiro, Brazil) (Armelin et al., 1989).

The procedure for determination of iridium consisted in irradiating the standard PCC-1 and marine sediments for 8 h, at a thermal neutron flux of 5 x 10^{12} n cm^{-2} s^{-1}, dissolving with a mixture of acids in a teflon bomb and separating interfering elements (REEs, Sc, Na, Fe, Co) by their retention in a cationic resin, Bio Rad AG 50WX8.

The effluent solution containing iridium was concentrated by evaporation and measured in the gamma-ray spectrometer for about 15 h, for quantitative determination of iridium.

The method was applied to the determination of iridium in the PCC-1 standard rock and in samples of sedimentary borehole cores taken at several depths in the Campos Basin, in the continental shelf of Rio de Janeiro, Brazil.

NEUTRON ACTIVATION ANALYSIS FOLLOWED BY DELAYED-NEUTRON COUNTING

Principles of the Method

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

Thermal neutrons can fission only fissile nuclides e.g., ^{233}U, ^{235}U, ^{239}Pu, *while fission of fertile nuclides, such as* ^{238}U and ^{232}Th, can be caused only by fast neutrons.

A technique to discriminate a fissile and fertile nuclide, in order to determine their ratio, is based on the difference between the fission cross section of several nuclides according to the incident neutron energy.

If we consider neutrons of thermal reactor, the energy of the incident neutron can be changed by covering or not the sample with material capable of absorbing lower energy neutrons.

This technique can be used for the determination of uranium and thorium in a sample (Armelin & Vasconcellos, 1986), as well as for the calculation of $^{235}U/^{238}U$ isotopic ratios (Armelin & Vasconcellos, 1986; Vasconcellos et al., 1987).

Experimental

Sample or standard were packed into polyethylene envelopes. Cadmium was used as filter for uranium and thorium analysis when both elements were to be determined while composite cadmium and boron carbide was chosen as filter for the determination of $^{235}U/^{238}U$ ratios.

Irradiations were carried out in the IEA-R1 research reactor, in a position where the neutron flux had the following intensities: thermal flux = 4.4×10^{11} n cm^{-2} s^{-1}, epithermal flux = 4.0×10^{10} n cm^{-2} s^{-1}, fast flux = 1.6×10^{11} n cm^{-2} 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 made up of pre-amplifier, monochannel analyser, scaler and timers.

Irradiation, decay and counting times were always 60, 20 and 60 seconds respectively.

RESULTS AND DISCUSSION

Analysis of Rare Earth Elements, Uranium, Thorium and Other Traces

The results obtained for G-2 and GS-N geological standard rocks are presented in Table 2. They show a good reproducitibility of INAA and pre-separation methods (Marques et al., 1989). The accuracy of the results was also good with relative error lower than 15% for the majority of REEs. The precision and the accuracy were not so good for some results of Lu probably due to the small quantity of this element in samples with concentrations lower than 0.1 ppm.

Significant differences between the results obtained by the INAA method and by the chemical procedure were not observed. This fact may be explained by the low concentration of U in these rocks. The chemical procedure is particularly useful for the analysis of uraniferous rocks.

Table 2 – Concentrations (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 (*)	This work (**)	Gladney et al., 1983	This work (*)	This work (**)	Govindaraju, 1984
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 ± 0.09	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 ± 0.01	0.113 ± 0.024	0.22 ± 0.04	0.19 ± 0.03	0.2

(*) - Results obtained by INAA and RNAA (for Nd and Gd)
(**) - Results obtained using chemical separation before irradiation
(-) - Analysis not made

Table 3 – Results (ppm) for the REEs and other traces in the Brazilian Geological Standards GB-1 and BB-1.

Element	GB-1		BB-1	
	This work	Literature	This work	Literature
La	66 ± 3	63[a]	32 ± 2	31.8[a]
Ce	119 ± 4	108[a]	68 ± 4	63.3[a]
Nd	38 ± 6	39[a]	32 ± 5	32.7[a]
Sm	6.6 ± 0.5	7.8[a]	6.7 ± 0.6	8.1[a]
Eu	0.98 ± 0.05	0.97[a]	1.60 ± 0.09	1.6[a]
Gd	3.9 ± 0.1	3.9[a]	5.6 ± 0.6	6.0[a]
Tb	0.40 ± 0.02		0.88 ± 0.07	
Dy	1.8 ± 0.2	1.6[a]	5.3 ± 0.1	5.1[a]
Yb	0.73 ± 0.09	0.61[a]	2.6 ± 0.2	2.5[a]
Lu	0.12 ± 0.01	0.079[a]	0.42 ± 0.04	0.34[a]
U	5.8 ± 0.5		1.42 ± 0.05	
Th	36.3 ± 0.5		7.4 ± 0.1	
Ba	634 ± 11	15-850[b]	531 ± 15	65-767[b]
Rb	236 ± 4	224[b]	76 ± 2	
Ta	4.30 ± 0.01		1.21 ± 0.01	63[b]
Hf	5.6 ± 0.2		4.83 ± 0.08	
Cs	6.9 ± 0.1		1.20 ± 0.07	
Co	3.20 ± 0.08	2-10[b]	32.8 ± 0.3	30-40[b]
Sc	2.22 ± 0.08		29 ± 3	35[b]

a. Dutra (1984); b. Linhares (1987)

The results obtained for the REEs and other trace elements in the Brazilian geological standards GB-1 and BB-1 (Table 3) (Figueiredo & Marques, 1989) also agreed well with literature values (Dutra, 1984; Linhares, 1987) (relative errors lower than 13%). With the exception of Gd, the other elements were determined by thermal and epithermal INAA.

The analysis of REEs and other traces in 158 samples of volcanic rocks from Paraná Basin was performed, in the Radiochemistry Division, for geochemical studies (Marques, 1988). In Table 4 are shown, as illustration, the results obtained for one basic rock (concentration of $SiO_2 <$ 55%) and one acid rock (concentration of $SiO_2 >$ 63%) from the Paraná Basin, and also the results obtained by INAA and RNAA for a carbonatite from the apatite mine of Jacupiranga. It can be seen that data were obtained with good precision, with standard deviations less than 15%.

In Table 5 are presented the results obtained for the concentration of REEs, uranium and thorium in some Brazilian uraniferous minerals (xenotime, tantalite and zircon). In this case, to correct the contribution due to fission products from uranium, samples were irradiated together with a natural uranium standard. It can be seen that this method allowed the determination of ten REEs (La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho and Yb), U and Th, with good precision (standard deviations less than 20%).

Analysis of Iridium

In order to check the accuracy and the precision of the method, 14 determinations of iridium were made in the PCC-1 standard rock. An average of 5.4 ± 1.4 ppb was obtained, which shows a reasonable agreement with literature values (Govindaraju, 1984, Ir = 5.2, Gladney et al., 1983, Ir = 4.8 ± 1.9).

Sixteen samples of sedimentary borehole core taken at several depths in the Campos Basin were analyzed, and the iridium concentrations ranged from (0.61 ± 0.10) ppb to (4.49 ± 0.68) ppb, which did not categorize an anomaly.

Table 4 – Results (ppm) for the REEs and other traces in Brazilian Geological Samples.

Element	Volcanic rocks from the Paraná Basin		Carbonatite from the apatite mine from Jacupiranga	
	Acid	Basic	INAA(*)	RNAA(**)
Sc	17 ± 2	39 ± 4	14.1 ± 0.8	15 ± 2
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
Ce	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	22 ± 1	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	1.7 ± 0.2	2.20 ± 0.20
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	-	-

(*) - Instrumental neutron activation analysis
(**) - Radiochemical neutron activation analysis
(-) - Analysis not made

Table 5 – Results (ppm unless indicated) for the concentration of the rare earth elements, uranium and thorium in some Brazilian uraniferous minerals.

Element	Xenotime	Tantalite	Zircon
La	25896 ± 326	416 ± 21	47 ± 7
Ce (%)	4.0 ± 0.4	0.15 ± 0.02	0.090 ± 0.004
Pr	4715 ± 576	-	36 ± 4
Nd	-	-	626 ± 96
Sm	2815 ± 365	56 ± 9	292 ± 12
Eu	37 ± 2	4.4 ± 0.2	3.3 ± 0.4
Tb	-	-	69 ± 5
Dy	3067 ± 75	27 ± 4	748 ± 64
Ho	655 ± 15	-	235 ± 27
Yb	2456 ± 215	-	2790 ± 70
U (%)	0.14 ± 0.02	0.025 ± 0.004	0.13 ± 0.01
Th (%)	1.2 ± 0.1	0.027 ± 0.003	0.98 ± 0.08

(-) - Analysis not made

Analysis of Uranium and Thorium by Delayed Neutron Counting

The limits of detection (from Kaiser's criterion; Kaiser, 1970) and limits of determination (from Long and Winefordner's criterion; Long & Winefordner, 1983) in conditions established for uranium and thorium analysis are shown in Table 6.

The accuracy and the precision of the method were evaluated by means of the analysis of geological samples provided by the IAEA, through an intercomparison programme for uranium and thorium analysis. Results obtained in this study for two Brazilian thorium ores are shown in Table 7.

Table 6 – Limits of detection and limits and determination for uranium and thorium analysis by neutron activation analysis and delayed-neutron counting.

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

Detection limits and determination limits were calculated for 1.5 g samples.

Table 7 – Results for the non destructive and simultaneous analysis of uranium and thorium in IAEA thorium ores and in Brazilian thorium ores by neutron activation analysis and delayed-neutron counting.

Sample	U (ppm)			Th (%)		
	This work	Pszonicki (1983)	Relative error %	This work	Pszonicki (1983)	Relative error %
S-14	(26 ± 2)	29	10.3	(0.067 ± 0.007)	0.061	9.8
S-15	(80 ± 2)	85	5.9	(0.037 ± 0.02)	0.363	1.9
S-16	(433 ± 5)	445	2.7	(1.71 ± 0.08)	1.68	1.8
Monazite	(1300 ± 24)		-	(5.0 ± 0.1)		-
Monazite with low Th content	(330 ± 10)		-	(1.11 ± 0.04)		-

Means and standard deviations for 6 determinations.

Since the method is much more sensitive for the determination of uranium than of thorium, the precision of uranium analysis is very little affected by the presence of thorium in the sample. It was considered that counting statistics is the main source of error in the precision of uranium and thorium analysis. Also it was considered that the accuracy of uranium analysis is independent of the presence of thorium in the sample, but reliable results for thorium depend on the U/Th ratio of the sample.

Once the delayed neutron counting system was assembled and the analytical parameters were entirely established, the method was applied for geochemical studies (Marques et al., 1987) as well as for geological prospection.

A few thousand samples were analyzed in the total.

One of the studies conducted was a collaboration with the Instituto de Geociências da Universidade de São Paulo. The study is part of the IAEA Research Contract: "Uranium Distribution in Brazilian Granitic Rocks-Identification of Uranium Provinces".

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