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BY EPITHERMAL NEUTRON ACTIVATION ANALYSIS**

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ABSTRACT

Uranium, in thorium matrixes or in minerals and ores containing thorium, is determined by epithermal neutron activation analysis (ENAA). In some minerals and ores, such as monazite sands, the analysis can be carried out by purely instrumental means with no chemical separation of uranium or thorium from the irradiated matrix. For thorium compounds matrixes with very low uranium content, a rapid radiochemical separation method, based on the retention of uranyl ion on anion exchange resins, is first carried out before counting the gamma-ray peaks for ^{239}U in multichannel analysers, coupled to NaI (TI) scintillators or to Ge-Li detectors.

INTRODUCTION

Uranium in thorium matrixes is often analysed by nonactivation methods. Activation of the sample with thermal neutrons followed by counting without chemical separation, cannot be fully exploited due to the large amounts of fission products formed by thermal neutrons with ^{235}U or formed by interaction with the ^{233}U that appears as daughter product in the decay chain started with ^{233}Th.

Ankner[1] applied X-rays fluorimetry to determine uranium in thorium oxide down to a detection limit of 0.02%. Hirokawa and Gotô[2] used the same method and were able to analyse amounts of uranium in thorium corresponding to 100 micrograms of uranium. Fluorimetry has been applied by Desai and Sudhalata[3] who obtained good results for the determination of uranium in thorium nitrate by applying solvent extraction and using ethylenediaminetetracetic acid to complex the thorium. Martres and Burastew[4] analysed monazite samples by a polarographic method with a detection limit corresponding to 50 parts per million of uranium.

Delayed neutrons technique has been apllied by Amiel[5], in the case of samples containing both elements, i. e., uranium and thorium, but interferences caused by the presence of thorium increase when the amount of thorium is very large as compared with the uranium to be analysed.

Activation by epithermal neutrons and counting of the ^{239}Np formed has been applied by Meyer[6] for traces of uranium and thorium in geological materials. The method was not applied for the case of thorium matrixes in which the amount of thorium was very large as compared with the amount of uranium.

The advantages of using epithermal neutrons for some activation analysis problems have been pointed out by Steinnes[7]. This type of activation should be patircularly favourable for

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uranium determination due to the high ressonance integral of uranium. Steines and Brune[8] analysed uranium, by activation with epithermal neutrons, in silicate minerals, with uranium and thorium present at tracer levels. Some iron ores were also analysed for uranium by the same authors, with good results.

Turkowsky et al.[9] also used epithermal neutrons for activation of uranium samples followed by chemical separation of the uranium by solvent extraction and ion exchange resins. Separation of uranium was not quantitative, requiring a chemical yeld determination in each analysis.

In this paper a method is presented for analysis of uranium in thorium matrixes and in thorium minerals or ores, making use of epithermal neutrons for activation of the sample and counting the 74.7 keV gamma rays of ^{239}U, with Ge-Li detectors or NaI scintillators. The method can be non-destructive in some cases, as the case of monazite sands and some other ores. For determination of traces of uranium in thorium salts of high purity a rapid radiochemical separation method, based on the behaviour of uranium, thorium and rare earths in sulfuric acid media, and anion exchange resins[10], was developed[11].

EXPERIMENTAL

Equipment - Gamma-ray spectra of irradiated samples and standards were obtained by means of a 400 channels analyser, "TMC", Model 406-2, coupled to a well type NaI(Tl) scintillator (Harshaw), 7.6 cm by 7.6 cm, or by a Hewlett-Packard, HP 5402A MCA/Basic System 4096 channels analyser coupled to a 25.6 cm^3 Ge-Li detector with FWHM equal to 2.1 keV for the ^{137}Cs 0.661 MeV peak.

Reagents - All reagents used were of analytical grade. The standards for uranium were prepared by dissolving uranium sesquioxide in nitric acid in order to have a final concentration of 10 mg of uranium per ml of solution. The other required standards were prepared from this stock solution.

The anion exchange resin used was of trade mark Bio-Rad AG-2-X8, 200-400 meshs. The original resin, in chloride form, was first treated with a 2 molar solution of sodium hydroxide, washed with deionized water and next treated with a 2 molar solution of ammonium sulfate. The anion exchange resin, in sulfate form, was used for retention of the uranyl ions during the analysis with chemical separation.

Standards - Standards for uranium were prepared by transfering volumes corresponding to 10, 25 or 100 microliters of uranyl nitrate stock solutions to filter paper discs of about one square centimeter area and drying the papers under infrared heat.

Preparation of Samples - Minerals, ores and thorium salts, in solid form, were placed in polyethylene envelopes which were again packed in another envelope of the same material. For the case of non-destructive analysis, with direct counting of the irradiated samples, only the external envelopes were removed. The samples, packed as described, were put inside cadmium cylinders with about 0.8 cm internal diameter and 2 cm length. The thickness of the cadmium sheets used to make the cylinders corresponded to 0.1 cm.

In the case of the analysis of thorium salts solutions, aliquots were taken and transfered

to the filter papers which were dried as before, or the solutions were irradiated in quartz ampoules, which were involved in cadmium sheets of 0.1 cm thickness.

NON-DESTRUCTIVE ANALYSIS

In order to test the epithermal neutron activation analysis without chemical separation, in the case of uranium ores, monazite sands of known content of uranium and thorium, were analysed. For the samples of monazite sands containing more than 0.1% of uranium, the amounts of samples analysed varied from 30 to 50 mg. For samples with very low uranium content, amounts from 100 to 150 mg were taken.

The samples were prepared for irradiation as described and irradiated in a reactor position were the thermal neutron flux corresponded to 5×10^{12} n/s.cm.^{2} and the gold cadmium ratio was equal to 3.52. The uranium standard used had masses equal to 100 μg. Irradiation time was equal to 30 seconds, cooling and counting times were equal to 15 and 10 minutes, respectively. The Ge-Li detector was used for counting. Results are shown in Table 1.

TABLE 1

Determination of Uranium in Monazite
Sands, Without Chemical Separation

Sample	U_3O_8 (%)	
	ENAA*	Gravimetric
1	0.22 ± 0.02 **	0.22
2	0.16 ± 0.01	0.15
3	0.026 ± 0.002	<0.05

* Epithermal neutron activation analysis.
** Standard deviations for 4 replicates.

The possibility of analysing uranium in thorium matrixes, without chemical separation, was checked by analysing high purity thorium oxalate, with less than 4 ppm of uranium, to which increasing amounts of uranium was added. Previous experiments had shown that the purely instrumental analysis, with no chemical separation of uranium, would not be feasible for thorium samples of very low uranium content. For this reason the checking of the instrumental method, for thorium matrixes, was made in such a way that the addition of uranium to thorium would give samples with, at least, 125 ppm of uranium.

For the prepared samples the relative amounts of thorium (as oxalate) to uranium varied from 10:1 to 8 000:1. Irradiation time was equal to 30 seconds and counting started 5 minutes after the end of irradiation. The Ge-Li detector was used, requiring a counting time equal to

20 minutes. Results are presented in Table 2.

TABLE 2

Analysis of Thorium Oxalate Samples with Increasing
Amounts of Uranium, Without Chemical Separation

Thorium Oxalate (mg)	Uranium Added (μg)	Uranium Found (μg)
40	5	5.0 ± 0.7*
40	10	9.5 ± 0.7
40	25	24.1 ± 1.8
40	50	48.5 ± 1.9
40	100	99.0 ± 3.2
20	100	97.5 ± 3.0
10	100	97.8 ± 2.8
5	100	98.4 ± 2.7
1	100	99.1 ± 2.7

* Counting standard deviations.

The values of uranium found as compared to uranium added may indicate some neutron self-absorption on irradiation, but the difference between uranium found and uranium added, in the majority of cases, is much less than 5%.

ANALYSIS WITH RAPID RADIOCHEMICAL SEPARATION

Ores and Minerals

For samples in which the proportion of thorium to uranium was higher than 8 000:1 a separation of uranium from the irradiated matrix was required. The general method of analysis for the minerals and ores was as follows: samples with masses from 30 to 200 mg were irradiated in the cadmium cylinders for a time from 10 seconds to 10 minutes, depending on the concentration of uranium on the samples. To the irradiated samples the amount of 0.5 mg of uranium (as uranyl nitrate) was added as carrier and the sample was melted with potassium fluoride in a platinum crucible. The melted sample was cooled to room temperature, 1.5 ml of concentrated sulfuric acid was added and the ,mass was then heated up to formation of fumes of sulfuric anhydride, cooled again to room temperature, treated with hot water and transferred to a 100 ml beaker. One or two drops of a 10% solution of potassium permanganate were added followed by 5 to 10 mg of thiourea crystals to reduce the permanganate ion. The pH of the solution was ascertained to 2.5, the final volume was made to about 80 ml and the solution was passed through an anion exchanger column, in sulfate form, at a rate of 12 to 15 ml per minute, applying slight suction to regulate the flow as desired. The ion exchange resin was then washed with 30 ml of a 0.2 molar solution of sulfuric acid. The resin was transferred to a

counting vial and counted using the NaI scintillator. The results of application of such a method to uranium minerals containing thorium at about the same level, supplied by the U.S.Geological Survey, are presented in Table 3.

TABLE 3

Determination of Uranium in Minerals
After Rapid Radiochemical Separation

Sample	Amount Taken (mg)	Found Uranium (expressed as U)	Existing Uranium (expressed as U)
Diabase (W1)	120	0.56 ± 0.06 * (ppm)	0.54 to 0.65(ppm) (a)
Dunite (DTS—1)	220	0.0040 ± 0.0008(ppm)	0.0037(ppm) (b)

* Standard deviation for 5 replicates

(a) Reference 17.

(b) Reference 13.

Analysis of Thorium Salts

In the case of thorium matrixes, the step of percolation of the irradiated sample through the anion exchanger showed that, due to high amount of thorium in the sample, some ^{233}Th would remain in the resin even after washing it with a mixture of hydrochloric and hydrofluoric acid. To reduce the amount of the remaining ^{233}Th in the resin, inactive thorium oxalate was used to dilute the ^{233}Th in the irradiated sample. This addition was made during the first step of the chemical treatment of the irradiated sample.

Thorium salts samples with masses corresponding to 10 or 40 mg of thorium oxide were used for analysis. After irradiation, the samples were transferred to a beaker containing a mixture formed by thorium oxalate, equivalent to 360 mg of thorium oxide, 1.5 ml of concentrated sulfuric acid and 0.5 mg of uranium carrier (as uranyl nitrate). The mixture was heated up to formation of fumes of sulfuric anhydride, cooled to room temperature, and water was then added. From there on the same previous procedure as applied to the minerals and ores, was followed. In the case of thorium matrixes, the washing of the ion exchange resin, which should be placed in polyethylene columns, was made with 30 ml of a 0.2 molar solution of sulfuric acid, plus 30 ml of a 10 molar solution of hydrochloric acid and, finally, by 20 ml of a solution 9 molar in hydrochloric acid and 1 molar in hydrofluoric acid, in order to eliminate the ^{233}Pa formed by beta decay of ^{233}Th[12]. The ion exchange resin was then transferred to a counting vial and counted in NaI scintillator. The total time spent on the separation corresponds to 45 to 50 minutes.

In order to check the chemical yield, irradiated standards of uranium were added to a mass of thorium sulfate, corresponding to about 400 mg of thorium oxide, and the thorium sulfate was submited to the described chemical separation procedure. The mean value for the recovery, in seven replicate analysis, was equal to 95.1% ± 0.8. For each actual analysis this

recovering factor was used to correct for the chemical yield.

The described method was applied to samples consisting of solid thorium oxicarbonate, nitric solutions of the thorium oxicarbonate and thorium oxalate. The content of uranium in the oxicarbonate samples was determined by the fluorimetric method of Desai and Sudhalata[3], giving a value of 9.6 parts per million in uranium with a standard deviation of 0.3 for 12 replicates. In the case of the nitric solutions of thorium oxycarbonate, water in the solution did not introduce any appreciable error due to eventual neutron thermalization of the epithernal neutrons, what was checked by adding increasing amounts of uranium to the samples. Results for the various samples are shown in Tables 4, 5 and 6. Masses used for irradiation, m, as well as irradiation and counting times, t_i and t_c, respectively, are listed in each Table.

TABLE 4

Determination of uranium
in thorium oxicarbonate

Sample	Uranium	
	(μg)	(ppm)
1	0.212	10.6
2	0.199	9.9
3	0.206	10.3
4	0.203	10.1
Mean:		10.2 ± 0.4

m = 20 mg.
t_i = 2 m.
t_c = 4 m.
Detector: NaI scintillator.

TABLE 5

Analysis of thorium oxycarbonate
(Samples Irradiated as Nitric Solution)

U Added (µg)	U Found (µg)	Uranium in the Sample (µg)	Uranium in the Sample (ppm)
	0.851	0.851	9.3
	0.935	0.935	10.3
0.04	0.924	0.884	9.7
0.10	0.980	0.880	9.7
0.40	1.375	0.975	10.7
0.60	1.463	0.863	9.5
1.00	1.902	0.902	9.9
		MEAN:	9.9 ± 0.5

$m = 91$ mg (0.5 ml)
$t_i = 2$ m.
$t_c = 4$ m.
Detector: NaI scintillator.

TABLE 6

Determination of Uranium in Thorium Oxalate

Mass of Sample (mg)	Added Uranium (µg)	Found Uranium (µg)	Uranium in the Sample (µg)	Uranium in the Sample (ppm)
20		0.055	0.055	2.8
20		0.041	0.041	2.0
40		0.101	0.101	2.5
40		0.096	0.096	2.4
20	0.01	0.053	0.043	2.2
20	0.02	0.067	0.047	2.3
20	0.04	0.076	0.036	1.8
20	0.05	0.093	0.043	2.1
20	0.06	0.102	0.042	2.1
20	0.08	0.117	0.037	1.8
20	0.10	0.138	0.038	1.9
			Mean:	2.17 ± 0.35

$t_i = 4$ m (NaI scintillator)
$t_c = 20$ m (Ge-Li detector)

FIGURE 1

Curve A : gamma-ray spectra of anion-exchange after retention of uranium from oxalate irradiated sample.

Curve B : standard of ^{233}Th.
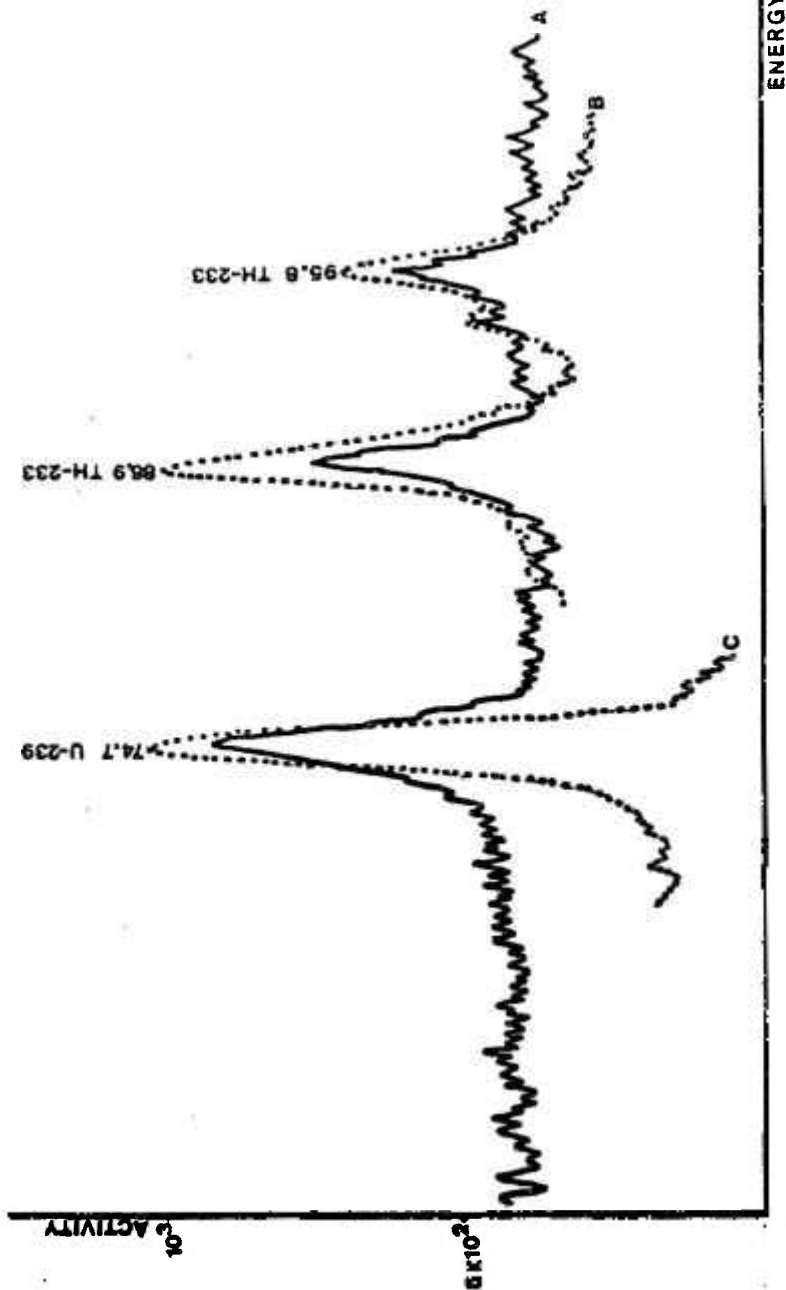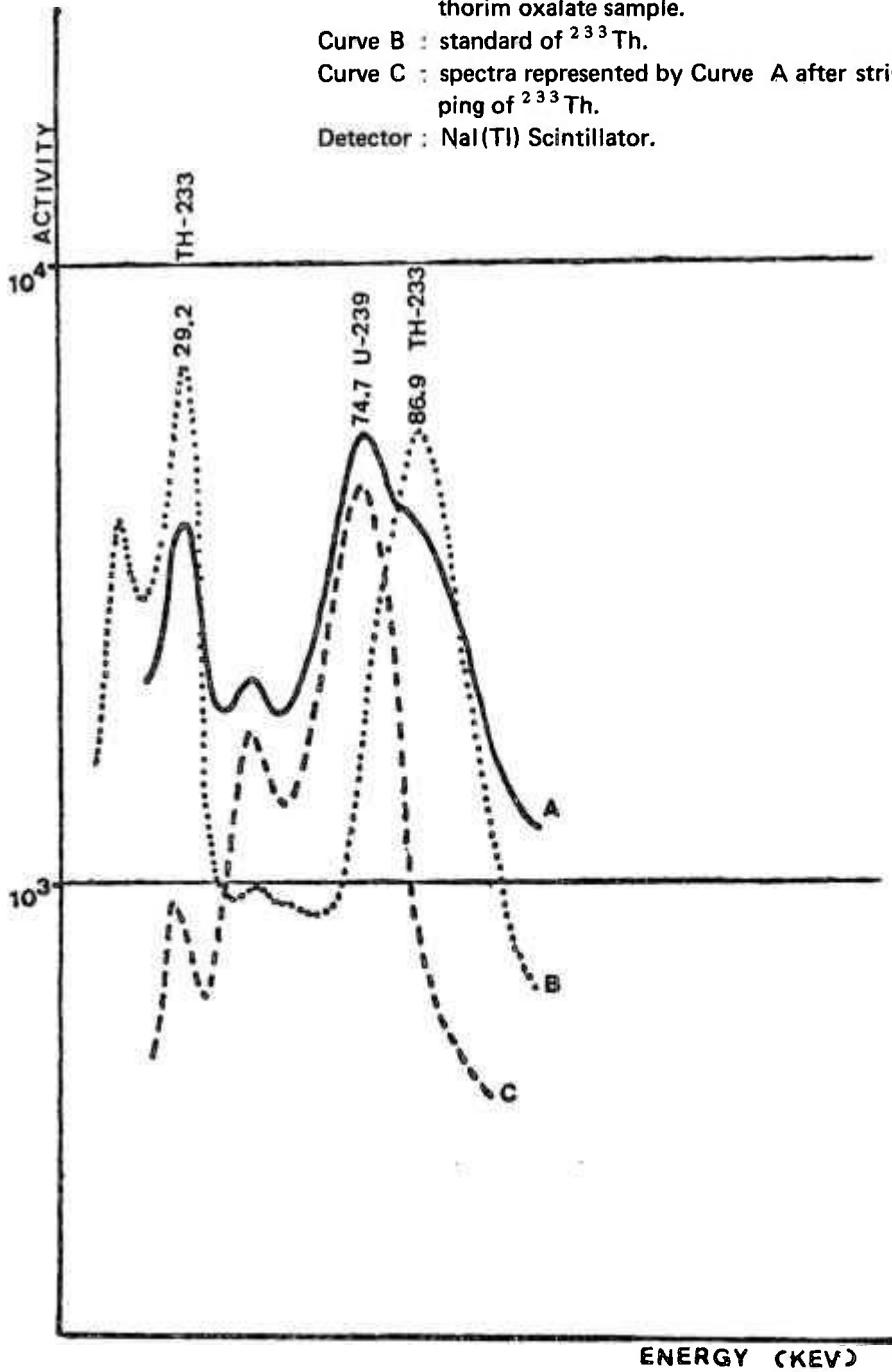Curve C : standard of ^{239}U.
Detector : Ge-Li.

FIGURE 2

Curve A : gamma-rays spectra of anion-exchange resin after retention of uranium from irradiated thorim oxalate sample.

Curve B : standard of ^{233}Th.

Curve C : spectra represented by Curve A after stripping of ^{233}Th.

Detector : NaI(Tl) Scintillator.

Due to the slight contamination of the ^{239}U with ^{233}Th retained in the anion exchange resin, counting of the resin should be made by using Ge-Li detectors. In this way the small amount of ^{233}Th does not interfere with the determination of uranium, since the resolution of the equipment is such that the ^{239}U peak of energy 74.7 keV is well separated from the ^{233}Th peak of energy 86.9 keV, as shown in Figure 1. However, NaI scintillator can also be used if a stripping of the ^{233}Th contribution is made. In order to do this a standard of thorium is irradiated together with the samples and, after the sample spectrum has been obtained, the spectrum of ^{233}Th is accumulated in a negative way untill the ^{233}Th peaks of 29.2 keV disappears (see Figure 2). The stripping technique does not introduce any appreciable error in the results as can be seen by the data in Tables 4, 5 and 6.

DISCUSSION

Precision of the method can be evaluated by means of the small values for standard deviations for the data of the various analysed samples, Tables 1 to Table 6. Accuracy can be calculated by comparison of found values for uranium with "true" values, when available, as will be shown.

In accordance with Mc Farren et al.[14] and Eckshlager[15] an analytical method can be accepted as "excellent" if the "total error", $\underline{E}$, calculated as

$$E = 100 (D + 2S) /u$$

is smaller than 25%. $\underline{D}$ is the absolute value of the mean error (difference between true value and found mean value, statistically significantly different from zero, at 95% level); $\underline{S}$ is the standard deviation and $\underline{u}$ the true value.

"Total errors" for the method applied to the various samples whose results have been listed in Tables 1, 3, 4 and 5 are presented in Table 7. Total errors were calculated only for those samples for which reliable indications were available concerning the "true" value of the uranium content of the sample. When possible, literature data were used as source for "true" values, but only in those cases for which these data were not too scattered, over a large range, varying too much from one laboratory results to another.

TABLE 7

"Total Errors E" For Results of Analysis
Listed on Tables 1, 3, 4 and 5

Sample	Table	E(%)
Monazite 1	1	18.2
Monazite 2	1	13.3
Diabase (W1)	3	11.5 – 23.1
Dunite (DTS–1)	3	43.3
Thorium oxycarbonate	4	8.3
Thorium oxycarbonate (solution)	5	10.4

Only in the case of the Dunite sample the total error was larger than 25% but smaller than 50%, what allows one to classify the method, for this sample, as "acceptable", in accordance with Mc Farren et al.[14] and Eckslager[15]. Since the amount of uranium in this sample is very small, on the level of parts per bilion, the criterion of "acceptable" for this sample, meaning a total error smaller than 50%, but larger than 25%, seems reasonable.

The values for the standard deviation for the results of the analysis of solid thorium oxycarbonate or of the same material in solution, Tables 4 and 5, indicate a good precision for the method. Accuracy is also good if one compares the 10.2 ppm and 9.9 found for those two samples with the amount of uranium found by fluorimetric method, i.e., 9.6 ppm.

The results for the analysis of thorium oxalate, Table 6 were not confronted with the ones obtained by some other method. However, the linearity of the results of analysis of samples with increasing amounts of uranium, indicates that the value found for the uranium content of the sample to which no uranium was added, is correct. The straight line passing through the points corresponding to the results of Tables 5 and 6, obtained by the least-squares method, are, respectively

$$y = 0.8970 + 1.0088\,x \tag{1}$$

$$y = 0.0948 + 0.9230\,x \tag{2}$$

in which x is the mass of uranium added to the samples and y the amount of uranium found.

An analysis of variance for the lines (1) and (2) shows the existence of linear regression at a confidence level of 95%, meaning that the value found for uranium, in those samples to which no uranium was added, indicates the amount of uranium in the original samples.

Sensitivity of the method was calculated by measuring the activity of uranium standards irradiated during 10 minutes with an epithermal neutron flux of the order to 10^{11} n/cm^2.s., which was the flux used to perfom the analysis presented in this paper. A quantitative "determination limit" was calculated in accordance with Currie[16] giving the result of 2×10^{-10} g, in the absence of interferences and using NaI scintillation for counting. The sensitivity can be increased by irradiating for times longer than 10 minutes. Longer irradiations are specially indicated in the cases were the analysis requires chemical processing since, during this step, the activity for ^{239}U decreases to about one fourth of the activity at the end of irradiation.

The advantages of using epithermal neutrons activation analysis for uranim can be seen in the gamma rays spectra obtained with Ge-Li detector for a sample of monazite sand and irradiated with and without cadmium covering, Figure 3. Although the peaks are well resolved in both cases, the total activity induced in the sample irradiated without the cadmium covering is too high, resulting in a dead time of the multichannel analyser larger than 30%. The peaks resolution for those samples of high total activity is larger than for the low total activity samples and quite often the high activities samples produced distorted gamma ray spectra. The high total activity is mainly due to the gamma rays of the various radioisotopes of other elements present in the samples, besides uranium, and this high activity is avoided by impeding the activation of these other elements, by irradiating with epithermal neutrons. For instance, the interference caused by the gamma peaks of ^{233}Th, ^{153}Sm and ^{155}Sm is much larger in the

case of irradiation of the samples without cadmium covering than when irradiation takes place with the cadmium shield, as can be seen by the spectra in Figure 3.
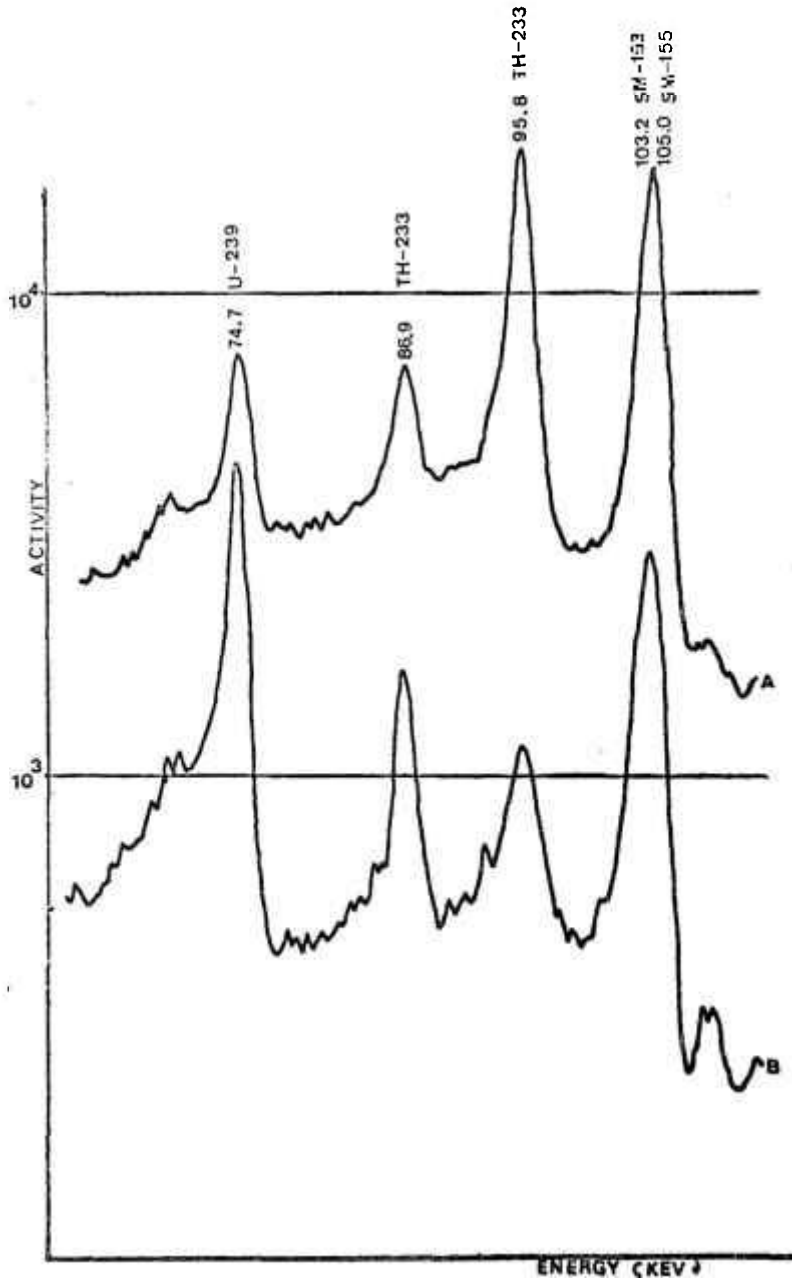
FIGURE 3 : gamma-rays spectra, obtained with Ge-Li detector, of irradiated monazite sands.
Curve A : sample irradiated without cadmium covering.
Curve B : sample irradiated with cadmium covering.

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RESUMO

É feito o estudo da determinação de urânio em matrizes constituídas por minerais e minérios de tório, bem como por sais de tório, usando análise por ativação com neutrons epitérmicos. Em alguns minerais e minérios tais como areias monazíticas, a análise pode ser feita por método puramente instrumental sem separação química do urânio ou tório da matriz. Para matrizes constituídas por sais ou outros compostos de tório contendo uma proporção muito baixa de urânio faz-se uma separação radioquímica rápida do ^{239}U antes da contagem do radioisótopo em cintilômetros de NaI(Tl) ou detectores de Ge-Li. A separação é feita por retenção do íon uranila em resinas trocadoras de anions.

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