*Journal of Radioanalytical and Nuclear Chemistry, Articles, 97/2 (1986) 293–300*

# NEUTRON ACTIVATION ANALYSIS OF THORIUM AFTER SEPARATION OF $^{233}$Th BY ISOTOPIC ION EXCHANGE*

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(Received February 5, 1985)

The procedure for thorium determination in ammonium diuranate (ADU) and rocks, by neutron activation analysis after chemical separation of $^{233}$Th, is presented. The separation of $^{233}$Th from the interfering radioisotopes is based on the retention of $^{233}$Th by a resin saturated with thorium (isotopic exchange) and on the elution of the interfering radioisotopes by a dilute solution of thorium in 0.5M HCl (ion exchange). The determination limit of thorium in rocks and ADU was found to be 0.56 and 9.3 μg, respectively, when a 20% relative standard deviation was assumed as acceptable. The highest value obtained for the determination limit of thorium in uranium compounds, on account of the $^{234}$Th activity present, is discussed.

## Introduction

Even though an analysis by neutron activation without chemical separation may now be used to solve many analytical problems, there are some cases in which the interferences in the gamma-ray spectrum of the radioisotope of interest, caused either by the presence of other radioisotopes or by the very high matrix activity, prevent such pure instrumental analysis.

In this case, it is necessary to use a radiochemical separation procedure which depends on the sample, on the elements to be analyzed and on the accuracy and precision required for the analysis. If the radioisotopes of interest have a relatively short half-life, as in the case of $^{233}$Th (22.3 m), the possibilities of a chemical separation are limited, since the sensitivity of the analysis diminishes.

Among the techniques used for radiochemical separations, isotopic exchange must be cited. Comprehensive papers about the possibilities of isotopic exchange in radioanalytical chemistry have been presented by TERA and MORRISON,[1] and by PETERS and DEL FIORE.[2] These authors associated isotopic exchange to ion exchange for the radiochemical separation of many elements, and they point out the feasibility of the method by emphasizing its simplicity and quickness in the case of the separation of short-lived radioisotopes.

*From a thesis submitted by C. S. Munita to the "Instituto de Pesquisas Energéticas e Nucleares (CNEN/SP)" University of São Paulo, in partial fulfillment for a Doctor of Science's Degree. Work supported by the Brazilian Atomic Energy Commission.

*Elsevier Sequoia S. A., Lausanne*
*Akadémiai Kiadó, Budapest*

In a previous paper MUNITA and ATALLA[3] presented the conditions for the highest isotopic exchange between $^{233}Th$ present in the solution and thorium saturating the resin. In order to determine the conditions which allow the highest exchange, some of the interfering radioisotopes in the $^{233}Th$ gamma rays spectrum were also considered. Generally, all the elements that activate very easily under a thermal neutron flux should be considered as interfering, especially when a short half-life radioisotope is to be used for the activation analysis.

The effects of four variables on thorium isotopic exchange, namely, thorium and HCl concentrations in the loading and washing solutions, concentration of interfering ions in the loading solution and resin cross-linkage degree were also analyzed.[3] The experiments were carried out through a four variable experimental design in order to allow a statistical interpretation. It was possible to infer which conditions allow a maximum isotopic exchange and, at the same time, to minimize the retention of interfering ions in the resin. The most favourable conditions found for the separation are: 0.50 mg Th/ml in the 0.5M HCl load and washing solutions; the concentration of the interfering ions did not present any effect between 1.0 and 10 $\mu$g/ml.; 4% DVB resin.

In the present paper, the possibilities of the technique for the determination of thorium in rocks and in uranium compounds are presented. Four samples of standard rocks, supplied by the United States Geological Survey and Geological Survey of Japan (GSJ), were analyzed, namely: GSP–1 (granodiorite), G–2 (granite), JB–1 (basalt), and BCR–1 (basalt), whose thorium content was determined by many researchers and the results were compiled by FLANAGAN.[4]

Samples of ammonium diuranate (ADU), provided by the Division of Chemical Engineering of this Institute, whose thorium content was previously determined by spectrophotometry were also analyzed.

Before neutron activation, the ADU samples were pretreated in order to separate most of the uranium from thorium. Uranium separation has been achieved by means of pure TBP as extracting agent.[5-7] After the uranium separation, thorium was co-precipitated with ferric hydroxide.

The purpose of this paper is to increase the possibilities of the neutron activation analysis of thorium and, at the same time, to propose a fast analytical method for the determination of microquantities of thorium.

## Experimental

*Equipment.* A gamma-ray spectrometer composed of a 400-channel "TMC" model 404–6 multianalyzer, coupled to a NaI(T1) scintillation crystal, well-type 7.5 cm× 7.5 cm, Harshaw. Automatic sample collector, "Fractomat", Buchler Instruments. Glass columns with 0.5 cm diameter and 5.0 cm length.

*Reagents.* All reagents were of analytical grade: 0.5M HCl solution containing 0.50 mg Th/ml. $^{234}Th$ tracer, prepared according to *ABRÃO*.[8] Thorium is sorbed in alumina when 0.3N HF uranyl nitrate solutions are percolated through alumina. Bio-Rad AG 50W X–4

resin, 100–200 mesh saturated with thorium, as indicated in a previous paper.[3] Thorium standard solutions: a standard solution with 1.00 mg Th/ml was prepared. From this solution, some more diluted ones were also prepared. Thorium standards for irradiation were obtained by drying 25 or 50 μl aliquots of standard solutions on a small piece of filter paper.

*Determination of thorium in rocks*

In order to develop and test the method, GSP–1 (granodiorite), G–2 (granite), BCR–1 (basalt) and JB–1 (basalt) rocks were used.

*Procedure.* The dissolution of the rocks was accomplished by means of a concentrated $HNO_3$-HF mixture. The solution was heated until dryness and some drops of HCl and 10% $H_2O_2$ were added to the residue; after heating, 5 ml water was added and $Fe(OH)_3$ was precipitated by means of a 10% NaOH solution. The precipitate was dissolved with 1M HCl and the ferric hydroxide was reprecipitated by means of ammonium hydroxide. The precipitate was filtered under vacuum through a small filter paper. After drying, the filter with the precipitate was placed in a polyethylene envelope and simultaneously irradiated with a thorium standard at a neutron flux of $5 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot s^{-1}$. After irradiation, the precipitate was dissolved with 5 ml of 0.5M HCl containing 0.50 mg Th/ml. This solution (loading solution) was percolated through the thorium saturated resin; afterwards, 50 ml of a solution with the same composition as the loading solution, except for the $^{233}Th$, was also percolated through the column at a flow rate of 2 ml/min. After washing, the resin was placed in a counting tube and the $^{233}Th$ activity was compared with that of the standard.

*Separation yield.* In order to calculate the thorium separation yield, the procedure described above was applied to samples to which known amounts of $^{234}Th$ tracer were added before the dissolution. The yield was calculated by comparing the activity of $^{234}Th$ recovered and the activity added. The average yield found in five determinations was 99.0±0.2%.

*Linearity of results.* The linearity of the method was studied in the range of 0.50 to 15.0 μg of thorium. The PCC–1 (peridotite) rock, which contains only 0.01 ppm[4] of thorium, was used in these experiments. Increasing known masses of thorium were added to 100 mg samples before its dissolution. The procedure described above was applied and the results, corrected according to the average yield value, are presented in Table 1. By applying the least squares[9] method the following equation $y = bx + a$ was obtained:

$$y = 1.0006x + 0.0154$$

where x is the thorium mass added and y is the value found. The linear correlation coefficient is 0.9997. The t test[10] applied to the parameters a (intercept) and b (slope) in order to verify the accuracy of the method showed that, at a 0.10 significance level, the values $a = 0$ and $b = 1$ may be assumed.

*Sensitivity of the method.* In order to calculate the determination limit, a relative standard deviation of ±20% was assumed as acceptable. The results shown in Table 1 and the following equation:[10,11]

$$s_{x'} = \pm 0.20 \left(\frac{y'-a}{b}\right) = \pm \frac{s_o}{b}\left(1 + \frac{1}{n} + \frac{(y' - \bar{y})^2}{b^2\,(\Sigma x_i^2 - n\bar{x}^2)}\right)^{1/2} \quad (1)$$

were used for the calculation, and the value of 0.56 $\mu$g of thorium was found

where $y'$ – result when the mass of thorium in the sample is the determination limit,
$x'$ – determination limit,
$s_{x'}$ – standard deviation of the determination limit,
$s_o$ – regression standard deviation,
$\bar{x}$, $\bar{y}$ – average of the n values $x_i$ and $y_i$, respectively,
$n$ – number of results.

The detection limit $x''$ was calculated by assuming as positive any result above twice the standard deviation, that is, $x'' > 2\,|s_{x''}|$. The value $x''$ was obtained after solving

$$x'' = \left(\frac{y'' - a}{b}\right) > 2\left|\frac{s_o}{b}\left(1 + \frac{1}{n} + \frac{(y'' - \bar{y})^2}{b^2\,(\Sigma x_i^2 - n\bar{x}^2)}\right)^{1/2}\right| \quad (2)$$

It was found that masses equal to or smaller than 0.22 $\mu$g of thorium cannot be detected by means the method proposed.

*Rock analyses.* 100 mg sample was used for the analysis and the procedure described above was followed. The results and the recommended values[4] are presented in Table 2. The standard deviation of the results was calculated by means of the variance $s_o^2$ which characterizes the dispersion of the experimental values $y_i$ with respect to the straight line.

Table 1
Results obtained in analyses of rocks to which increasing masses of thorium were added. Samples: 100 mg PCC–1 (peridotite) rock

| Th added ($x_i$), $\mu$g | Th Found ($y_i$), $\mu$g |
|---|---|
| 0.50 | 0.49 |
| 1.25 | 1.28 |
| 1.75 | 1.86 |
| 2.00 | 1.91 |
| 2.50 | 2.48 |
| 3.00 | 2.96 |
| 4.00 | 4.10 |
| 6.00 | 5.92 |
| 8.00 | 8.10 |
| 10.0 | 10.2 |
| 15.0 | 14.9 |

*Determination of thorium in uranium compounds*

An ADU sample stored for more than 5 years, containing less than 1 ppm of thorium, was used for the experiments carried out to develop the method.

Table 2
Results for thorium determination in rocks supplied by USGS. Sample mass = 100 mg

| Rock | Source | Thorium concentration, ppm | |
|---|---|---|---|
| | | This work | Recommended value[4] |
| GSP–1 (Granodiorite) | USGS | 103.6±1.3<br>104.1±1.3<br>103.3±1.3 | 104 |
| G–2 (Granite) | USGS | 25.7±1.3<br>24.3±1.3<br>25.5±1.3 | 24.2 |
| JB–1 (Basalt) | GSJ | 10.7±1.3<br>10.0±1.3<br>10.3±1.3 | 9.4 |
| BCR–1 (Basalt) | USGS | 7.1±1.3<br>6.7±1.3<br>6.5±1.3 | 6.0 |

Thorium determination in uranium compounds by means of this technique is more complicated than in other kinds of samples, since it is necessary to take into account the presence of the natural uranium radioactive daughters, among them $^{234}$Th.

There is a partial overlapping of the main peaks of $^{233}$Th and $^{234}$Th gamma-ray spectra when a NaI(T1) detector is used. As the final activity measured for the activation analysis comes from both, $^{234}$Th and $^{232}$Th, the subtraction of the $^{234}$Th spectrum is necessary. By doing this operation, an error is introduced in the analysis. On the other hand, by means of the measurement of the activity of $^{234}$Th in the sample, it is possible to calculate the separation yield of thorium for each determination. In order to do it, the correspondence between $^{234}$Th activity and the uranium mass must be calculated. This correspondence was established by measuring the activities corresponding to the energy of $^{234}$Th (93 keV) associated with increasing masses of ADU. The ADU was placed in counting tubes to which 1 ml of 5M $H_2SO_4$ was added. By integrating the area under the peak at 93 keV, the activity of $^{234}$Th was determined. For ADU masses up to 400 mg, there is a linearity between activity and mass, but for higher masses of ADU a shading effect caused by uranium was observed.

*Analytical procedure.* 10 ml of 5M HCl and 1 g of ADU were introduced into a separatory funnel. The solution was shaken for 15 m with 10 ml of pure TBP. The aqueous phase was separated and the operation was repeated twice. The aqueous phases were washed with 10 ml of chloroform in order to extract the residual TBP, whose solubility in water is 0.039%.[12] The aqueous phase was then evaporated until near dryness and a few drops of concentrated $H_2SO_4$ and $HNO_3$ were added. After heating, 10 ml $H_2O$ and 2.5 mg of iron (as $FeCl_3$) were added and the ferric hydroxide was precipitated by means of ammonium hydroxide. From this point on, the procedure was the same as that described for the rocks.

Before irradiation, the gamma-ray spectrum of the radioisotopes coprecipitated with ferric hydroxide was recorded in the first half of the multichannel analyzer memory, where it was kept. By comparing the $^{234}$Th activity after separation with the initial activity of $^{234}$Th in the sample, the separation yield was established. The average yield of thorium separation in 9 experiments was 97.8±0.7%. After the precipitate irradiation, the gamma-ray spectrum was recorded in the second half of the analyzer memory, and the preserved spectrum was subtracted. The activity of $^{233}$Th obtained after subtraction was compared with that of the standard irradiated simultaneously with the ferric hydroxide precipitate.

*Linearity of results.* The linearity of the method was verified by means of the addition of increasing, known masses of thorium to several portions of 1 g of ADU sample containing less than 1 ppm of thorium. Thorium was added as thorium chloride solution. The procedure described above was followed and the results obtained are presented in Table 3. By applying the least squares method[9] the following equation was obtained:

$$y = 1.002x - 0.260.$$

The correlation coefficient calculated for the straight line is 0.9995.

Like the case of the rocks, the t test applied to the linear parameters showed that the values a = 0 and b= 1 may be assumed at a significance level of 0.10.

*Sensitivity of the method.* The sensitivity of the method was calculated by means of the results presented in Table 3 and Eq. (1), as in the case of the rocks.

Assuming as acceptable the same relative standard deviation adopted for the rocks, the determination limit of 9.3 μg of thorium was found for ADU samples. The detection limit, assuming as positive any value above twice the standard deviation was found to be 3.8 μg of thorium.

*Practical application.* The method was applied for thorium determination in ADU samples, previously analyzed by spectrophotometry.[13] Three analyses were performed for each sample and the values obtained are shown in Table 4. The standard deviation of each result was calculated as for the rock analysis.

Table 3
Results obtained for analyses of ADU to which increasing masses of thorium were added. Samples: 500 mg ADU

| Th added ($x_i$), μg | Th found ($y_i$), μg |
|---|---|
| 10 | 9 |
| 15 | 15 |
| 25 | 26 |
| 50 | 49 |
| 60 | 61 |
| 75 | 74 |
| 100 | 98 |
| 125 | 128 |
| 150 | 149 |

Table 4
Results of thorium analyses in ADU samples

| Sample | Thorium concentration, ppm | |
|---|---|---|
| | This work | Spectrophotometry |
| 1 | 25.8±1.8<br>25.2±1.8<br>25.9±1.8 | 24.4 |
| 2 | 19.8±1.8<br>19.5±1.8<br>20.0±1.8 | 19.1 |
| 3 | 13.9±1.8<br>13.8±1.8<br>13.7±1.8 | 12.2 |

*Discussion.* The separation of thorium from rocks by the method proposed presented a good reproducibility, allowing analysis without tracer addition. As spectrum subtraction was not needed a low determination limit was obtained.

The t test applied to the straight line parameters showed that the method is not affected by systematic error. Since it is possible to determine 0.56 $\mu$g of thorium with a ±20% error, it may be concluded that a good sensitivity is achieved.

The results of standard rock analysis, listed in Table 2, confirmed the reproducibility and accuracy of the method.

It must be noted that the method may not be applied to all kinds of mineral samples. For instance, if the percentage of lanthanides is high, prior separation of thorium from this group of elements, before the coprecipitation of thorium with ferric hydroxide, may be necessary. The study of the performance of the method for thorium determination in rocks like monazite is the aim of further work.

In the case of uranium compounds, a previous separation of thorium from uranium is necessary, because of the mass disparity and of the interference between $^{233}$Th and $^{239}$U gamma-ray spectra. $^{234}$Th follows thorium in the separation and its activity can be used to calculate the separation yield. In order to use $^{234}$Th as a tracer for this calculation, it was necessary to determine the correspondence between $^{234}$Th activity and uranium or ADU mass used for the analysis. It was experimentally confirmed that a shading effect caused by uranium by masses up to 400 mg of ADU is not observed. By extrapolating, the $^{234}$Th activity in 1 g of ADU, the mass used for the analyses was calculated. It was possible to verify that the reproducibility of the separation yield is good and that the thorium loss is approximately 2%.

The results listed in Table 4 are slightly higher than those obtained by means of spectrophotometry, but they are compatible if the standard deviation is taken into account.

The sensitivity of the method proposed is lower for thorium determination in uranium compounds (9.3 $\mu$g) than for rock samples (0.56 $\mu$g). This limitation is caused by the

subtraction of $^{234}Th$ gamma rays spectrum from the final gamma rays spectrum ($^{233}Th$ + $^{234}Th$). Even so, the method proposed can be used to control thorium percentage in nuclear grade uranium, since ASTM specifications[14] recommend that thorium content in uranium must be less than 10 ppm.

Even though the suitability of the method for other kinds of samples was not investigated, it seems that it is applicable in most of the cases.

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The authors wish to express their thanks to Dr. F. W. LIMA by the encouragement throughout the work.

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