

DETERMINATION OF THORIUM AND URANIUM ISOTOPES IN THE MINING LIXIVIATION LIQUOR SAMPLES

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ABSTRACT

The alpha spectrometric analysis refers to determination of thorium and uranium isotopes in the mining lixiviation liquor samples. The analytical procedure involves sample preparation steps for rare earth elements, thorium and uranium separation using selective etching with hydrofluoric acid and further radiochemical separation of these using TRU chromatographic resins (Eichrom Industries Inc. USA) besides electroplating of the isolated radionuclides. An isotopic tracer is used to determine the overall chemical yield and to ensure traceability to a national standard. The results are compared to results obtained for the same samples by Becquerel laboratory. We improved the method looking for reproducibility and isotopes isolation as required by alpha spectrometry and the method showing effective in analysis of mining liquor.

1. INTRODUCTION

Radionuclides of both the uranium and thorium decay series can be often present to a high degree in the materials occurring in mining activities. It has been observed that mining milling and processing of uranium and thorium bearing minerals alter the natural constituents of radionuclides and sometimes lead to enhanced radiation exposures [1; 2]

The present study was aimed at evaluating the activity concentration of radionuclides of the uranium and thorium series in order to verify the natural activity concentration unbalance resulted from mining lixiviation of minerals rich in rare earths using radioanalytical techniques.

In radiochemistry, separation techniques are very common, for example, when a radionuclide is purified of other radioactive elements [3]. Techniques used for separation include coprecipitation, liquid-liquid extraction, ion exchange and extraction chromatography. In some cases, two or more of these techniques are combined.

In this work, the radiochemical procedure consists of two steps performed by precipitation techniques and extraction chromatography using TRU chromatographic resin column.

The alpha spectrometric analysis was applied to determination of thorium and uranium isotopes in the mining lixiviation liquor samples. The analytical procedure involves sample preparation steps for rare earth elements, thorium and uranium separation using selective etching with hydrofluoric acid and further radiochemical separation of these using TRU

chromatographic resins (Eichrom Industries Inc USA) besides electroplating of the isolated radionuclides.

In order to account for the inevitable loss of the sample during separation, a specific isotope or tracer is added to the sample. A tracer represents the addition to an aliquot of sample a known quantity of a radioactive isotope that is different from that of the isotope of interest but expected to behave the same. Activity results for the samples are normally corrected assuming the tracer is homogeneously mixed and is brought into chemical equilibrium with her.

The adaptation of the separation method will be done from the development of separation methods previously used in other analyzes using alpha-spectrometry [4,5]. The results are compared to results obtained for the same samples by Becquerel Laboratory, Canada.

2. MATERIAL AND METHODS

2.1. Reagents and Apparatus

All reagents used were analytical grade. Certified radionuclides were obtained from the Instituto de Radioproteção e Dosimetria (IRD), Rio de Janeiro, Brasil and the certified absolute activity level for each of them is: ^{230}Th 10.047 kBq and ^{232}U 4.26 kBq. Working solutions were prepared by transferring a known weight of the tracer followed by volumetric dilution in an appropriate working concentration.

The alpha-spectrometry measurements were carried out with Canberra PIPS (passivated ion implanted planar silicon) detectors. The alpha-energy calibration and the measurement of counting efficiency of the detector were performed using a source from Analytics Inc. Analytics maintains traceability to the National Institute of Standards and Technology through Measurements Assurance Programs as described in USNRC Regulatory Guide 4.15, Rev. 1 [6]. The spectrometer used was a Canberra Model S509 Genie 2000 Alpha Analyst.

2.2. Methodology

50 mL of the liquid samples (leach liquor) were initially heated to dryness at 200 ° C. The solid obtained was then treated with 50 mL of cold water (75 mL of concentrate hydrochloric acid + 25 mL of concentrate nitric acid) and taken to dryness. The solid obtained was taken up in 50 mL of hydrofluoric acid (60%) and taken to dryness. This solid was dissolved in deionized water and filtered. The solid collected by the filter was dissolved in 30 mL of concentrate nitric acid to obtain the nitrate of the retained elements: rare earths and thorium and uranium. It was taken to dryness and the solid obtained was dissolved in 10 ml of 1 M HNO_3 solution.

The solution obtained was eluted on a TRU chromatographic resin column (Eichrom Industries Inc. USA). The rare earths were separated by eluting them with 0.05 M HNO_3 . The

thorium was eluted with 30 mL of aq. 0.25 M HCl and uranium with 0.1 M of ammonium oxalate solution. Flowchart for obtaining Th and U separately is presented in Figure 1.

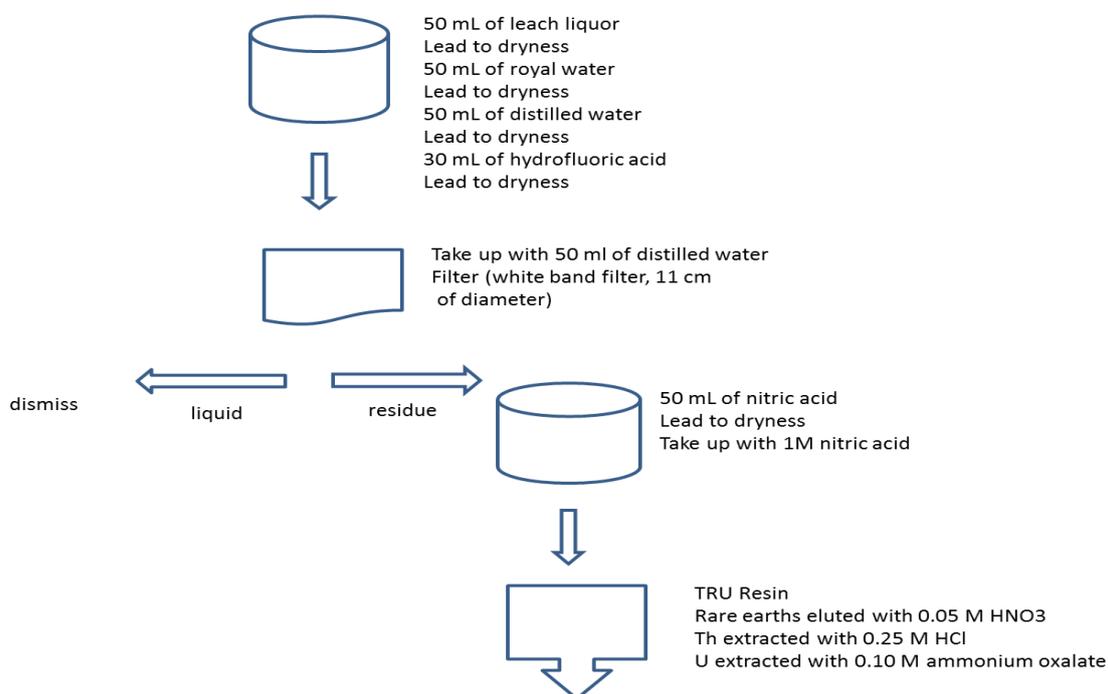


Figure 1: Flowchart for obtaining thorium and uranium, separately, from a Leach liquor solution

2.3 Determination of Uranium and Thorium

Determination of U and Th was carried out by using alpha-spectrometry. Solutions of isolated radionuclides were evaporated to dryness and dissolved in a mixture of nitric acid, 10 mL, and perchloric acid, 5 mL. The samples were evaporated to dryness and retaken in a solution of 3 M H_2SO_4 and 0,8 M $(NH_4)_2SO_4$ with the pH adjusted in a range of 1.2-2.8 (Thymol blue indicator) with concentrate NH_4OH . Electrodeposition disks were prepared from 0,90 mm thick sheets of stainless steel, by machining sections to 24.8 mm diameter planchets. The electroplating was done at an applied current of 1.0 A for U and Th [7].

3. RESULTS AND DISCUSSION

The alpha spectra obtained in the sample analyses are shown in the Figure 2, spectrum for the thorium, and Figure 3, spectrum for the uranium. As can be seen, in the spectra is shown that the radiochemical procedure utilized it was successful in the separation of thorium and uranium.

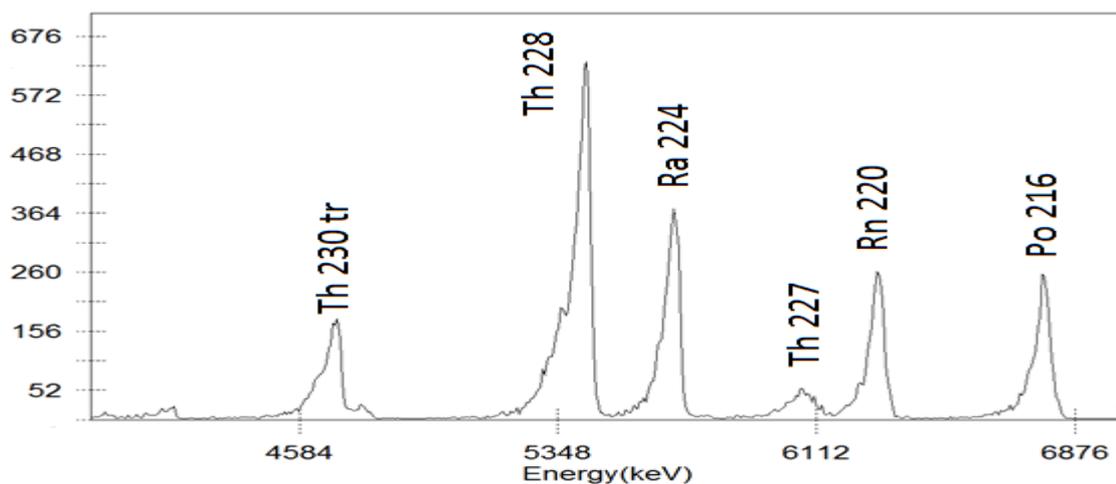


Figure 2: Alpha spectrum obtained after use of the radiochemical procedure showing the characteristics peaks for the isotopes in the ^{232}Th series for the sample.

Results obtained in the analysis for quantitative determination of thorium and uranium isotopes using the experimental procedure for separation and isolation of the Th and U isotopes by precipitation with hydrofluoric acid and using the TRU resin in column chromatography are presented in Tab. 1, for column leaching, and Tab. 2, for agitated leaching.

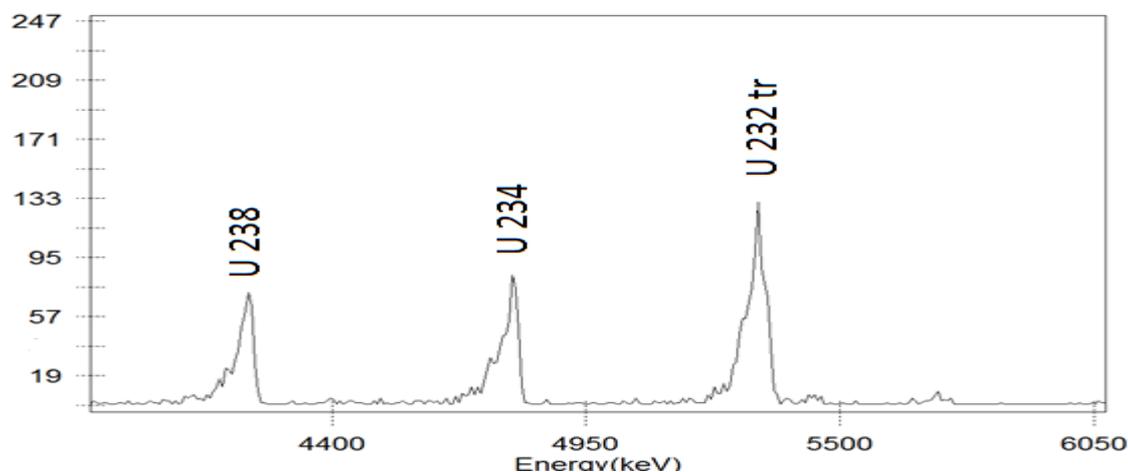


Figure 3: Alpha spectrum obtained after use of the radiochemical procedure showing the characteristics peaks for the uranium isotopes for the sample.

In both tables are presented the activity concentration results obtained by us and those obtained by Becquerel laboratory for the same samples. This being done we can compare the result which allows us an analysis of such form to make an evaluation of the procedure by us used. As can be seen there is a discrepancy between the various isotopes in analyses, suggesting that different methods were used in the determinations by the two laboratories. Besides, for the same isotopes different values for activity concentration were determined by the two laboratories. This means that different chemical yields were obtained when using the different methods. The most interesting result is for the reason ($A_{\text{U-238}}/A_{\text{U-234}}$) that in natural

minerals, in secular equilibrium, is approximately 1. The results for CDTN are in according with this approximation ($0.43 \pm 0.04 / 0.6 \pm 0.1$ for column leaching and $1.79 \pm 0.09 / 2.0 \pm 0.2$ for agitated leaching). In the CDTN case, we performed experiments involving data points with three replicates and the results are presented with standard deviation.

One must also consider the method used in leaching (column or agitation) since the results for activity are different in the determination methods used by the two laboratories. For example, ^{232}Th does not appear in column leaching and appears in agitated leaching. When we analysis the results obtained for CDTN laboratory in the case of ^{228}Th the activity is much higher in column leaching than that in agitated leaching and the activities for ^{238}U and ^{234}U are much larger in the case of agitated leaching than those for column leaching.

Table 1: For column leaching the results of activity for thorium and uranium isotopes are inserted in Tab.1

Isotopes	Unit	CDTN	BECQUEREL Lab
		Activity concentration	
Thorium 232	Bq/L	nd	<0,6
Thorium 227	Bq/L	$2,4 \pm 0,4$	1,20
Thorium 228	Bq/L	$20,6 \pm 1,7$	6,78
Thorium 230	Bq/L	nd	<5,0
Radio 224	Bq/L	$11,1 \pm 2,5$	ND
Radon 220	Bq/L	$9,4 \pm 0,8$	ND
Polonius 216	Bq/L	$9,5 \pm 0,9$	ND
Uranium 238	Bq/L	$0,43 \pm 0,04$	<1,38
Uranium 234	Bq/L	$0,6 \pm 0,1$	ND
Uranium 235	Bq/L	nd	<0,50

nd = not appeared in alpha spectrum. ND = not determined

Table 2: For agitated leaching the results of activity for thorium and uranium isotopes are inserted in Tab.2

Isotopes	Unit	CDTN	BECQUEREL Lab
		Activity concentration	
Thorium 232	Bq/L	$1,49 \pm 0,02$	1,8
Thorium 227	Bq/L	$1,7 \pm 0,2$	<0,50
Thorium 228	Bq/L	$9,6 \pm 2,9$	5,50
Thorium 230	Bq/L	nd	<5,0
Radio 224	Bq/L	$5,9 \pm 1,1$	ND
Radon 220	Bq/L	$4,91 \pm 0,02$	ND
Polonius 216	Bq/L	$4,9 \pm 0,2$	ND
Uranium 238	Bq/L	$1,79 \pm 0,09$	5,4
Uranium 234	Bq/L	$2,0 \pm 0,2$	ND
Uranium 235	Bq/L	nd	<0,50

nd = not appeared in alpha spectrum. ND = not determined

As can be seen in Figure 4 the daughter ^{232}Th alpha emitters appear in the spectrum, Figure 2. The half-life of the father is much greater than those of the children, which would guarantee the balance in the activities. However, this is not observed in relation to ^{228}Th and its children, for which there is a difference in the activities of the isotopes, which is more accentuated in the case of column leaching.

With this in mind, it is possible to establish that the isotopes can be retained in the column or removed from the mineral selectively.

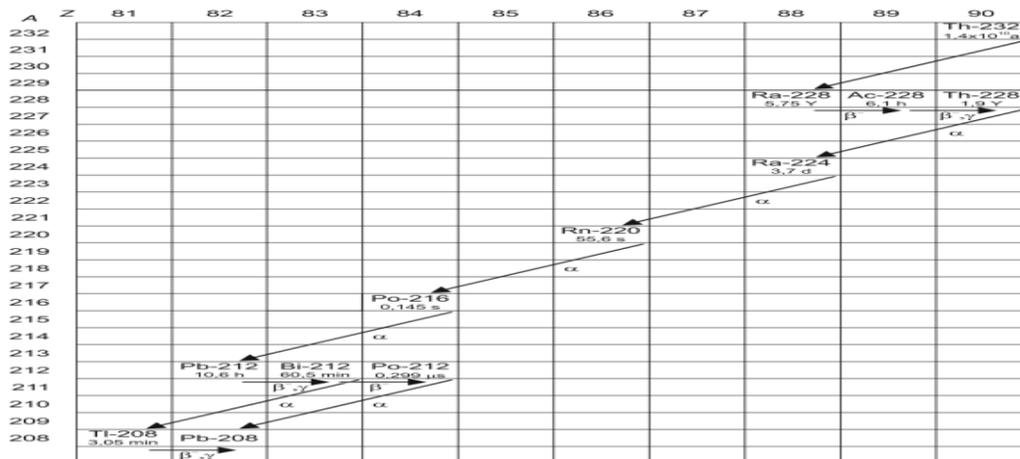


Figure 4: The Thorium series

90-Th-232

Half-life: 14 billion years
 E_{α} (keV) I_{α} (%)
 3947.2 21.7
 4012.3 78.2

86-Rn-220

Half-life: 55.6 seconds
 Mode of decay: alpha into Po-216
 E_{α} (keV) I_{α} (%)
 6288.08 99.886

90-Th-228

Half-life: 1.9 years
 Mode of decay: alpha into Ra-224
 E_{α} (keV) I_{α} (%)
 5340.36 27.2
 5423.15 72.2

84-Po-216

Half-life: 0.145 s
 Mode of decay: alpha into Pb-212
 E_{α} (keV) I_{α} (%)
 6778.3 99.9981
 6050.78 70
 6089.88 27

88-Ra-224

Half-life: 3.7 days
 Mode of decay: alpha into Rn-220
 E_{α} (keV) I_{α} (%)
 5448.6 5.06
 5685.37 94.92

84-Po-212

Half-life: 0.299 μs
 Mode of decay: alpha into Pb-208
 E_{α} (keV) I_{α} (%)
 8784.37 100

4. CONCLUSIONS

The determination of Th and U in leach liquor samples was done using an adapted separation method. The results were compared with results obtained by the Becquerel laboratory. The

results presented significant differences, what can be attributed to application of methods different of analysis that result in different chemical yields.

The results for the activities concentrations determined by us were justified and it was possible to establish that the differences between agitated and column leaching may be due to the selectivity of retention and removal of the isotopes from the mineral.

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