

THORIUM: DETERMINATION BY CDTN, BRAZIL

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One of the tasks of the Radiochemical Sector, CDTN/CNEN, Brazil, is to meet the clients' analytical needs. The Sector has been facing the challenges of determining several elements in diversified matrixes from all over the country since the sixties. It has been giving analytical support to universities, industries, environmental monitoring programs, research institutes. Due to the growing need to determine thorium isotopes through the years it was necessary to work out a routine procedures. Nowadays the determination of thorium consists of a well established routine whose procedures are applied to grouped samples according to their kind, physical state, matrix interference, detection limits and number of samples. This paper describes the methods used by CDTN to determine ^{232}Th by neutron activation analysis and ^{230}Th and ^{228}Th by radiochemical separations and alpha spectrometry in several matrixes.

1 Introduction

Thorium is not a very rare element, comprising 0.001 - 0.002% of the earth's crust. It is found in many minerals, usually associated with rare-earths (RE), and often with titanium, niobium, tantalum, and uranium. Two of the richest thorium minerals are thorite, a thorium silicate containing about 60% thorium, and thorianite, a thorium-uranium oxide containing 90%, but both are quite rare and have no practical importance. The only important commercial, primary source is monazite, a RE-thorium orthophosphate containing from 1.4 to 28 % of thorium. The average ThO_2 content of about 6% in Brazilian monazite makes the country one of the major suppliers of the world production [1, 2, 3].

In Brazil there are about 15,000 miners employed in thorium mining. Their work consists of basically two activities: – the monazite mining and its processing in order to obtain RE chloride and thorium as a by-product, – and the mining and processing of other minerals with Th and U associated to the crystal structure. This processing transforms these radionuclides and daughters into products, by-products or waste [3]. Besides commercial interests, it is important to emphasise thorium radiological toxicity. The occurrence of thorium isotopes and the daughters of natural series of ^{232}Th is an environmental problem, which should be given special attention to, mainly in Brazil and India [2, 4].

2 Thorium analysis demand

The CDTN, Centro de Desenvolvimento da Tecnologia Nuclear (Nuclear Technology Development Centre), sponsored by CNEN, Comissao Nacional de Energia Nuclear (Nuclear Energy National Commission), is located in Belo Horizonte, capital of the Brazilian state of Minas Gerais. The Centre began its activities in 1960 right after

starting up of the TRIGA MARK I IPR-R1 research reactor. At that time the need for the determination of natural thorium had just began in pyrochlore, a niobium ore that would be exported. The X-ray fluorescence and delayed neutron techniques were then applied. The mineral uranium prospecting associated with thorium occurrence increased the necessity to determine thorium. Meanwhile, several analytical techniques such as colorimetry, potentiometry, gravimetry and volumetry to determine thorium have been also worked out. Their application depended on the thorium concentration, matrix interference, and the time requested to obtain analytical results.

Nevertheless in the seventies it was necessary to determine thorium at low levels, ranging from 0.05 to 20 $\mu\text{g L}^{-1}$ in water and leachates and 0.05 to 20 $\mu\text{g g}^{-1}$ in residues. The instrumental neutron activation analysis that had been applied to determine other elements, was applied to ^{232}Th analysis by measuring short half-life ^{233}Th and long half-life ^{233}Pa . Radiochemical procedures were introduced afterwards, in order to reduce the matrix interference. At the same time, the interest in determining thorium in environmental samples increased. The Monitoring Environmental Programs co-ordinated by CDTN in nuclear facilities and mining industries diversified the matrixes to be analysed: pasture, air filters, biomaterial and food.

In the eighties the radiochemical method to separate ^{228}Th and ^{230}Th and the measurement by alpha spectrometry were introduced. The matrixes analysed were surface, drinking and groundwater, and air filters.

Nowadays the procedures applied by the Radiochemical Sector to determine ^{232}Th , ^{230}Th and ^{228}Th [6, 7, 8, 12, 13, 14] in several matrixes are well established in order to meet analytical needs from all over the country, giving analytical support to industry, mining, research centres and environmental monitoring programs.

3 Thorium radiological hazard

The thorium isotopes are important to radiological protection due to their nuclear characteristics [4, 5]: ^{232}Th is a natural radionuclide, 100% natural abundance, alpha emitter (4.01 and 3.95 MeV) with the half-life of 1.39×10^{10} years, and it is the parent substance of the 4n or thorium series; ^{228}Th is one of the ^{232}Th 's daughters and alpha emitter (5.42 and 5.34 MeV) of the half-life of 1.9 years; ^{230}Th is one of ^{238}U 's daughters and alpha emitter (4.68 and 4.61 MeV) of the half-life of 7.5×10^4 years [4, 5]. The Comissao Nacional de Energia Nuclear in Brazil classifies these radionuclides as Class 1, the most restricted group among the classes of radiotoxicity [5]. One of the main radiological risks of thorium isotopes is their capacity to remain in bones for 8,000 days of biological half-life [8, 9, 10].

4 Determination of ^{232}Th , ^{230}Th and ^{228}Th

^{232}Th by Neutron Activation Analysis.

The neutron activation (NA) process consists of exposing a chemical element to a neutron flux in which the reaction (n, γ) produces a new radioactive nuclide [4, 5]. At CDTN the irradiation is performed in the TRIGA MARK I IPR-R1 reactor. This reactor is equipped with three facilities for irradiations: the rotary specimen rack outside the core, a central thimble and a pneumatic tube transfer system. The rotary rack facility (the thermal neutron flux at 100 kW is $6.6 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$, the fast neutron flux is 4.7

$\times 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}$) is often used for irradiating the routine samples because it is able to irradiate 40 samples in the lower layer and 40 more in the upper one simultaneously. This facility is used in neutron activation technique for comparative and parametric methods.

To determine ^{232}Th (cross-section 7.3 barns) an exposure to the thermal neutron flux is required for a period of time long enough to produce the activity of at least $2.5 \times 10^4 \text{ Bq}$ of ^{233}Th . The reaction (n, γ) produces ^{233}Th , with half-life of 22.4 min and main γ -rays 86.6, 162.3, 169.3, 459.2 keV. After β -particle emission, ^{233}Pa , with half-life of 27 d and main γ -rays of 299.9(15%), 311.8(100%), 340.3(4%) keV, is produced. Due to these nuclear characteristics ^{232}Th can be determined by means of short half-life ^{233}Th and long half-life ^{233}Pa [4, 5]. By means of ^{233}Th , the measurements are carried out after the shorter half-life radionuclides decay – 30 minutes – and by ^{233}Pa after the middle half-life radionuclides decay, about 10 days.

The determination through ^{233}Th is rarely applied due to the background interference and number of samples. In the Radiochemical Sector the gamma spectrometry is carried out using a coaxial HPGe detector with 11.8% relative efficiency and 1.66 keV FWHM resolution at 1,332.5 keV γ -rays for ^{60}Co .

Nowadays the common matrixes analysed are the surface, drinking and ground-water, aqueous and organic effluents, soil, sediment, ore, pasture, biomaterial, air filters, mud, aqueous and organic leachates, solid and liquid waste, industrial residues, petroleum, several precipitates, and others. The ^{232}Th analyses performed at the request of clients amount in average to about 60%. The established routine procedures [6, 11] have been applied to samples grouped according to the physical state of the matrix, whether the Solid Sample Group (SSG) is considered biomaterial, soil, sediment, residues, precipitates, mud, or the Liquid Sample Group (LSG) is surface, drinking and underground water, aqueous and organic effluent, leachate. The air filter matrix is a special group. The procedures used are comparative methods, therefore in each group of samples to be analysed thorium standards must be included and treated as the samples. The work with inner-standards and replicated samples is a routine approach. The thorium standards are solutions prepared from ThO_2 , dissolved with hydrochloric acid, H_2O_2 and perchloric acid and diluted with deionized water in order to obtain the limit concentration of 1.0 mg L^{-1} . The concentration is determined by gravimetry.

The determination of ^{232}Th can be done by instrumental neutron activation analysis (INAA) or radiochemical neutron activation analysis (RNAA), depending on the concentration of uranium and/or rare-earths in the sample. Samples of aqueous and organic leachates, waste, residues and precipitates are usually first analysed by delayed neutron technique in order to verify the presence of uranium. The uranium seriously interferes as it increases the background of the sample and causes manipulation hazards due to the exposure rate.

The summary of the procedures is:

1. Instrumental Procedure (U concentration is less than $100 \mu\text{g g}^{-1}$ or 100 mg L^{-1}):
 - solid samples from SSG are dried, powdered (less than 100 mesh), homogenised, weighed, and transferred to the irradiation tubes. The liquid standards are pipetted straight into the irradiation tubes and the self-absorption correction is applied afterwards;

- air filter samples are folded and put into the tubes. The liquid standards are pipetted on paper filter, which is dried, folded and also put into their tubes;
- liquid samples from LSG follow different procedures: the aqueous samples are pipetted straight into the tubes or concentrated in advance and transferred to the tubes; the organic samples can also be pipetted straight into the tubes or whenever they are concentrated. In this case the aliquot must be digested with HNO_3 and HClO_4 , 2:1 and transferred to the tubes. If the samples consist of the aqueous and organic phases, both phases must be separated and the procedure to be followed as aforesaid. The decision whether to concentrate the sample or not depends on the desirable detection limit.

The irradiation time is usually 2 hours for environmental samples and 1 hour for other matrixes. The decay time is at least 10 days in both cases because the determination has been carried out by ^{233}Pa in order to allow for the decay of the short and medium half-life radionuclides.

2. Chemical Separation Procedure (U concentration is more than $100 \mu\text{g g}^{-1}$ or 100mg L^{-1}):

- solid samples from SSG (dried, powdered, homogenised, and weighed) and air filters: yttrium carrier is added and the sample is dissolved with HNO_3 and HClO_4 , 2:1, and HF , if necessary. H_2SO_4 is added, pH is adjusted to 1.8, oxalic acid is added and Th and Y are precipitated as oxalates. The precipitate is filtered and vacuum dried. The paper filter is inserted in the irradiation tube;
- liquid samples from LSG: yttrium carrier is added, whenever the organic material is acid digested. H_2SO_4 is added and then the samples are treated in the same way as the solid samples.

For the determination using ^{233}Pa the irradiation time is usually 1 hour and the decay time is about 3 days. Using ^{233}Th , the irradiation time is 15 minutes and the decay time is about 30 minutes.

3. Radiochemical Separation Procedure (samples obtained after the Instrumental Procedure #2 and showing activated rare-earth elements in the gamma spectrum):

- solid samples from SSG, and air filters samples: the activated samples are dissolved with HNO_3 and HClO_4 , 2:1, until nitrogen oxides fumes appear;
- liquid samples from LSG: the organic ones are digested with acids and the aqueous ones need no preparation.

After that, KMnO_4 and MnSO_4 is added in order to precipitate the ^{233}Pa . The filter is inserted in the tube, the tube is closed and counted. The activated rare-earths in the supernatant liquid are collected and sent to waste treatment.

4. Chemical and Radiochemical Separation Procedure (applied when uranium is detected in advance, and the interference from activated rare-earths is observed during the counting):

- solid from SSG and liquid from LSG samples: first the Chemical Separation Procedure, #2, is applied. After the counting the Radiochemical Separation Procedure, #3, is applied.

^{230}Th and ^{228}Th by Alpha Spectrometry.

Alpha spectrometry (AS) is the primary technique used to analyse α emitters [7, 12, 13, 14]. High-resolution α spectrometry begins with chemical separations of the alpha

emitters and α particle source-preparation procedures. The usual approach to α spectrometry is to accumulate a spectrum in a multi-channel analyser and then the spectrum is evaluated. The α particle source is a stainless steel disc on which the radionuclides from the sample are deposited. In the Radiochemical Sector the α spectrometry [7, 12, 13, 14] has been performed using a silicon gold surface-barrier detector, FWHM 35 keV resolution for 5.486 MeV alpha from ^{241}Am . The counting has been carried out during 4 hours at least. The procedure has been used for the determination of ^{228}Th and ^{230}Th in air filter and surface, drinking and groundwater. In each group of samples to be analysed ^{228}Th and ^{230}Th standards are added that are treated as the samples because this procedure is a comparative method. The Sector controls the quality working with inner-standards and replicated samples. The procedure for preparing the disc involves four steps:

- preparation of the sample: the air filter is dissolved with HNO_3 , and the water sample is concentrated. If there is organic material the ash should be wetted with HNO_3 and HClO_4 , 2:1;
- co-precipitation: lanthanum carrier and HF are added, the solution is spun down, the fluorides are dissolved with H_2SO_4 , 1:1. The solution is boiled until fumes appear, spun down again, the precipitate is discarded, the hydroxides are spun down with NH_4OH , pH 10. The solution is filtrated discarding the aqueous phase and the hydroxides are dissolved with HNO_3 , 2 mol L^{-1} ;
- solvent extraction, separation of thorium from the lanthanum carrier and rare-earth: ascorbic acid is added and pH is adjusted to 1.5. The extraction with 10% (TTA) thenoyltrifluoroacetone in xylene is repeated three times while discarding the aqueous phases. HNO_3 , 2 mol L^{-1} , is added for extraction of thorium that will be in aqueous phase. If necessary the organic material is wet ashed with nitric and perchloric acids and the residue is dissolved with nitric and sulfuric acid, the solution is evaporated until fumes appear, water is added and the solution is neutralised to pH 2;
- electrodeposition: ^{228}Th , ^{230}Th and ^{232}Th are plated on the disc mounted in the electrodeposition cell with the mirror side facing out. The platinum electrode is the anode and the copper is the cathode. The electrolysis is conducted at a mean reversed current of 1.2 A for 1 hour.

In spite of presenting nuclear characteristics to be measured by α spectrometry, ^{232}Th is performed by NA not only because it is an easier and faster technique but also because it is suitable to meet high demands and satisfy the detection limit often required. The recovery is estimated using ^{232}Th as a tracer, whose activity was determined by INAA in advance.

5 Conclusions

^{232}Th presents nuclear characteristics that make their determination by neutron activation analysis easier at CDTN [6, 11]. ^{228}Th and ^{230}Th have been determined by radiochemical separations and alpha spectrometry [7, 12] because of the characteristic of the samples the activity of which is lower than 20 Bq L^{-1} for water and 20 Bq m^{-3} for air filter.

Table 1. ^{232}Th in water – National Intercomparison Program

| Date | True Values Bq L^{-1} | Results Reached Bq L^{-1} | Accuracy % | Precision % |
|---------------|-----------------------------------|---------------------------------------|---------------|----------------|
| December/1996 | 8.67 ± 0.25 | 7.8 ± 1.2 | 1.25 | 3 |
| April/1997 | 0.058 ± 0.009 | 0.057 ± 0.001 | 0.20 | 2 |
| August/1997 | 0.34 ± 0.51 | 0.313 ± 0.006 | 0.91 | 2 |
| December/1997 | 0.154 ± 0.031 | 0.157 ± 0.006 | 0.15 | 4 |

Table 2. Data of procedures

| Routine Matrixes | Radionuclide | Detection Limits | Precision, % [15] |
|-----------------------------------|-------------------|------------------------------|----------------------|
| Aqueous effluent | ^{232}Th | 20 mBq L^{-1} | 5 |
| Leachate, waste | ^{232}Th | 20 mBq L^{-1} | 4 |
| Surface, drinking and groundwater | ^{232}Th | 10 mBq L^{-1} | 10 |
| | ^{230}Th | 50 mBq L^{-1} | |
| | ^{228}Th | 50 mBq L^{-1} | |
| Biomaterial | ^{232}Th | 10 mBq g^{-1} (ash) | 3 |
| Pasture | ^{232}Th | 10 mBq g^{-1} (ash) | 3 |
| Soil, sediment | ^{232}Th | 10 mBq g^{-1} (ash) | 3 |
| Air filter | ^{232}Th | 0.01 mBq m^{-3} | 6 |
| | ^{230}Th | 50 mBq m^{-3} | 10 |
| | ^{228}Th | 50 mBq m^{-3} | 10 |

Both methods are applied with calibrated thorium standards treated as samples, inner-standards, and replicated samples. By this procedure the Radiochemical Sector verifies the experimental conditions and determines the precision [15]. Quality assurance concerning ^{232}Th in water has been demonstrated by the National Intercomparison Program, co-ordinated by Dosimetry and Radioprotection Institut (IRD - Instituto de Radioprotecao e Dosimetria), Brazil. Table 1 shows the values recently determined for ^{232}Th in water, and the accuracy and precision, which were calculated by IRD. In Brazil there is no program to determine the accuracy for other ^{232}Th matrixes and for ^{228}Th and ^{230}Th in water and air filter. Reference certified materials are not available for these matrixes. In this case inner standards, secondary reference standards and spike (4, 14) are used in order to assure quality. Through the years, the majority of thorium isotopes results for environmental samples range from below the detection limit to twenty times higher than this limit. For other matrixes, such as leachates, residues, waste, precipitates, the ^{232}Th concentration depends on the situation. There are no typical values. Table 2 gives the routine matrixes, the detection limits and the precision (confidence limit of 95%) [15] of the procedures. These detection limits are usually required by the clients. The procedures have been successfully applied since the eighties. They belong to few methods suitable for a large number of samples from several matrixes, measured at low cost, safely handled and in a relatively short time.

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