Determination of ^{238}U, ^{232}Th and ^{40}K in Zircon Sand Products from a Processing Plant in Brazil

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Abstract

The presence of natural radionuclides from the thorium and uranium series in beach sands is a well-recognized fact. The radioactivity is normally attributed to the presence of zirconium along with other heavy minerals such as kyanite, ilmenite and rutile (density 2.9 $g.cm^{-3}$). Potassium-40 is another important radionuclide found in beach sands, although in concentrations relatively lower than the ones derived from the progeny of the uranium and thorium series. Zircon sands may contain a significant concentration of natural radioactivity, because thorium and uranium may substitute zirconium in the zircon crystal lattice. Processing of ores containing small amounts of natural radionuclides by the industry may enhance the activity concentration in the products forming the so-called TENORM (Technologically Enhanced Naturally Occurring Radioactive Materials). This work was carried out aiming to determine the ^{238}U, ^{232}Th and ^{40}K contents of the mineral products extracted from the sands processed by an industry located in northeast Brazil, with emphasis on zircon. Measurements were performed through gamma spectrometry, by using a high purity germanium detector (HPGe) coupled to a multichannel analyzer. The results obtained by this technique were compared with the ones obtained (for ^{238}U and ^{232}Th) by alpha spectrometry by means of a surface barrier detector. Activity concentrations in zircon sands, determined by gamma spectrometry, ranged from 4,490 ± 198 to 13,972 ± 24 $Bq.kg^{-1}$ and from 891 ± 9 to 7,864 ± 13 $Bq.kg^{-1}$, for ^{238}U and ^{232}Th, respectively. By using the alpha spectrometry technique, on the other hand, activity concentrations ranged from 3,969 ± 388 to 12,256 ± 885 $Bq.kg^{-1}$ and from 852 ± 83 to 7,205 ± 718 $Bq.kg^{-1}$, for ^{238}U and ^{232}Th, respectively

Key Words: Natural radionuclides; beach sands; zircon sands

1 INTRODUCTION

The public concern about issues related to preservation of the environment has led to an increasing demand for the implementation of control measures to minimize the impact of human activities on the environment. These measures involve, in most cases, the quantification of contaminants, such as metals and radionuclides, in soil, water and air. Although they are present in all compartments of the environment, generally in low concentrations, natural radionuclides may have their concentrations altered due to industrial processes. Consequently, it becomes important to determine the content of those radionuclides in environmental samples the environment.

The radionuclides starting the main natural radioactive series are ^{238}U and ^{232}Th. These radionuclides are commonly referred to as primordial radionuclides and have great importance from the viewpoint of radiation protection (UNSCEAR, 2000). All minerals and raw materials contain radionuclides of natural origin, such as the radionuclides from the ^{238}U and ^{232}Th decay

series, and ^{40}K, which are the main radionuclides of interest. The activity concentrations of natural radionuclides in normal rocks and soil are variable but generally low. However, certain minerals contain uranium and/or thorium series radionuclides at significantly elevated activity concentrations, even the ones that are commercially exploited. Additionally, during the extraction of minerals from the earth's crust and posterior processing, the radionuclides may become unevenly distributed between the various materials and selective mobilization of radionuclides can disrupt the original decay chain equilibrium. As a result, radionuclide concentrations can be increased as compared with the original mineral or raw material (IAEA, 2006).

As an example of the radionuclides presence and concentration in minerals one can cite the concentration of natural radionuclides in beach sands. The processing of mineral sands for the extraction of kyanite, ilmenite, rutile and zircon, can lead to higher than normal concentrations of uranium and thorium (IAEA, 2011).

Due to its physicochemical properties and the occurrence of U and Th, zircon is one of the most important minerals for geochronological investigations in igneous and metamorphic rocks. Zircon is resistant to metamorphic and tectonic processes, but its internal structure undergoes a process called metamictization, resulting from replacement of zirconium by uranium and thorium (WOODHEAD et al., 1991). Due to this process, the levels of radionuclides from the uranium and thorium series in zircon sands are higher the ones found in rocks and soils, ranging from 0.2 to 74 $kBq.kg^{-1}$ and 0.4-40 $kBq.kg^{-1}$, respectively. However, other minerals present in the same mineral deposit as zirconium may also exhibit relatively high natural radionuclides contents. Activity concentration for Rutile was 3.8 $kBq.kg^{-1}$ for ^{238}U series and 0.56 $kBq.kg^{-1}$ for the elements of the ^{232}Th series. Meanwhile, these same values for ilmenite were 2.3 $kBq.kg^{-1}$ and 1.2 $kBq.kg^{-1}$, respectively, for the ^{238}U and ^{232}Th series (UNSCEAR, 2000).

^{238}U is the precursor of the natural decay series which has the main radionuclides responsible for most part of the dose undertaken by humans, among them ^{226}Ra, which can be absorbed in the bones due to its chemical similarity to calcium, depositing the energy from alpha decay in the surrounding tissues. At the same time the ^{232}Th series represents minor risk in relation to the uranium series, but one of its radionuclides, ^{228}Ra, can also be assimilated into the bone increasing the dose to the body tissues. Finally, the radionuclides from these series, together with ^{40}K, are responsible for the occupational absorbed radiation dose undertaken by the population (WICKER; SCHULTZ, 1982, UNSCEAR, 2000).

The measurement of radionuclides concentration in environmental samples such as beach sands involves small quantities to be determined by techniques of nuclear instrumentation. This way, it is important to study and improve those techniques in order to obtain reliable results, as far as precision and accuracy are concerned (AYRANOV et al. 2008; VESTERBACKA et al., 2009; KILIARI&PASHALIDIS, 2010).

Therefore, the present study aimed to compare the techniques of alpha spectrometry and gamma spectrometry for the determination of ^{238}U and ^{232}Th in mineral sands. The validation of the methodologies was carried out by using reference materials provided by the International Atomic Energy Agency.

2 MATERIAL AND METHODS

2.1 Study Area and Sample Collection and Preparation

The samples used in this study were mineral sands separated from the mining of placers, from Northeastern Brazil. Almost all production of heavy minerals from beach sand in Brazil comes

from the operation of two industries: one of them in Paraíba State, and the second one in Rio de Janeiro (SABEDOT, 2004).

The determinations were performed on samples from a mine located in the municipality of Mataraca, in the coastline of Paraiba, 96 km from the city of João Pessoa. The minerals extracted from coastal sand dunes included the titanium minerals ilmenite ($FeTiO_3$) and rutile (TiO_2) (used in the production of welding electrodes and alloys), a zircon mineral, zirconite (raw material for ceramics and refractory), and an aluminum mineral kyanite (raw material for ceramics industry) (SABEDOT; SAMPAIO, 2008).

The main product of the mining is ilmenite. Zircon appears as co-product of the mineral processing of coastal sand dunes, where it is found widespread with other heavy minerals, which are considered contaminants. The mineral zircon, also commonly called zirconia, is a tetragonal orthosilicate of zirconium with composition ZrSiO4.

The sample analyses were performed at the Environmental Monitoring Division from the Northeast Regional Center of Nuclear Sciences - DIAMB/CRCN-NE which besides the conventional analytical techniques, focuses on the analysis of the main natural radionuclides from the major decay series (^{238}U and ^{232}Th) and of important natural radionuclides like ^{40}K in geological matrices.

2.2 Sample preparation

For the determination of activity concentrations by gamma spectrometry, 50 g of each sample were placed in plastic cylindrical containers, sealed and directly analyzed, being counted for 80,000s. The gamma lines used for determining ^{238}U and ^{232}Th were 1,001 keV and 911 keV, respectively (VESTERBACKA et al., 2009).

For the determination of ^{238}U and ^{232}Th by alpha spectrometry, samples were digested by alkaline fusion (20 mL of HF, 25 mL of HNO_3 and 25 mL of HCl were added to RM test portions of 2.50 g), spiked with ^{229}Th and ^{232}U tracers. The solution was evaporated, followed by the addition of 25 mL of HCl 1 $mol.L^{-1}$ to facilitate the chemical purification. Samples were then purified by passing through an ion exchange resin, electrodeposited on stainless steel disks and counted.

2.3 Alpha Spectrometry

The detector used in this technique was of the surface barrier type, model 7200-02, manufactured by Canberra®. This detector is associated with a microcomputer which uses the data acquisition software GENIE 2000 from Canberra®. This program controls various parameters used in data acquisition, such as the potential difference used in acquisitions (45 V), the pressure inside the chamber where the sample is placed (<0.25 Torr) and the counting time (80,000 seconds). Furthermore, it stores and analyzes the main peaks in the generated spectra.

2.3.1 Calibration of the Alpha Detection System

In order to identify the energies observed from the alpha spectra a previous calibration of the detection system was required. For a system in good operating conditions there is a linear relationship between the intensity and the recording channel of the pulse generated. Therefore, this situation is valid for the relation between the energy of the particle and the channel where such generated pulse is recorded. The detection system was calibrated in energy through a mixed source ^{233}U, ^{241}Am and ^{244}Cm with an activity of 2891 $\alpha.s^{-1}$ (reference date 02.09.1997) in a 2π geometry.

The efficiency calibration was performed with an ^{241}Am (77S97) source provided by IRD/ CNEN (Radiation Dosimetry Institute, Brazilian Nuclear Commission), with an emission rate 1025.3 $\alpha.s^{-1}$ (reference date 02/09/1997), in a 2π geometry, electrodeposited in a stainless steel disc. A source-detector distance of 5 mm was used and the counting time was 60 minutes. As a result, the estimated value for the detector efficiency was 29.65 ± 0.04 %.

2.4 Gamma Spectrometry

The system used for the gamma spectrometry measurements was based on a hyper-pure germanium (HPGe) detector from Canberra® model BEGe GX2518 (broad energy detector) with 40% relative efficiency and 1.8 keV resolution for the 1,332.5 keV energy of ^{60}Co. The detector was placed inside a low background radiation lead shielding and cooled with liquid nitrogen. This detector was connected to an analogical electronic system including a preamplifier Canberra® model 2002CSL and a Canberra multichannel analyzer where the gamma ray spectrum is accumulated in 8192 channels. Data analysis was performed using the software Genie 2000 Canberra® and a counting time of 80,000 seconds was used. The detector efficiency was determined using a mixed standard solution of known activity containing ^{152}Eu, ^{133}Ba and ^{241}Am in the same sample geometry. In this work, the empirical function was obtained according to the methodology presented by Genesini (2004).

3 RESULTS AND DISCUSSION

3.1 Results Obtained for ^{238}U

The samples had an alpha spectrum with good resolution (full width at half maximum ranging between 70 and 90 keV). The sample purification allowed the sequential analysis of ^{232}Th and ^{230}Th, i.e., if the purification had not been performed thorium present in the samples would prevent discrimination in the spectrum of the particles emitted by the uranium and thorium. The Minimum Detectable Activities (MDA) obtained in this method are shown in Table 1.

Table 1 Minimum detectable activities for the determination of U and Th by alpha spectrometry

Energy (MeV)	Nuclide	MDA (Bq.kg^{-1})
4.2	^{238}U	13
4.7	^{234}U	28
4.0	^{232}Th	11
4.7	^{230}Th	21

The results obtained by alpha spectrometry for uranium-238 are shown in Table 2. They show activity concentrations ^{238}U varying from 3,969 to 12,256 Bq.kg^{-1}. The results show that among the minerals present in the sand deposit, the ones that deserve more attention from the point of view of radiological protection are those of zirconium.

Table 2 also presents, for the sake of comparison, the values of activity concentrations of uranium-238 measured by gamma spectrometry in the same zircon sands. By using this technique, values ranging from 4,490 to 13,972 Bq.kg^{-1} were found for that radionuclide. The similarity of the results of the activity concentration of uranium-238 found by the two techniques shows that either of them can be successfully used for determining the concentration of this radionuclide in mineral sand samples.

Table 2 Activity concentrations for ^{238}U in the zircon sands by alpha and gamma spectrometry

Mineral	**^{238}U (alpha)** ($Bq.kg^{-1}$)	**^{238}U (gamma)** ($Bq.kg^{-1}$)
Zircon I	3,969 ± 388	4,490 ± 198
Zircon II	5,882 ± 470	5,607 ± 227
Zircon III	4,203 ± 373	4,745 ± 405
Zircon B	9,829 ± 663	9,560 ± 282
Zircon E	4,807 ± 406	5,132 ± 160
Zircon F	12,256 ± 885	13,972 ± 24

* Uncertainty for 95% confidence level

Table 3, on the other hand, shows the results obtained by alpha spectrometry for ^{232}Th. For this thorium isotope, activity concentrations varying from 852 to 7,205 $Bq.kg^{-1}$ were found. The results show that among the minerals present in the sand deposit, the ones that deserve more attention from the point of view of radiological protection are those of zirconium.

Table 3 also presents the values of activity concentrations of ^{232}Th measured by gamma spectrometry in the same zircon sands. By using this technique, values ranging from 891 to 7,864 $Bq.kg^{-1}$ were found for that radionuclide. The similarity of the results of the activity concentration of ^{232}Th found by the two techniques shows that either of them is adequate for determining the concentration of this radionuclide in mineral sand samples. Besides, the results show ^{238}U concentration values consistently higher than those for ^{232}Th, as expected.

Table 3 Activity concentrations for ^{232}Th in zircon sands by alpha and gamma spectrometry

Mineral	**^{232}Th (alpha)** ($Bq.kg^{-1}$)	**^{232}Th (gamma)** ($Bq.kg^{-1}$)
Zircon I	852 ±83	891 ± 9
Zircon II	1,443 ± 95	1,452 ± 12
Zircon III	915 ± 110	965 ± 18
Zircon B	2,500 ± 227	2,795 ± 12
Zircon E	1,014 ± 50	1,081 ± 5
Zircon F	7,205 ± 718	7,864 ± 13

* Uncertainty for 95% confidence level

The activity concentration of ^{40}K in the zircon sands was also determined by the gamma spectrometry technique. The results of this determination are presented in Table 4, together with the values found for ^{238}U and ^{232}Th, determined by the same technique.

Table 4 Activity concentrations for ^{238}U, ^{232}Th, and ^{40}K in zircon sands determined by gamma spectrometry

Mineral	**^{238}U** ($Bq.kg^{-1}$)	**^{232}Th** ($Bq.kg^{-1}$)	**^{40}K** ($Bq.kg^{-1}$)
Zircon I	4,490 ± 198	891 ± 9	153.8 ± 18.7
Zircon II	5,607 ± 227	1,452 ± 12	258.4 ± 23.5
Zircon III	4,745 ± 405	965 ± 18	115.4 ± 20.5
Zircon B	9,560 ± 282	2,795 ± 12	390.7 ± 28.9
Zircon E	5,132 ± 160	1,081 ± 5	125.1 ± 18.0
Zircon F	13,972 ± 24	7,864 ± 13	972.1 ± 37.0

* Uncertainty for 95% confidence level

As shown in Table 5, there is an apparent positive correlation between the concentrations of the three radionuclides. Due to the small number of points and their uneven distribution in the activity concentration interval, it was not possible to present the graphs showing the correlations. This correlation can be seen, however, through the matrix shown in Table 5, for the activity concentrations of ^{238}U, ^{232}Th, and ^{40}K, determined by gamma spectrometry.

Table 5 Matrix correlation based on the activity concentrations of ^{238}U, ^{232}Th, and ^{40}K, determined by gamma spectrometry

Radionuclide	**^{238}U**	**^{232}Th**	**^{40}K**
^{238}U	1		
^{232}Th	0.9677	1	
^{40}K	0.9701	0.9946	1

4 CONCLUSIONS

The outcome of the measurements performed by alpha and gamma spectrometry for determining the activity concentrations of ^{238}U and ^{232}Th in zircon sands shows that both techniques can be successfully used for the analyses of environmental samples.

The results also show the importance of performing this kind of survey, as the products of the beach sand processing have their radionuclide content increased posing, therefore, a risk for those workers which handle these materials, from the point of view of radiation protection.

ACKNOWLEDGMENTS

The authors are indebted with the staff from the Environmental Monitoring Division of the Northeast Regional Center of Nuclear Sciences (DIAMB/CRCN-NE) and with CNPq, for the technical and financial support, respectively

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