Determination of Uranium and Thorium using Gamma Spectrometry: a pilot study

OLIVARES, D M M, KOCH, E S, MANSO GUEVARA, M V, GARCIA VELASCO, F.

Universidade Estadual de Santa Cruz km 16 Rodovia Jorge Amado, Ilhéus-BA, Brazil.
Email: *diango.mo87@gmail.com*

Abstract. This paper presents the results of a pilot experiment aimed at standardizing procedures for the CPqCTR/UESC Gamma Spectrometry Laboratory (LEG) for the quantification of natural radioactive elements in solid environmental samples. The concentrations of ^{238}U, ^{232}Th and ^{40}K in two sediment matrix belonging to the Caetité region were determined, by using the absolute method with uncertainties about 5%. The results were obtained using gamma spectrometry with a high-resolution p-type HPGe detector. As a closure, the absorbed dose, radium equivalent activity and the annual effective dose were calculated.

Keywords: Gamma spectrometry, ^{238}U and ^{232}Th concentration, outdoor dose.

1. INTRODUCTION

Environmental assessments are one of the permanent activities, in which universities and their research centers are involved, and they can impact on a positive way in a given region.

Gamma-ray spectrometry is one of the most widely used techniques for environmental radioactivity assessment (HANNAN et al., 2015; SANTOS JÙNIOR et al., 2017). It allows to perform a precise quantitative analysis of the radionuclide concentration (natural or anthropogenic) in different types of environmental samples, without the application of laborious sample preparation (AGBALAGBA; AVWIRI; CHAD-UMOREH, 2012).

However, the quantification of radionuclide in extended sources, by using the absolute method, requires the knowledge of the efficiency detection. The efficiency curve can be experimentally obtained by using a "polyenergetic standard source" with geometry and a matrix composition similar to the studied samples. When these "standard sources" are not available, the efficiency curve for volumetric sources can be obtained from point-like sources of calibration using the efficiency transfer method (VARGAS; DÍAZ; SÁNCHEZ, 2003). Two sediment samples belonging to Caetité region, where it is concentrated nowadays the uranium ore activity in Brazil were analyzed. The efficiency curve determined by Olivares, D. (2016) was used for quantifying the amount of uranium, thorium and potassium in both samples.

This paper presents the results of a pilot experiment aimed at standardizing procedures from the Research Center in Sciences and Technologies of Radiations (CPqCTR/UESC) LEG for the quantification of natural radioactive elements (^{238}U, ^{232}Th and ^{40}K) in solid environmental samples.

Based on the fact, that mining is catalogued by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) as a potential source of exposure to natural

radioactive elements (UNSCEAR, 2000), different radiological magnitudes were also calculated.

2. SAMPLES COLLECTION AND PREPARATION

The sediment samples (SS1 and SS2) were collected from two specific sites of the influence region of uranium mining in Caetité, Bahia.

The samples were stocked and sealed in plastic bags in order to avoid any external contamination. After that, the samples were sent to our Environmental Samples Preparation Laboratory at the CPqCTR. and prepared according to the procedure established in (IAEA, 2003).The granulometric reduction of the collected samples was done using a sieve of 170 mesh (90 µm). After the homogenization procedure, samples were dried in the oven at a temperature of 110 ºC. At intervals of 2 hours, the mass of the samples was verified, until achieving a stable difference (lesser than 5 mg) in the dry weight, in temperature and humidity conditions about 20 ºC and 40%, respectively. The dried samples were hermetically sealed in two plastic containers (vessels) with a cylindrical geometry (6.2 cm^2 x 2.7 cm), previously identified. Finally, both samples were stored during 30 days in a desiccator in order to reach the secular equilibrium of radon with other elements of the natural radioactive series.

3.EXPERIMENTAL SETUP

The experimental measurements were carried out using a coaxial p-type HPGe detector (model **GC2518**), manufactured by Canberra. The geometrical dimensions and spectrometric characteristics of the detector were verified by Olivares, D. (2016) and compared with those provided by the manufacturer. This detector has a nominal relative efficiency about 25% compared to 7.62 cm x 7.62 cm NaI (Tl) detector. The measured resolution (FWHM) and the Peak-to-Compton ratio (P/C) for the ^{60}Co gamma-ray energy of 1.33 MeV were 1.72 keV and 58:1, respectively. These characteristics were in disagreement with those reported by the manufacturer for the same energy (1.62 keV and 61.6:1, respectively). The detector is installed in a 10-cm-thick lead shield, model 747 (CANBERRA, 2013). The HPGe is connected to a pre-amplifier (model **2002C**) and a Digital Spectrum Analyzer (DSA-200), with a shaping time of 4 µs. The course and fine gain were fixed in 40x and 1.0502x, respectively. A high voltage of 4000 V was applied to the detector.

The energy calibration function, which establishes the relation between gamma-ray energies and the electronic channels, was obtained in the energy range from 59-1408 keV.

Adjustment of the experimental data was achieved by an excellent linear fit (r^2=0.999), whose parameters are: m=0.2302 keV channels^{-1} and b= -0.6077 keV.

The full-energy peak efficiency calibration was performed in the same energy range with point-like standard sources of: ^{22}Na, ^{60}Co, ^{133}Ba, ^{137}Cs, ^{152}Eu, ^{155}Eu and ^{241}Am. The spectrum acquisition time was chosen depending on the activity of the source to keep the statistical uncertainty in the peak area below 1%. Background radiation was measured for 72 h, and its contribution was subtracted from the corresponding standard source spectra.

4. METHODS AND RESULTS

The samples were measured at 5 cm from the top of the detector for 72 h. Spectra were acquired using the software Genie 2000 (CANBERRA, 2006). Gamma-ray energies of 351 keV (^{214}Pb), 1120 and 1764 keV (^{214}Bi) were used for ^{238}U calculations. The energies of 583 keV (^{208}Tl) and 968 keV (^{228}Ac) were used for ^{232}Th calculations, and for ^{40}K quantification was used its own gamma-ray energy (1460 keV). The measured spectrum of the sample SS2, is shown in figure 1.

Due to the analytic lines, used in the quantification procedure (highlighted in red), were above 350 keV, the spectrum is shown for energies greater than 300 keV. The specific activity of ^{238}U, ^{232}Th and ^{40}K, corresponding to both sediment samples from Caetité region, were obtained using the Absolute Method (Eq. 1):

$$A = \frac{CPS_s - CPS_g}{\varepsilon \cdot I_\gamma \cdot m} \quad \left(Bq \cdot kg^{-1} \right) \qquad (1)$$

where CPS_s and CPS_g represent the count rates in the full-energy peak and the background count rates, ε is the efficiency corresponding to energy E of interest, $I\gamma$ represents the photon yield or photon-emission probabilities to energy E, and m is the dried mass of the sample in kg.

Energy and photon yield values were taken from the database of the International Atomic Energy Agency (IAEA, 2007). Background spectra were used for the calculation of the detection limits (DL) and the Minimum Detectable Activity (MDA). In this work was used the Currie modified criterion for the calculation of detection limit and therefore to MDA (KNOLL, 2010).
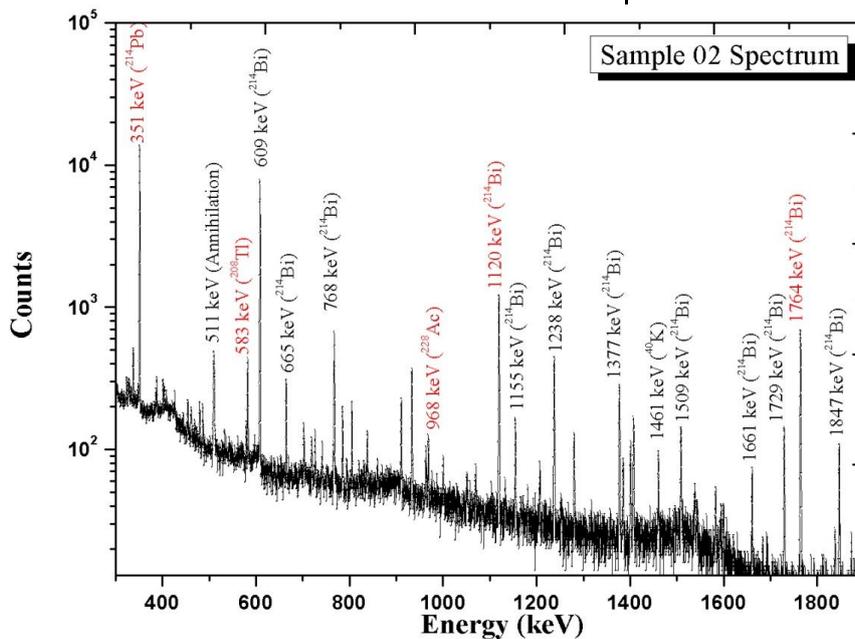
The efficiency curve was obtained after adjusting the nominal detector parameters using a Monte Carlo N-Particle eXtended (MCNPX) transport code (PELOWITZ, 2008), and using the efficiency transfer method. Correction factors such as solid angle for the volumetric sample and self-absorption correction factors ($F_{self-abs}$) were also taken into account to calculations. If the reader is interested, additional details can be found in Olivares, D (2016).
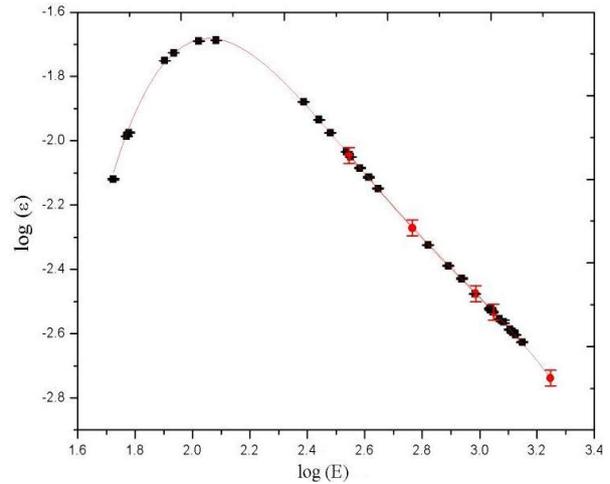

Figure 2: The ε_{vol} curve in log-log scale as a function of photon energies (E). Solid line represents polynomial logarithmic fit (r^2=0.998).

Figure 2 shows the efficiency curve in the energetic range of 53-1764 keV for the studied volumetric sample. Red points represent the efficiency values for the analytical gamma lines of interest.

The ^{238}U, ^{232}Th and ^{40}K concentration values (table 1) were estimated from the specific activity Eq. (1), with a mean relative error of 5%. Due to the spectrum acquisition time was chosen to keep the statistical uncertainty in the peak area below 1% (Type A uncertainty), and the photon

Figure 1: Measured spectrum of the sample SS2 acquired using GENIE 2000.

yield of this lines are lower than 0.3 % (Type B uncertainty); the concentration values' uncertainties were given mainly by the uncertainties in the estimative of the efficiency. For all the efficiency values, the uncertainty was computed as the quadratic sum of the individual uncertainties of the factors used in the efficiency calculation. These factors and their relative errors are listed in table 2.

Table 1: Main results for ^{238}U and ^{232}Th concentration for both sediment samples

Energy (keV)	SS1		SS2	
	A (kBq kg^{-1})	C (mg kg^{-1})	A (kBq kg^{-1})	C (mg kg^{-1})
^{238}U				
351	2.8 ± 0.2	22 ± 1	8.1 ± 0.4	64 ± 3
1120	2.7 ±0.2	21 ± 1	7.7 ± 0.4	61 ± 3
1764	3.1 ± 0.2	24 ± 1	8.5 ± 0.5	67 ± 4
^{232}Th				
583	0.20 ± 0.01	68 ± 4	0.35 ± 0.02	117 ± 7
968	0.22 ± 0.02	74 ± 5	0.33 ± 0.02	111 ± 8
^{40}K				
1460	0.68 ± 0.04	-	0.61 ± 0.03	-

Table 2: Uncertainty sources contributing to the total uncertainty of the efficiency (ε)

Uncertainty source	Type	Relative error
Count rate	A	~1 %
Radioactive decay	A	~1 %
Photon yield	B	< 0.7 %
Geometric factor	B	~3 %
Self-Absorption factor	B	~2-3 %
Error interpolation	A	~2%

As a closure for this work, radiological protection magnitudes such as: the absorbed dose rate (D), the radium equivalent activity (Ra$_{eq}$) and the annual effective dose equivalent (H) for 1 m from the surface for adults were calculated according to UNSCEAR (2010).

The absorbed dose, due to gamma radiation resulting from exposure to the primordial radionuclide for both samples were: 1.4 ± 0.1 μGy h^{-1} and 3.7 ± 0.1 μGy h^{-1} for SS1 and SS2 respectively. The Ra$_{eq}$ values for the two samples were: 3204 ± 127 Bq kg^{-1} (for SS1) and 8624 ± 260 Bq kg^{-1} (for SS2) and the annual effective dose values were: 1.7 ± 0.1 mSv y^{-1} for SS1 and 4.5 ± 0.1 mSv y^{-1} for SS2.

The annual effective dose values do not exceed the accepted as safe limit for occupationally exposed persons (20 mSv y^{-1}) (UNSCEAR, 2010). They are even included in the radiation dose limits to mine workers at different uranium operations around the word (< 4.8 mSv) (NIELSEN; ROOS; ANDERSSON, 2015).

5. CONCLUSIONS

The pilot experiment carried out in the CPqCTR/UESC LEG established a methodology to perform quantitative procedure of radionuclides by using the Absolute Method. It successful application allowed to determine the concentration of ^{238}U, ^{232}Th and ^{40}K in two sediments samples belonging to the Caetité region and the assessment of the outdoor dose, which do not exceed the regulated levels. This work itself do not constitute an environmental study, because there are not enough sampling points for characterizing the region.

REFERENCES

AGBALAGBA, E.O.; AVWIRI, G.O.; CHAD-UMOREH, Y.E. 2012. *γ-Sprectroscopy measurement of natural radioactivity and assessment of radiation hazard indices in soil samples from oil fields environment of Delta State, Nigeria*. **Journal of Environmental Radioactivity**, 109:64-70. DOI: 10.1016/j.jenvrad.2011.10.012.

CANBERRA, 2013. Model 747 and 747E Lead Shield Canberra industries, Inc.

_____.2006. Genie™ 2000 Spectroscopy Software, Version 3.01, Canberra Industries, Inc.

HANNAN, M.; WAHID, K.; NGUYEN, N. 2015 *Assessment of natural and artificial radionuclides in Mission (Texas) surface soils*. **Journal of Radioanalytical and Nuclear Chemistry**, 305: 573-582. DOI: 10.1007/s10967-015-4018-4.

INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA) 2003 *IAEA - TECDOC -1360 Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements*, International Atomic Energy Agency, Vienna.

INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA), 2007. Update of X-Ray and Gamma-Ray Decay Data Standards for Detector Calibration and Other Applications, International Atomic Energy Agency, Vienna.

KNOLL, G. F. 2010. **Radiation Detection and Measurements**. 4th Edition. United States of America: John Wiley & Sons, Inc.

NIELSEN, S. P., ROOS, P., ANDERSSON, K. G. 2015. **Predicted Radiation Exposure from Mining at Kvanefjeld**: Introduction to Radiation, Review of Baseline Information, and Predicted Radiation Exposures from Kvanefjeld Mining, Mineral Processing and Refining. Technical University of Denmark (DTU). (DTU-Nutech-R; No. 11(EN)).

OLIVARES, D. M. M. Caracterização de um espectrômetro gama de baixo fundo para a determinação de urânio e tório em amostras ambientais sólidas. 2016. 108p. Dissertação (Mestrado em Física) – Programa de pós-graduação em Física – PROFÍSICA, Universidade Estadual de Santa Cruz, 2016.

PELOWITZ, D.B. (Ed.). 2008. **MCNPX User's Manual**, **Version 2.6.0**, Los Alamos, New Mexico, LA-CP-07-1473.

SANTOS JÚNIOR, J.A.; AMARAL, R.S.; MENEZES, R.S.C.; ÁLVAREZ, J.R.E.; SANTOS, J.M.N.; FERNÁNDEZ, Z.H.; BEZERRA, J.D.; SILVA, A.A.; DAMASCENA, K.F.R.; MACIEL NETO, J.A. 2017. *Influence of terrestrial radionuclides on environmental gamma exposure in a uranium deposit in Paraíba, Brazil*. **Ecotoxicology and Environmental Safety**, 141: 154-159. DOI: 10.1016/j.ecoenv.2017.02.004.

UNITED NATIONS SCIENTIFIC COMMITTEE ON THE EFFECTS OF ATOMIC RADIATION (UNSCEAR). 2010. Annex B: Exposures from natural sources. In: **Sources and Effects of Ionizing Radiation**: UNSCEAR 2008 Report to General Assembly, with scientific annexes, Volume I: Sources. United Nations, New York.

_____. Source and effects of Ionizing Radiation: UNSCEAR 2000 Report to General Assembly, with scientific annexes, Volume I: Sources. United Nations, New York.

VARGAS, M. J., DÍAZ, N. C., SÁNCHEZ, D. P. 2003. *Efficiency transfer in the calibration coaxial p-type HPGe detector using the Monte Carlo method*. **Applied Radiation & Isotopes**, 58:707-712. DOI: 10.1016/S0969-8043(03)00091-5.