



## **Thorium, Uranium and Potassium Levels of Brazil geological sediment by Gamma-Ray Spectrometer and Instrumental Neutron Activation Analysis**

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### **1. Introduction**

In Brazil, most of the marine sediments that are suitable for dating by thermoluminescence (TL), luminescence optical stimulated (OSL), and electron paramagnetic resonance (EPR) is composed of either essential quartz. The most precise measurement of the  $\gamma$ -ray dose rate is by the burial of a dosimeter in a suitable capsule, but in the situation of low dose rates, it may be necessary for the pill to be buried for 12 months [1]. For many reasons, this may not be practical. So usually, the total dose rate is calculated either from the determination of the elemental concentration of the radionuclides Th, U and K. The mass fractions of the elements can be determined by analytical techniques such as instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF) or  $\gamma$ -ray spectroscopy [2]. The strategy adopted to calculate the total dose rate must provide results with reasonable accuracy. This article reports lab comparison analysis techniques INAA and  $\gamma$ -ray spectrometry for some Brazilian marines sediment samples. It concludes that the precision study between two analytical methods, INAA and  $\gamma$ -ray spectroscopy, show a high correlation.

### **2. Methodology**

#### **2.1. Study area, sample collection and initial preparation**

This works area of study is the continental place of the city of São Vicente, the state of São Paulo, Brazil. The geographic location is 23°59'05,7"s, 46°29'58,5"w. A mountain range surrounds the sampling site to the north and the bay of São Vicente to the south. The six selected sites were sampled to represent the entire study area. Sampling was performed at the "Sand and Foundry Technical Society"(STAF) to represent six undisturbed areas containing sealed quaternary sand-sized marine terraces. In an area of 1 km<sup>2</sup> and using polyvinyl acrylic tubes were collected eight samples. Each sample was oven-dried at 100.7 °C until it reached a constant dry weight, homogenized and then sieved through a 100 mesh to obtain a uniform grain size.

## 2.2. Instrumental Neutron Activation Analysis (INAA)

To perform the analysis, about 100 mg of dry powder of each sample was used. It was weighed and packed in polyethylene wrappings protected with Al foil. Then, a set of eight samples was assembled together with approximately 100 mg of Standard Reference Material NIST-SRM 1633b Constituent Elements in Coal Fly Ash and the Sediment candidate certified reference material, RM, from Wageningen University, Environmental Sciences, Netherlands. After grouping the samples in parallel to receive the same neutron flux, they were irradiated for 8 hours in the IEA-R1 reactor of IPEN-CNEN/SP, under a thermal neutron flux of the order  $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$  [3]. The measurements were performed in two stages, one after 7 days of decay to determine U and K elements concentrations, and another after 25 to 30 days to determine Th. All measurements were performed using the Ge hyperpuro detector, model GX 1925 from CANBERRA, resolution of 1.90 keV at the 1332.49 keV gamma peak of  $^{60}\text{Co}$ , with S-100 MCA of CANBERRA with 8192 channels. To determine the uranium concentration a Cd capsule and neutron epithermic flux was used. The Genie-2000 Gamma Acquisition & Analysis software, v.3.1a, developed by CANBERRA, was used to analyze the gamma-ray spectra [4]. Equation 1 describes the relative method which it is assumed that the neutron flux, cross section, irradiation times, and all other variables associated with the count are identical for both the standard and the sample [5].

$$\frac{R_{\text{std}}}{R_{\text{sam}}} = \frac{W_{\text{std}}(e^{-\lambda t_d})_{\text{std}}}{W_{\text{sam}}(e^{-\lambda t_d})_{\text{sam}}} \quad (1)$$

where R is the counting rates of the gamma-ray of interest for sample (sam) or standard (std), W is mass of the element,  $\lambda = \ln 2/t_{1/2}$  and  $t_d$  is the decay time.

## 2.3. $\gamma$ -ray spectroscopy

The homogenized samples were weighed, conditioned and sealed in polyethylene pots with a volume of 42  $\text{cm}^3$ . The samples are stored for 30 days for secular equilibrium. The activities of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  determined by means of the natural gamma ray. A single gamma transition of 1460.81 keV determined the potassium concentration. The natural concentrations of  $^{238}\text{U}$  and  $^{232}\text{Th}$  were considering the radioactive balance of the radioactive series of uranium and thorium. Radium and its decay products account for 98.5% of the radiological effect of the radioactive uranium series. The  $^{226}\text{Ra}$  activity data replaced the  $^{238}\text{U}$  activity data. The gamma transitions of 295 keV, 352 keV of  $^{214}\text{Pb}$  and 609 keV of  $^{214}\text{Bi}$  were considered to determine  $^{226}\text{Ra}$ . The transitions of 238 keV, 300 keV of  $^{212}\text{Pb}$  and 911 keV, 969 keV of  $^{228}\text{Ac}$  were considered for  $^{232}\text{Th}$  [6]. The concentrations of natural gamma activity were obtained using Equation 2 [7].

$$A_{\text{Eg}} = \frac{C}{E_g I_g t_m} f_{\text{Eg}} \quad (2)$$

where  $A_{\text{Eg}}$  represents the concentration of natural gamma activity given in ( $\text{Bq kg}^{-1}$ ). C is a net area of the peak of interest.  $E_g$  is detection efficiency,  $I_g$  is emission probability. m is the sample mass in kg, and  $f_{\text{Eg}}$  is the attenuation factor for the related gamma transition. The average of the activities weighted by the uncertainties of the respective changes was obtained in Equation 3 [7].

$$A (\text{Bq kg}^{-1}) = \frac{\frac{A_1}{\sigma_1^2} + \frac{A_2}{\sigma_2^2} + \dots + \frac{A_n}{\sigma_n^2}}{\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2} + \dots + \frac{1}{\sigma_n^2}} \quad (3)$$

The concentration of activity for the radionuclides in each studied sample was defined using the gamma spectrometer system by an HPGe detector with electronic circuit DSPLynx. The power resolution (FWHM) is 1.80 keV, and the relative efficiency is 40% to 1.332MeV of  $^{60}\text{Co}$ . Analysis of the results was performed by Genie2000 software. In all measurements, the dead time is less than 10%, and the Genie2000 software performed the correction automatically. The conversion factors used to convert  $\text{Bq kg}^{-1}$  to fracing mass

were:  $^{238}\text{U}$ ; 1 ppm = 12.35 Bq kg<sup>-1</sup>, for  $^{232}\text{Th}$ ; 1 ppm = 4.06 Bq kg<sup>-1</sup>. Where 1 % of  $^{40}\text{K}$  = 313 Bq kg<sup>-1</sup>[8].

### 3. Results

This work studied the precision of INAA to determine the elemental concentration for the candidate to Reference Material (RM) in soil. Table 1 shows the measured mean value, RSD, and the recommended values.

Table 1: Mass fraction and RSD in the RM for Th, U and K determined by INAA

Element	Measured Value	RSD	Recommended Value	RSD
	Mean ± SD	(%)		(%)
Th (mg kg <sup>-1</sup> )	5.54 ± 0.69	12.54	5.69 ± 0.62	10.98
U (mg kg <sup>-1</sup> )	1.78 ± 0.24	13.76	1.75 ± 0.26	14.9
K (%)	1.42 ± 0.15	10.65	1.27 ± 0.66	51.8

The measured concentration of Th in the RM was 5.54 ± 0.69 (mg kg<sup>-1</sup>) compared to the recommended value of 5.69 ± 0.62 (mg kg<sup>-1</sup>). The concentration found of U in the same material was 1.78 ± 0.24 and the value recommended is 1.75 ± 0.26 and for K found it was 1.42 ± 0.15 and the value recommended is 1.27 ± 0.66. The determined concentrations were obtained from the analysis of seven replicate samples. The precision of the INAA analysis for the samples was 12.54 % for Th, 13.76 % for U and 10.65 % for K. It can be observed that  $^{40}\text{K}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  presented excellent analytical performance. Table 2 introduces the value obtained for activity concentrations by  $\gamma$ -ray spectroscopy measurements of reference material samples for soil (IAEA-327).

Table 2: Determination of  $^{232}\text{Th}$ ,  $^{238}\text{U}$ , and  $^{40}\text{K}$  in reference material IAEA-327.

Radionuclide	Measured Value	RSD	Certificate Value	
	Value ± SD	(%)	Recommended	Range
$^{232}\text{Th}$ (Bq kg <sup>-1</sup> )	35.26 ± 4.03	11,43	38.7	37.2 – 40.2
$^{238}\text{U}$ (Bq kg <sup>-1</sup> )	29.88 ± 4.42	14,79	32.8	31.4 – 34.2
$^{40}\text{K}$ (Bq kg <sup>-1</sup> )	579.47 ± 24.65	4,25	621	612 – 630

The RSD value estimated the accuracy of the measures for standard reference materials. From the results obtained, we can say that  $\gamma$ -ray spectroscopy produces successful outcomes for marine samples, displaying satisfactory accuracy. The elemental concentrations of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  using both  $\gamma$ -ray spectroscopy and INAA techniques are showing in Table 3.

Table 3: Mass fraction for Th, U, and K using INAA and  $\gamma$ -ray spectroscopy, n=7.

Samples	Mean ± SD					
	INAA			$\gamma$ -ray spectroscopy		
	Th (mg kg <sup>-1</sup> )	U (mg kg <sup>-1</sup> )	K (%)	$^{232}\text{Th}$ (mg kg <sup>-1</sup> )	$^{238}\text{U}$ (mg kg <sup>-1</sup> )	$^{40}\text{K}$ (%)
STAF01	1.12 ± 0.06	0.47 ± 0.05	0.40 ± 0.01	1.20 ± 0.13	0.49 ± 0.01	0.43 ± 0.013
STAF02	1.26 ± 0.13	0.57 ± 0.12	1.09 ± 0.13	1.23 ± 0.38	0.54 ± 0.10	1.10 ± 0.19
STAF03	1.31 ± 0.21	0.56 ± 0.11	0.47 ± 0.08	1.30 ± 0.18	0.45 ± 0.05	0.51 ± 0.04
STAF04	1.46 ± 0.15	0.80 ± 0.07	0.68 ± 0.05	1.41 ± 0.28	0.76 ± 0.34	0.68 ± 0.06
STAF07	1.23 ± 0.07	0.98 ± 0.04	1.31 ± 0.08	1.17 ± 0.61	0.97 ± 0.34	1.26 ± 0.04
STAF08	1.27 ± 0.15	0.24 ± 0.03	0.65 ± 0.03	1.18 ± 0.06	0.26 ± 0.03	0.62 ± 0.01
CCM01	1.28 ± 0.05	0.74 ± 0.08	0.27 ± 0.01	1.23 ± 0.96	0.79 ± 0.37	0.27 ± 0.01
CCM02	2.11 ± 0.33	0.56 ± 0.03	0.24 ± 0.10	2.03 ± 0.46	0.56 ± 0.07	0.18 ± 0.01

The difference between the two techniques was more negligible for  $^{40}\text{K}$  and slightly higher for  $^{232}\text{Th}$  and  $^{238}\text{U}$ . The results presented in Table 3 highlight the close agreement between the techniques of  $\gamma$ -ray spectroscopy and INAA. Linear regression graphs and their respective linear regression coefficients for the potassium, uranium and thorium elements has been observed. Figure 2 shows the relationship between the measured values of  $^{40}\text{K}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  obtained using  $\gamma$ -ray spectroscopy and INAA.

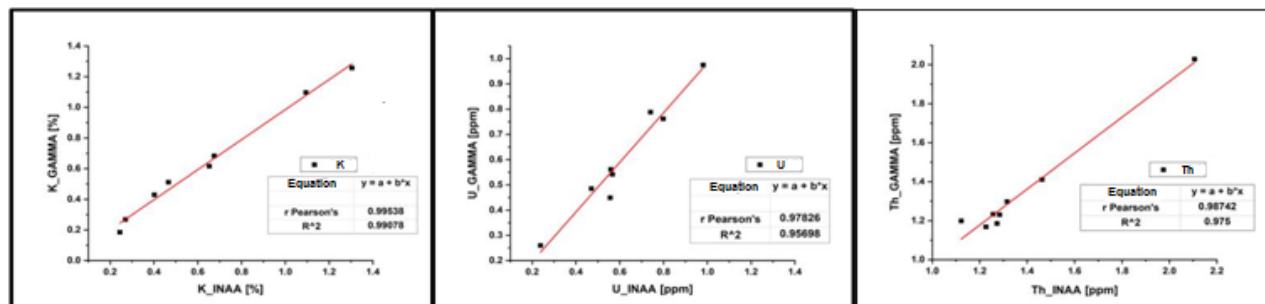


Figure 2: The relation of measured elemental concentrations of Th, U, and K using  $\gamma$ -ray spectroscopy technique and INAA.

The K element presented a clear, strong correlation with a linear regression coefficient of  $R^2 = 0.99$ . The correlation between the measured value of U had a linear regression coefficient of  $R^2 = 0.95$ , while the correlation between the measured value of Th had a linear regression coefficient of  $R^2 = 0.97$ .

#### 4. Conclusion

Good agreement was observed in determining  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  by  $\gamma$ -ray spectroscopy for certified or recommended reference material value (IAEA-327). Eight marine sediment samples from miner sites (STAF01, STAF02, STAF03, STAF04, STAF07, STAF08, CCM01 and CCM02 in Brazil) were analyzed by  $\gamma$ -ray spectroscopy and INAA technique. Elemental mean concentrations correlated with the 95% value or more when comparisons were performed between the two analytical techniques.

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