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COMPARATIVE STUDY OF THE DETERMINATION OF ^{238}U, ^{232}Th, AND ^{40}K IN GEOLOGICAL SAMPLES USING INAA AND GAMMA-RAY SPECTROSCOPY

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ABSTRACT

Physical dating methods including thermoluminescence (TL), optically stimulated luminescence (OSL) and electron paramagnetic resonance (EPR) require the precise determination of the dose rate of experimental ionizing radiation. To determine the age of sediment by TL and OSL or EPR, it is necessary to accurately determine the exact mass fractions of ^{238}U, ^{232}Th, and ^{40}K, since these concentrations are used in the calculation of the annual radiation dose. This work presents a comparative study of the determination of ^{238}U, ^{232}Th, and ^{40}K using two analytical techniques: instrumental activation analysis (INAA) and γ-ray spectroscopy. The results presented in this paper are concordant between the two techniques.

1. INTRODUCTION

The majority of marine sediments from the Brazilian coast that are suitable for dating by thermoluminescence (TL), optically stimulated luminescence (OSL) and electronic paramagnetic resonance (EPR) are composed of pure quartz or a mixture of feldspar and quartz. The aluminosilicates, in this case, have very low natural radioactivity amounts. The accuracy of any data obtained by TL, OSL or EPR depends on the precision of the measurement of such low dose rates and the assurance that they remain constant. Probably, the most accurate measurement of the dose rate of gamma rays is obtained by the burial of the dosimeter at the collection site. In the case of low dose rate, it may be necessary for the dosimeter to be buried for a period of up to 12 months, a procedure which can be very expensive and impractical [1, 2]. Alternatively, the total dose rate can be calculated from the determination of the elemental concentration of radionuclides ^{40}K, ^{232}Th and ^{238}U by analytical methods such as instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF) or γ-ray spectroscopy [3, 4, 5, 6]. This work compares the precision study between two analytical

techniques, INAA and γ-ray spectroscopy for the elemental determination of ^{40}K, ^{238}U, and ^{232}Th in marine sediment samples from a Brazilian site.

2. EXPERIMENTAL

2.1. Study area

The sampling site is located in the continental area of the city of São Vicente in the State of São Paulo, on the southeast coast of Brazil. The geographic location is 23º59'05,7"S, 46º29'58,5"W. The sampling site is surrounded by a mountain range to the north, and the bay of São Vicente to the south. The three selected sites (Fig. 1) were sampled in order to provide a representation of the entire study area.

2.1.1. Sample collection and initial preparation

Sample collection was carried out at the "Sociedade Técnica de Areia e Fundição" (STAF) in order to represent three undisturbed areas containing sealed Quaternary sand-sized marine terrace. The samples were collected in an area of 1 km^2 using polyvinyl-acrylic tubes. At each site, a representative sample was collected. The collected samples were evenly mixed after removal of the upper layer of vegetation and roots.

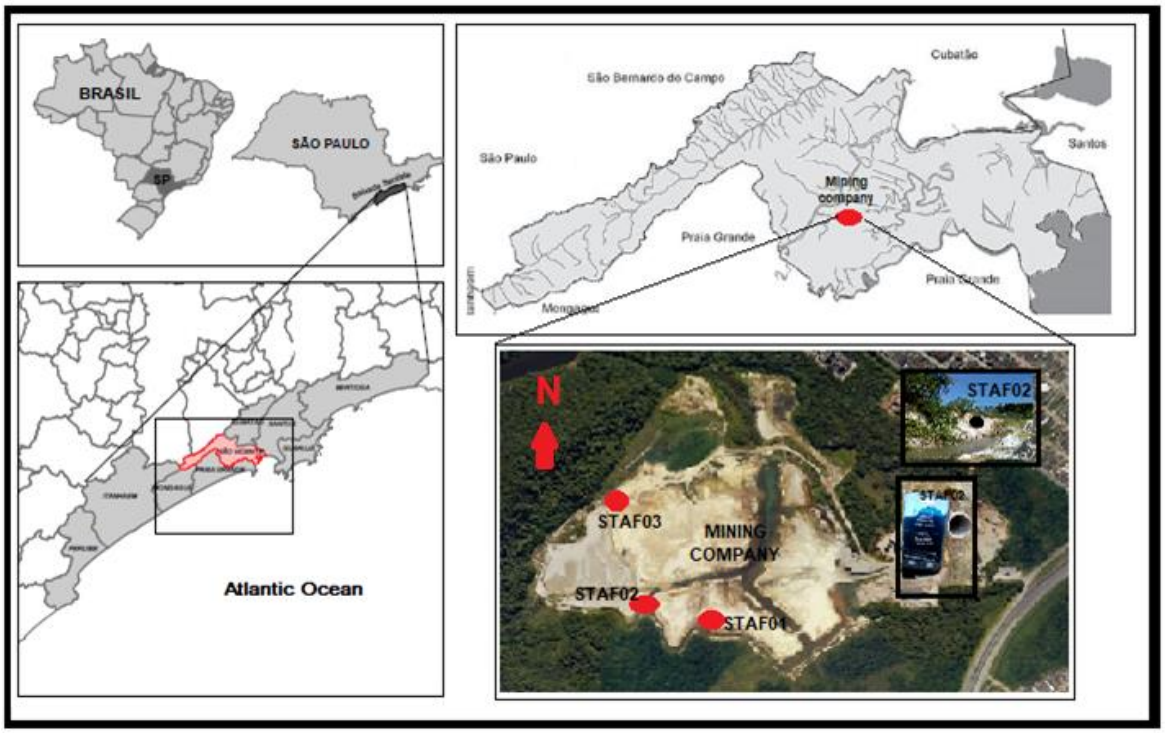

Figure 1: Study area showing the sampling locations around the STAF mine site.

To obtain moisture-free samples, each sample was oven-dried at 100.7 °C until it reached a constant dry weight. The dried samples were homogenized and then sieved through a 100 mesh to obtain a uniform grain size.

2.1.2. Instrumental Neutron Activation Analysis (INAA)

Around 100 mg of each sample were sealed in a polyethylene envelope. Each involucre was wrapped in Al foil. Groups of up to 8 aliquots and two geological standards, Standard Reference Material, NIST-SRM 1633b, Constituent element in Coal Fly Ash were used as a standard for analysis and the Sediment candidate certified reference material, named RM in this work, was used for the analytical quality control. Both reference materials were irradiated in the swimming pool research reactor IEA-R1 of the Instituto de Pesquisas Energetics e Nucleares, IPEN-CNEN/SP at a thermal neutron flux of about $1{,}33x10^{12}$ cm^{-2} s^{-}. The Measurements were performed using a Canberra GX 1925 (hyperpure) detector with a resolution of 1.90 keV at the peak range of ^{60}Co 1332.49 keV and S-100 MCA with 8192 channels. For the determination of K and Th the samples were irradiated with thermal neutron. The measured were made after 6 and 25 days for K and Th analysis, respectively. In the case of the analysis of U, the samples were irradiated in Cd capsule using epithermal neutron analysis (ref Regina). Gamma-ray spectra analysis and concentrations were performed using the Canberra Genie-2000 Neutron Activation Analysis Processing Procedure. Relative INAA method was used to calculate the concentration of Th, U, and K in geological samples. In the relative method, a standard containing a known amount of the element to be determined is irradiated along with the unknown samples. It is assumed that the neutron flux, cross-section, irradiation times are identical for both the standard and the sample. It is then possible to write an equation for INAA as follows [7].

$$\frac{R_{std}}{R_{sam}} = \frac{W_{std}\left(e^{-\lambda t_d}\right)std}{W_{sam}\left(e^{-\lambda t_d}\right)sam} \tag{2}$$

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.

2.1.3. γ-ray spectroscopy

The homogenized samples were weighed, conditioned and sealed in polythene pots with a volume of 42 cm^3. The pots were stored for 30 days for secularization, reaching equilibrium with the short-lived daughters of ^{222}Ra and their radionuclides. The natural gamma activity was determined from the activities of ^{238}U, ^{232}Th, and ^{40}K. The concentration of ^{40}K natural gamma activity was estimated by its unique gamma transition of 1460,81 keV. The natural gamma activity concentrations of ^{238}U and ^{232}Th were obtained considering the radioactive balance of the uranium and thorium radioactive series. Radium and its decay products account for 98.5% of the radiological effect of the radioactive uranium series. The ^{238}U activity data were replaced by the ^{226}Ra activity data. The gamma transitions 295 keV, 352 keV of ^{214}Pb and 609 keV of ^{214}Bi were considered for ^{226}Ra. The transitions of 238 keV, 300 keV of ^{212}Pb and 911 keV, 969 keV of ^{228}Ac were considered for ^{232}Th [8, 9, 10]. The concentrations of natural gamma activity were obtained using Equation 3 [11].

$$A_{Eg} = \frac{C}{E_g\, I_g\, tm} f_{Eg} \tag{3}$$

where A_{Eg} represents the concentration of natural gamma activity given in ($Bq.kg^{-1}$), C is a net area of the peak of interest, E_g is detection efficiency, I_g is emission probability, t is

acquisition time, *m* is mass of the sample in Kg and f_{Eg} is the attenuation factor for the related gamma transition. The average of the activities weighted by the uncertainties of the respective transitions was obtained in Equation 4 [11].

$$A\ (Bq.kg^{-1}) = \frac{\frac{A_1}{\sigma_1^2} + \frac{A_2}{\sigma_2^2} + \ldots + \frac{A_n}{\sigma_n^2}}{\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2} + \ldots + \frac{1}{\sigma_n^2}} \quad (4)$$

where A_1,..., An are the activities calculated from each gamma transition and σ_1,..., σ_n represent their respective uncertainties. The uncertainty of the respective transitions can be obtained from Equation 5.

$$\sigma_A = \sqrt{\frac{1}{\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2} + \ldots + \frac{1}{\sigma_n^2}}} \quad (5)$$

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}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 Bq kg^{-1} to fracing mass were: ^{238}U; 1 ppm = 12.35 Bq kg^{-1}, for ^{232}Th; 1 ppm = 4.06 Bq kg^{-1}. Where 1% of ^{40}K = 313 Bq kg^{-1}[12].

2.1.4. Analytical quality control of γ-ray spectroscopy and INAA methods

The analytical quality control of a method is confirmation by means of a systematic evaluation to demonstrate the scientific consistency of the method under the conditions of its application. The parameters used for formal analytical quality control of the trace elements studied in this work were: accuracy (relative percentage error and Z-score), precision (relative standard deviation), the limit of detection (LD) and limit of quantification (LQ). The Equations 6, 7, 8, 9 and 10 present the formulas for the determination of these quantities [13].

$$RE(\%) = \frac{100(x - x_r)}{x_r} \quad (6)$$

where,

RE(%) is the percentage relative error
x is the measurement value;
x_r is the reference value.

and the Z-score was determined by means of the expression.

$$Z = \frac{x - x_r}{s_r} \quad (7)$$

where,

z is the value of the z-score for the measured value;
s_r is the standard deviation of the reference value;

The precision of the analysis was studied by means of the relative standard deviation (RSD).

$$\mathrm{RSD}(\%) = 100\left(\frac{s_r}{\bar{x}}\right) \tag{8}$$

where,

$\bar{x}$ is the mean of the measured values.

The values for the limit of detection and limit of quantification were estimated for a known sample and follow the model proposed by Currie in 1999, which uses [14].

$$LD = 3{,}29\ \frac{\sqrt{b}}{t} \tag{9}$$

The limit of quantification is determined by.

$$\mathrm{LQ}=10\frac{\sqrt{b}}{t} \tag{10}$$

where,

b is the number of counts of the background radiation for the peak studied (cps);
t is the counting time.

3. RESULTS

This work studied the precision of INAA to determine the elemental concentration for the Sediment candidate to reference material, in which all sources of error were known and the uncertainties were estimated by the Department of Environmental Sciences, Wageningen University, The Netherlands. This candidate to RM was analyzed by 41 INAA laboratories and the results of this work were statistically compared to the data from these other laboratories in order to evaluate the analytical process for ^{238}U, ^{232}Th, and ^{40}K. Table 1 shows the measured mean value, the RSD and the recommended values for the elements under analysis in the RM reference material samples.

Table 1: Mass fraction and uncertainties for ^{232}Th, ^{238}U, and ^{40}K in reference material RM.

Radionuclide	Measured Value (n=7) Mean ± SD	RSD (%)	Recommended Value
^{232}Th, PPM	5.72 ± 0.31	5.42	5.69 ± 0.62
^{238}U, ppm	1.74 ± 0.10	5.74	1.75 ± 0.26
^{40}K, %	1.36 ± 0.07	5.14	1.29 ± 0.07

The activation converts ^{238}U and ^{232}Th into ^{239}Np and ^{233}Pa, respectively, by neutron capture and successive β-decay. The γ-rays can be detected using γ-ray spectrometry. The measured concentration of ^{232}Th in the reference material RM was 5.72 ± 0.31 (mg kg^{-1}) compared to the recommended value of 5.69 ± 0.62 (mg kg^{-1}). The concentration value of ^{238}U measured on the same material was 1.74 ± 0.10 compared to the certified value of 1.75 ± 0.26 and for ^{40}K it was 1.36 ± 0.07 compared to 1.29 ± 0.07. The determined concentrations were obtained from the analysis of seven replicate samples. The precision of the INAA analysis for the samples was 5.42% for ^{232}Th, 5.74% for ^{238}U and 5.14% for ^{40}K. The percentage relative error of the determined was 0.53% for ^{232}Th, 0.57%, for ^{238}U, and for ^{40}K, 5.43% over the recommended value. The z-score with 95% confidence level was 0.05 for ^{232}Th, 0.04 for ^{238}U and 1.00 for ^{40}K. The z-score values for all the studied elements of the reference material are satisfactory ($\leq$ 2) [13]. It can be observed that ^{40}K, ^{238}U and ^{232}Th presented excellent analytical performance. Table 2 introduces the value obtained for activity concentrations by γ-ray spectroscopy measurements of reference material samples for soil (IAEA-327). The activity of ^{238}U, ^{232}Th, and ^{40}K is reported throughout this article in dry weight (Bq kg^{-1}).

Table 2: Active concentration (Bq kg^{-1}) for ^{232}Th, ^{238}U, and ^{40}K in reference material IAEA-327.

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

Gamma rays emitted from ^{238}U and ^{232}Th through the decay of isotopes. These isotopes are at the end of the decay series and for measurements of γ-ray spectroscopy to be related to uranium and thorium, each series must be in secular equilibrium. The accuracy of the measurements was estimated from the RSD value for standard reference materials. From the results obtained, can say that γ-ray spectroscopy produces successful results for marine samples, displaying satisfactory accuracy. The accuracy of ^{232}Th and ^{238}U was within the range of 10% of the reference values. For 40K, the precision value was very good (<5.0%). The percentage relative error of the determined value for ^{232}Th was 9.7%, for ^{238}U, 9.8%, and for ^{40}K, 7.2% with respect to the certified value. The same procedure was applied in three samples of the marine terrace from the STAF mining company Brazil. The measured concentrations of radionuclide activity are shown in Table 3.

Table 3: Active concentration (Bq kg^{-1}) for ^{232}Th, ^{238}U, and ^{40}K in samples (n=3).

Samples	Mean ± SD		
	^{232}Th	^{238}U	^{40}K
STAF01	4.85 ± 0.65	5.95 ± 0.62	134.35 ± 4.08
STAF02	6.29 ± 1.41	6.79 ± 0.63	343.46 ± 5.91
STAF03	5.55 ± 0.38	5.51 ± 0.71	160.11 ± 13.94

The elemental concentrations of ^{238}U, ^{232}Th, and ^{40}K measured using both γ-ray spectroscopy and INAA techniques are shown in Table 4. The concentration values presented in Table 4 by γ-ray spectroscopy are obtained by multiplying the decay rate of the radionuclide (Bq kg^{-1}) by the transformation factor quoted earlier in the article.

Table 4: Mass fraction for ^{232}Th, ^{238}U, and ^{40}K from INAA and γ-ray spectroscopy in samples.

	Mean ± SD					
	INAA (n=7)			γ-ray spectroscopy (n=3)		
Samples	**Th, ppm**	**U, ppm**	**K, %**	**Th, ppm**	**U, ppm**	**K, %**
STAF01	1.13 ± 0.05	0.46 ± 0.03	0.45 ± 0.03	1.19 ± 0.16	0.48 ± 0.05	0.43 ± 0.01
STAF02	1.32 ± 0.04	0.50 ± 0.04	1.05 ± 0.03	1.55 ± 0.35	0.54 ± 0.05	1.10 ± 0.02
STAF03	1.22 ± 0.06	0.41 ± 0.04	0.51 ± 0.03	1.36 ± 0.09	0.44 ± 0.05	0.51 ± 0.04
LD	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.09 ± 0.03	0.10 ± 0.02	0.04 ± 0.01
LQ	0.13 ± 0.02	0.11 ± 0.03	0.12 ± 0.02	0.28 ± 0.05	0.32 ±0.06	0.13 ±0.03

The difference between the two techniques was less for ^{40}K and ^{238}U, and a little higher for ^{232}Th. The results presented in Table 4 highlight the close agreement between the techniques of γ-ray spectroscopy and INAA. The potassium element showed higher agreement, followed by thorium and uranium. We must, however, be cautious in extrapolating our results due too the issue of a sample size. The use of a larger number of samples would be more appropriate and is recommended for future work. Table 4 also shows the calculated LD and LQ values. It is important to note that the elemental concentration values obtained for the geological samples by the two techniques are above the calculated values of LD and LQ. Linear regression graphs and their respective linear regression coefficients for the potassium, uranium and thorium elements are presented below. Figure 2 shows the relationship between the measured values of ^{40}K, ^{238}U and ^{232}Th obtained using γ-ray spectroscopy and INAA. The equation used to adjust the linear regression curve for the three elements was of the type ($y = a + bx$).

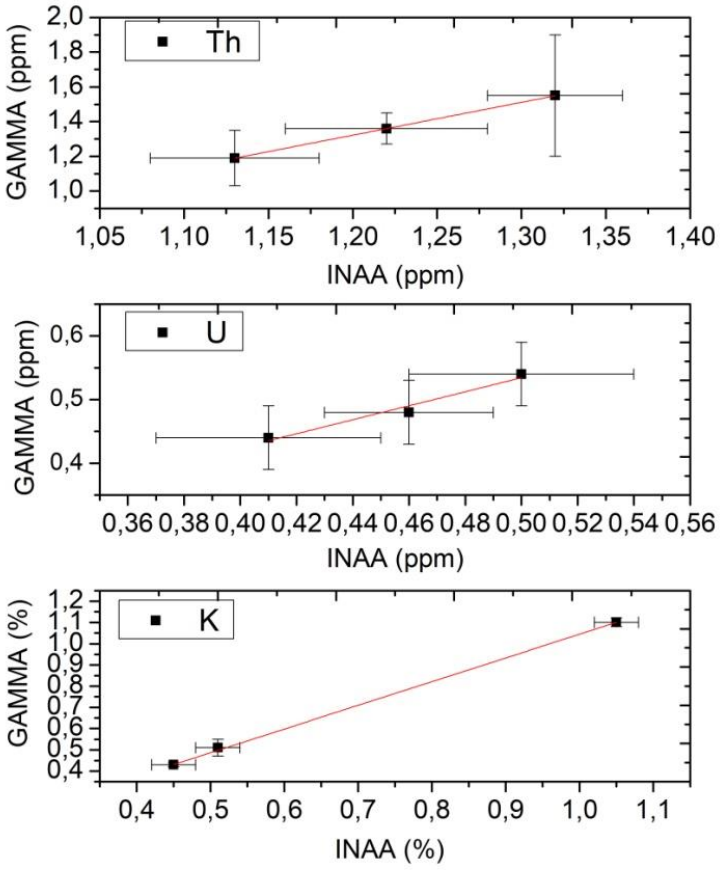

Figure 2: The relation of measured elemental concentrations of ^{232}Th, ^{238}U, and ^{40}K using γ-ray spectroscopy technique and INAA.

^{40}K presented a clear, strong correlation with a linear regression coefficient of $R^2 = 0.99$. The correlation between the measured value of ^{238}U had a linear regression coefficient of $R^2 = 0.94$, while the correlation between the measured value of ^{232}Th had a linear regression coefficient of $R^2 = 0.99$.

4. CONCLUSION

This work measured the concentrations of the specific activity of natural radionuclides ^{238}U, ^{232}Th and ^{40}K, as well as their elemental concentration, in marine sediment samples from three sites within a single location in Brazil, using γ-ray spectroscopy and INAA. A strong correlation was observed between radionuclides measured with γ-ray spectroscopy and INAA. Through inter-technique comparisons, we show that the natural radionuclides, their radiation dose and their elementary concentration corresponding to our systems presented excellent performance. It can, therefore, be concluded that INAA and γ-ray spectroscopy techniques can be used to determine the elemental uranium, thorium and potassium concentration in geological samples and that these results can be subsequently used to calculate dose rate.

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