



Levels of thorium, uranium and potassium in Brazilian geological sediment determined by gamma-ray spectroscopy and instrumental neutron activation analysis.

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ABSTRACT

The Brazilian coast of the terrace contains a wealth of evidence that can be used to explain the evolution of the coastline over the past 120k years. These studies include marine sediment geochronology based on dosimetry dating methods, in particular thermoluminescence. To determine the age of the terrace using luminescence dosimetry methods, it is necessary to decide on the exact mass fractions of ^{238}U , ^{232}Th , and ^{40}K . These mass fraction values are used to calculate the annual dose rate of ionized radiation. In this context, in the present work, we studied eight marine sediment samples collected in the city of São Vicente on the coast of São Paulo state, Brazil, and determined the mass fractions of elements ^{238}U , ^{232}Th , and ^{40}K by instrumental neutron activation analysis (INAA) and γ -ray spectroscopy. Linear regression mathematical methods are used to evaluate analytical methods accuracy. The results show a good correlation with a R^2 value of more than 0.71. Therefore, it is possible to calculate the resulting mass fraction, calculate the dose rates of these sediments, and contribute to their date.

Keywords: sand terrace, dose rate, INAA, γ -ray spectroscopy, ^{238}U , ^{232}Th , ^{40}K .



1. INTRODUCTION

In recent years, luminescence dating science has advanced significantly, particularly thermoluminescence. Several studies have shown that thermoluminescence dating from marine sediments can be carried out successfully [1,2,3]. Thermoluminescence results from light emission due to electrons' liberation and metastable entrapment states' vacancies in crystalline defects. When quartz is heated, electrons and holes are ejected and recombined with opposite charge carriers. The intensity of the emitted photon is proportional to the equivalent dose (ED) [4]. The age of a given geological material is obtained by the relationship between ED and the annual dose rate of radiation and is assumed to be constant over time [5].

Thus, one of the essential factors in luminescence dating involves estimating the annual radiation dose. If the annual dose rate is low, it may be necessary to bury the dosimeter for up to 12 months, which can be expensive and impractical [6].

Analytical methods capable of determining the mass fractions of radionuclides ^{40}K , ^{232}Th , and ^{238}U (in mg kg^{-1} or Bq kg^{-1}) shall be further converted into terms of the energy absorbed by a unit mass over time (Gy a^{-1}) [7].

Among the analytical methods most commonly used to determine the mass fractions of ^{40}K , ^{232}Th , and ^{238}U include instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF) and γ -ray, α -ray or β -ray spectroscopy [5,7,8]. Some problems in determining mass fractions of ^{40}K , ^{232}Th and ^{238}U include the effects of fluctuations in soil humidity. Measurement time of in situ dosimeters, cosmic radiation dose rates calculation, and the difficulty of measuring natural radioactivity in situ marine sediment.

In this study, two methods, γ -ray spectroscopy and INAA were used to determine the mass fractions of ^{40}K , ^{232}Th , and ^{238}U mass fractions in eight samples of marine sediment collected on the Brazilian coast, and linear regression was used to evaluate the precision of the analytical methods. Each technique has its advantages. The indirect method's estimated annual dose rate measurement takes only a few weeks. However, difficulties can arise due to shallow radioactivity values in marine sediments. In this case, using more than one method can be advantageous.

2. MATERIALS AND METHODS

2.1. Study area, sample collection, and initial preparation

The study is in the coastal area of São Vicente city, located in the state of São Paulo, Brazil (-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 (Figure 1). Six sites (STAF01, STAF02, STAF03, STAF04, STAF07, and STAF08) were sampled to represent the entire study area. The sampling was carried out at the "*Sociedade Técnica de Areia para Fundação*" (STAF) to represent six undisturbed areas containing sealed quaternary-sized marine terraces. Eight samples were collected using polyvinyl acrylic tubes. Each sample was oven dried at 100.7 ° C until it reached a constant dry weight, homogenized, and then sieved through a 100 µm to obtain a uniform grain size.

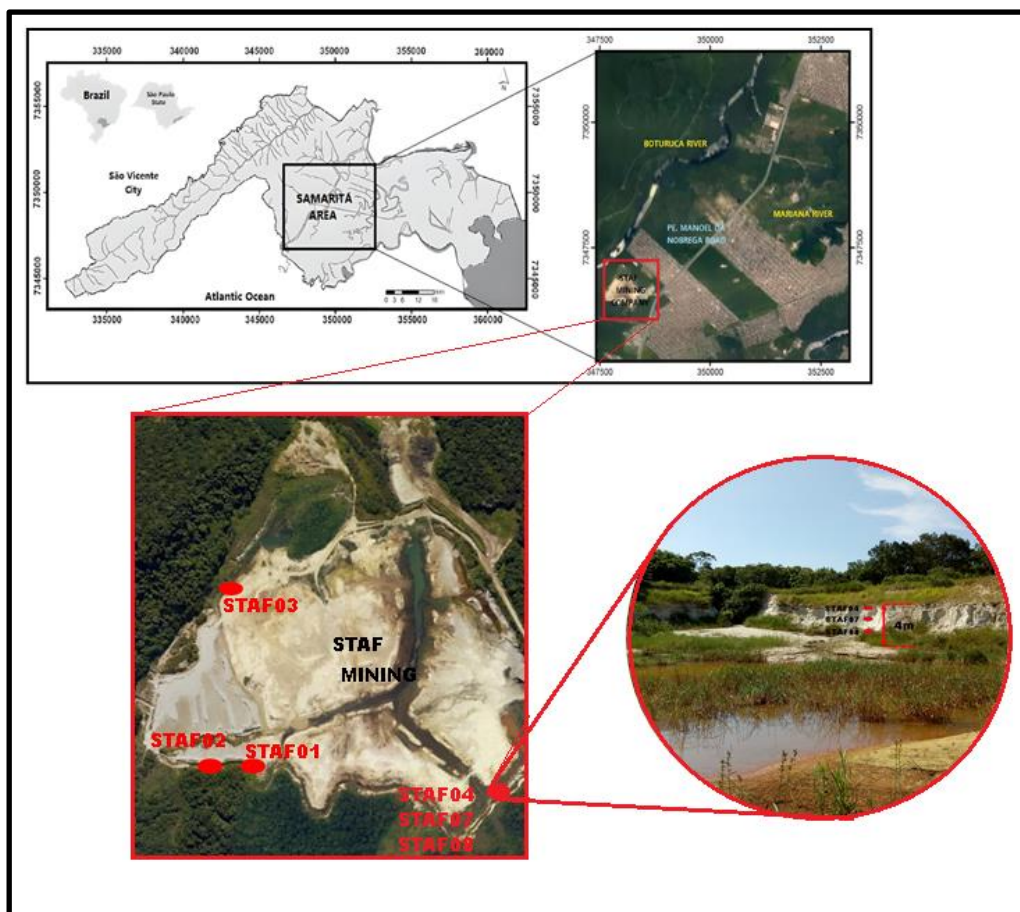


Figure 1: Location of the study area.

2.2. Instrumental Neutron Activation Analysis (INAA)

About 100 mg of dry powder was weighed and packed in polyethene wrap protected with Al foil for each sample. Eight samples were assembled with approximately 100 mg of the NIST-SRM 1633b constituent elements in coal fly ash and the certified reference material, RM, from Wageningen University, Environmental Sciences, the Netherlands. After grouping the samples in parallel to receive the same neutron flux, they were irradiated for eight hours in the IEA-R1 reactor of IPEN-CNEN / SP with a thermal neutron flux of the order of $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ [9]. Measurements were made in two stages: after seven days of decay to determine the concentrations of the U and K elements and after 25 to 30 days to assess the Th. All measurements used the Ge hyperpure detector, model GX 1925 from CANBERRA, with a resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co , with S-100 MCA of CANBERRA with 8192 channels. A Cd capsule and neutron epithermal flux were used to determine U concentration. The Genie-2000 Gamma Acquisition & Analysis software, v.3.1a, developed by CANBERRA, was used to analyze γ -ray spectra [10].

Equation 1 describes the comparative method in 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 sample [11].

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

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

2.3. 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 radionuclides. Natural gamma activity was determined from ^{238}U , ^{232}Th , and ^{40}K . The ^{40}K natural gamma activity concentration was estimated by its unique

gamma transition of 1460.81 keV. Natural gamma activity concentrations of ^{238}U and ^{232}Th were obtained considering the radioactive series of a radioactive balance of uranium and thorium. Radium and its decay products account for 98.5 % of the radiological effect of the radioactive uranium series. The ^{226}Ra activity data replaced the ^{238}U activity data. The 295 keV gamma transitions, 352 keV of ^{214}Pb , and 609 keV of ^{214}Bi were considered for ^{226}Ra . Transitions of 238 keV, 300 keV of ^{212}Pb and 911 keV, 969 keV of ^{228}Ac were considered for ^{232}Th [12, 13, 14]. Concentrations of natural gamma activity were obtained using Equation 2 [15].

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

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 the mass of the sample in kg, and f_{Eg} is the attenuation factor for the related gamma transition. The average of activities weighted by the uncertainties of the respective changes was obtained in Equation 3 [15].

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

where A_1, \dots, A_n are the activities calculated from each gamma transition and $\sigma_1, \dots, \sigma_n$ represent their respective uncertainties. The uncertainty of the individual changes can be obtained from Equation 4.

$$\sigma_A = \sqrt{\frac{1}{\frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2} + \dots + \frac{1}{\sigma_n^2}}} \quad (4)$$

The activity concentration for the radionuclides in each studied sample was defined using the gamma spectrometer system using an HPGe detector with an electronic DSPLynx. The power resolution (FWHM) is 1.80 keV, and the relative efficiency is 40 % to 1.332MeV of ^{60}Co . The

analysis of the results was performed with Genie2000 software. The dead time is less than 10% in all measurements, and the Genie2000 software performed the correction. The conversion factors used to convert Bq kg⁻¹ to mass fraction were: ²³⁸U; 1 ppm = 12.35 Bq kg⁻¹, for ²³²Th; 1 ppm = 4.06 Bq kg⁻¹ and 10000 ppm of ⁴⁰K = 313 Bq kg⁻¹ [16].

3. RESULTS AND DISCUSSION

The precision of the INAA method was studied by determining the elemental concentration of the candidate sediment reference material (RM). All error fonts are known, and uncertainties were estimated by the Environmental Sciences Department of Wageningen University. 41 INAA specialising laboratories analysed the RM candidate. The results of the elemental concentration obtained in the present study were compared with these data to evaluate the analysis of radionuclides ²³⁸U, ²³²Th, and ⁴⁰K. Table 1 shows the mean values, RSD, and recommended values for the RM sample.

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 ⁻¹)	5.54 ± 0.69	12.45	5.69 ± 0.62	10.89
U (mg kg ⁻¹)	1.78 ± 0.24	13.48	1.75 ± 0.26	14.86
K (mg kg ⁻¹)	14200 ± 1500	10.56	12700 ± 6600	51.96

RSD=Relative Standard Deviation; SD=Standard Deviation

In INAA, radionuclides ²³⁸U are ²³²Th, converted into ²³⁹Np and ²³³Pa, respectively, by neutron capture and decay. The γ -rays can be detected using γ -ray spectroscopy. The measured concentration value of ²³²Th in the RM was 5.54 ± 0.69 (mg kg⁻¹) compared to the recommended value of 5.69 ± 0.62 (mg kg⁻¹). The measured concentration value of ²³⁸U was 1.78 ± 0.24 compared to the certified value of 1.75 ± 0.26, and for ⁴⁰K, it was 14200 ± 1500 compared to 12700 ± 6600. The mean concentrations were obtained by analyzing seven replicates of the samples. The precision of INAA can be studied by analysing the RSD of the RM. In this study, the RSD values were 12.45

% for ^{232}Th , 13.48 % for ^{238}U and 10.56 % for ^{40}K . It can be concluded that ^{40}K , ^{238}U and ^{232}Th presented excellent analytic performance.

Table 2 presents the values of the activity concentrations determined by γ -ray spectroscopy measurements on IAEA-327. The activity of ^{238}U , ^{232}Th , and ^{40}K is reported throughout this article regarding dry weight (Bq kg^{-1}).

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

Radionuclide	Measured Value	RSD	Certificate Value	
	Value \pm SD	(%)	Recommended	Range
^{232}Th (Bq kg^{-1})	35.26 ± 4.03	11.43	38.7	37.2 – 40.2
^{238}U (Bq kg^{-1})	29.88 ± 4.42	14.79	32.8	31.4 – 34.2
^{40}K (Bq kg^{-1})	579.47 ± 24.65	4.25	621	612 – 630

RSD=Relative Standard Deviation; SD=Standard Deviation

The ^{238}U and ^{232}Th emit gamma rays through the decay of radioactive isotopes. These isotopes are at the end of a decay series. Each series must be in secular equilibrium for the γ -ray spectroscopy measurements to be related to uranium and thorium. The precision of the measurements was estimated using the RSD value for IAEA-327. From the value obtained, it can be said that the method produced successful results for the marine sediments, producing satisfactory accuracy. The precision of ^{232}Th and ^{238}U is within the acceptable range of the reference values.

For ^{40}K , the precision value was less than 5.0 %. The percentage error of the value determined for ^{232}Th was 11.43 % for ^{238}U , 14.79 %, and for ^{40}K , 4.25 %. The elemental concentrations for ^{238}U , ^{232}Th and ^{40}K measured using γ -ray spectroscopy, and INAA techniques are shown in Table 3.

The mass concentration values presented in Table 3 for γ -ray spectroscopy are obtained by multiplying the decay rate (Bq kg^{-1}) by the conversion factor. The difference between the two techniques was slight for ^{40}K and ^{238}U and slightly higher for ^{232}Th . The results presented in Table 3 highlight the strict agreement between γ -ray spectroscopy and INAA.

Table 3: Mass fractions of Th, U, and K using INAA and γ -ray spectroscopy.

Samples	Mean \pm SD					
	INAA			γ -ray spectroscopy		
	Th (mg kg ⁻¹)	U (mg kg ⁻¹)	K (mg kg ⁻¹)	²³² Th (mg kg ⁻¹)	²³⁸ U (mg kg ⁻¹)	⁴⁰ K (mg kg ⁻¹)
STAF01	1.12 \pm 0.06	0.47 \pm 0.05	4000 \pm 100	1.20 \pm 0.13	0.49 \pm 0.01	4300 \pm 130
STAF02	1.26 \pm 0.13	0.57 \pm 0.12	10900 \pm 1300	1.23 \pm 0.38	0.54 \pm 0.10	11000 \pm 1900
STAF03	1.31 \pm 0.21	0.56 \pm 0.11	4700 \pm 800	1.30 \pm 0.18	0.45 \pm 0.05	5100 \pm 400
STAF04	1.46 \pm 0.15	0.80 \pm 0.07	6800 \pm 500	1.41 \pm 0.28	0.76 \pm 0.34	6800 \pm 600
STAF07	1.23 \pm 0.07	0.98 \pm 0.04	13100 \pm 800	1.17 \pm 0.61	0.97 \pm 0.34	12600 \pm 400
STAF08	1.27 \pm 0.15	0.24 \pm 0.03	6500 \pm 300	1.18 \pm 0.06	0.26 \pm 0.03	6200 \pm 100
CCM01	1.28 \pm 0.05	0.74 \pm 0.08	2700 \pm 100	1.23 \pm 0.96	0.79 \pm 0.37	2700 \pm 100
CCM02	2.11 \pm 0.33	0.56 \pm 0.03	2400 \pm 100	2.03 \pm 0.46	0.56 \pm 0.07	1800 \pm 100

SD=Standard Deviation

However, the analysis of more samples is recommended for future studies. Linear regression graphs and their respective potassium, uranium, and thorium coefficients are presented below. Figure 2 shows the relationship between the ⁴⁰K, ²³⁸U and ²³²Th obtained by γ -ray spectroscopy and INAA. The equation used to adjust the linear regression curve for three elements was the type ($y = a + bx$). The ⁴⁰K showed a clear and strong correlation, with a linear regression coefficient of $R^2 = 0.99$. The correlation between the measured value of ²³²Th had a linear regression coefficient of $R^2 = 0.97$, and that of ²³⁸U was $R^2 = 0.94$.

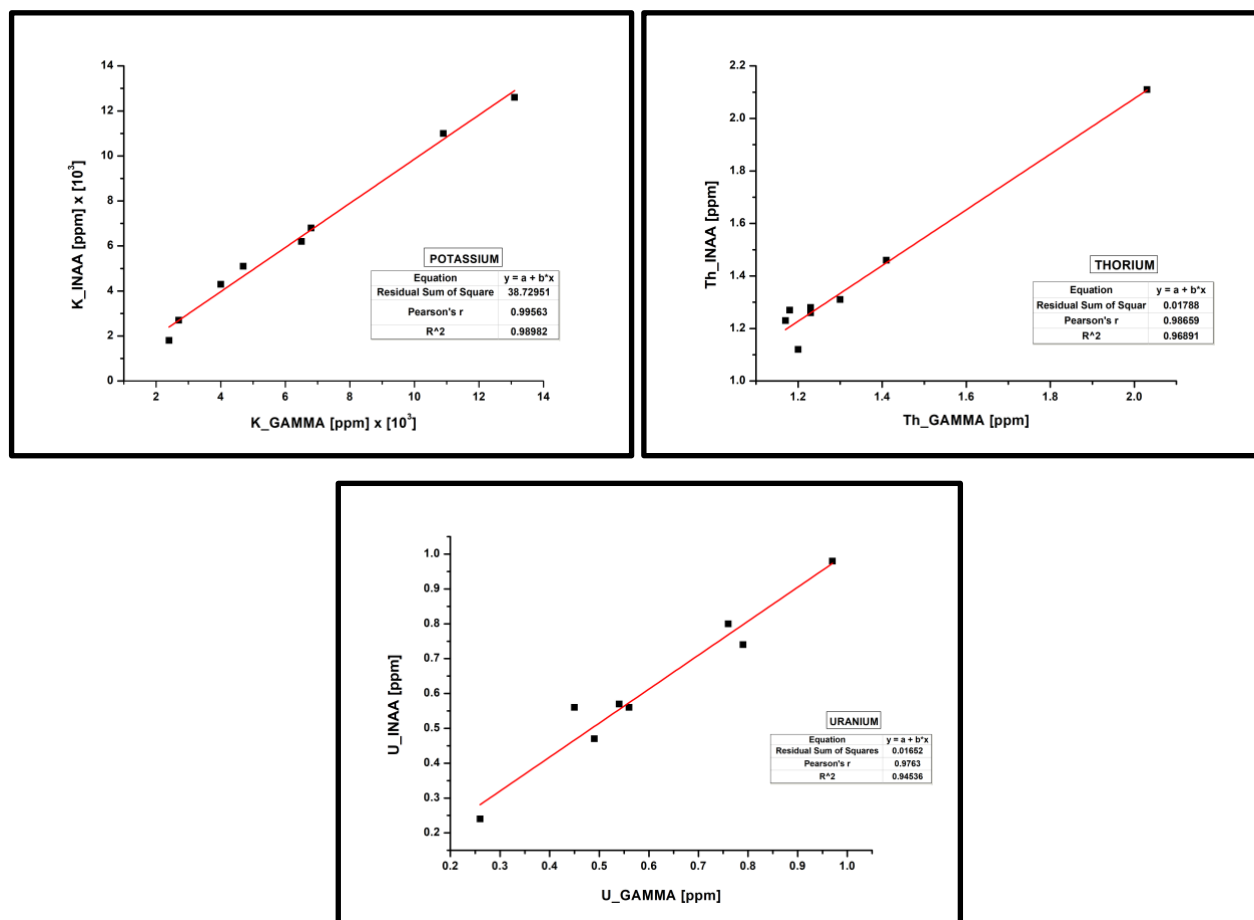


Figure 2: The relation of measured elemental concentrations of Th, U and K using γ -ray spectroscopy and INAA.

Figure 3 shows the mean concentrations of elements U, Th and K obtained by INAA and γ -ray spectroscopy and their respective uncertainties. One can observe that the means produced by both analytical methods are close. One can also keep how the delay for Th and U obtained by γ -ray spectroscopy was more significant than the uncertainty brought by INAA. The best results were obtained for the element K.

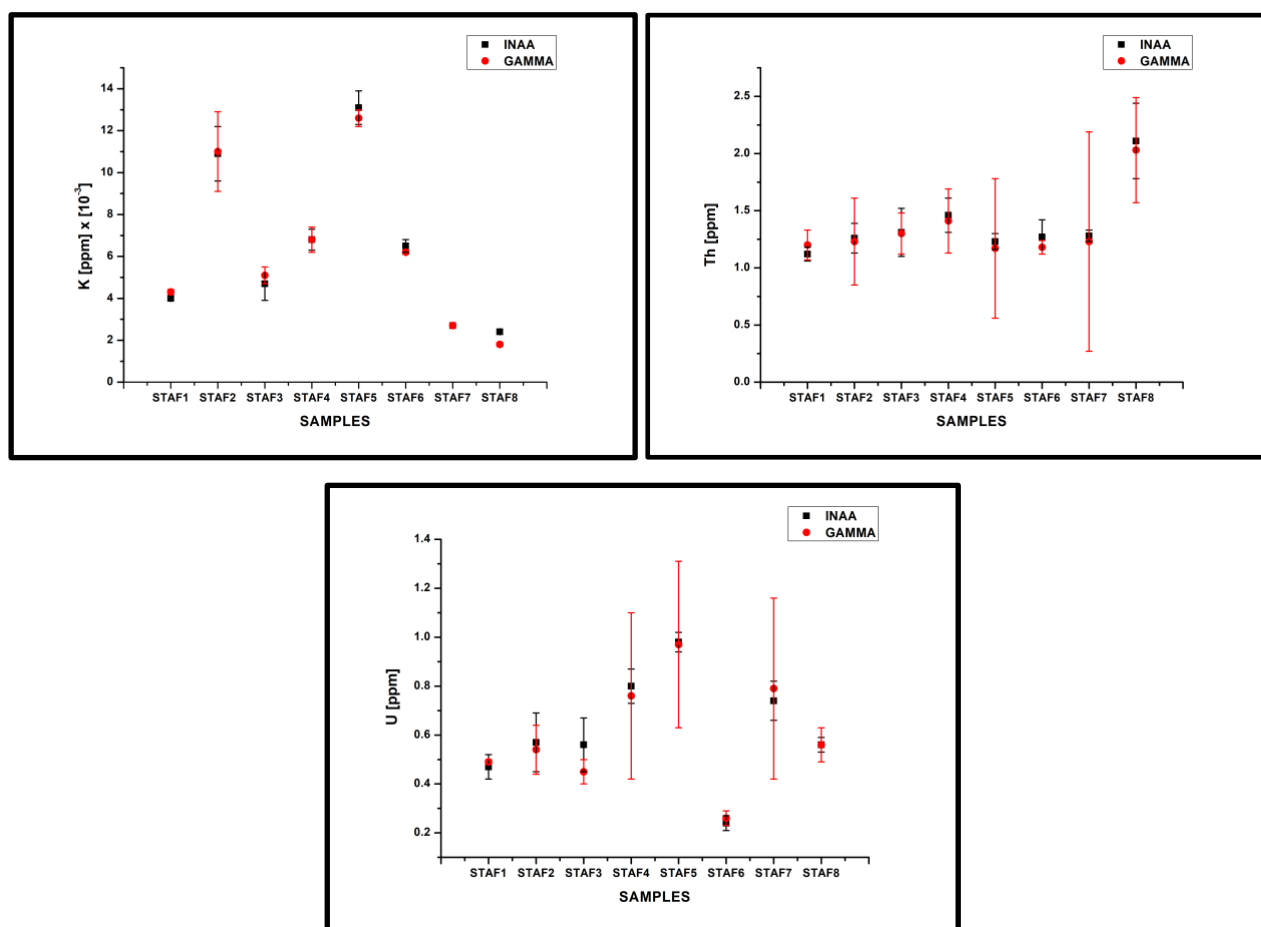


Figure 3. Comparison of the mean element concentration values measures with *INAA* and *γ-ray spectroscopy*.

4. CONCLUSION

This article measured the concentrations of specific activity of natural radionuclides ^{238}U , ^{232}Th , and ^{40}K and the mass fraction of 8 marine sediment samples from the Brazilian coast employing γ -ray spectroscopy and INAA. Good agreement was observed in the determination of the elements uranium, thorium, and potassium. We showed that the natural radionuclides, radiation dose, and elemental concentrations corresponding to our systems showed excellent performance through intertechnical comparisons. The mean element concentrations were correlated with a value of 95 % or more when comparing the two techniques. Therefore, it can be concluded that INAA and γ -ray spectroscopy techniques can be used reliably to determine the elemental concentration of uranium,

thorium, and potassium in geological samples. Subsequently, these results can be used to calculate the dose rate.

ACKNOWLEDGMENTS

The authors thank the National Council for Scientific and Technological Development (CNPq), the Foundation for Research Support of the State of São Paulo (FAPESP), the University of São Paulo (USP-SP) and the Nuclear and Energy Research Institute (IPEN-CNEN/SP) for technical and financial support.

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