PREPARATION OF A SOIL REFERENCE MATERIAL WITH HIGH THORIUM CONCENTRATION FOR DETERMINATION OF RADIONUCLIDES FROM THORIUM AND URANIUM NATURAL SERIES

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Abstract – It was prepared a reference material from a soil with high thorium concentration from a region with high natural radioactivity. Performed tests using gamma spectrometry and statistical programs showed that the prepared material was homogeneous and enough stable to be used as an in-house reference material in intercomparison exercises.

Keywords: reference material, radionuclides, soil.

1. INTRODUCTION

Brazil has big uranium and thorium reserves [1], so that the influence of these elements and their decay family on the environment can be significant in some regions. Industrial activities can also contribute to increase the background related to uranium and thorium content. So the monitoring of radionuclides in these regions is compulsory. The monitoring of radionuclides in environmental samples needs reference material to produce reliable analytical data. Through intercomparison exercises participants laboratories can evaluate their analysis methods.

Intercomparison exercises for radiochemical laboratories in Brazil are coordinated by Institute of Radioprotection and Dosimetry (IRD) trough the National Intercomparison Program (PNI) of radionuclides assays in environmental samples [2,3,4]. This program sends three times a year to users samples of radionuclides in several matrices like water, sediments, soils, and air filters.

The participating laboratories are mainly involved in monitoring the control of radioactivity in nuclear plants and environmental control.

Usually Certified Reference Materials (CRMs) are very expensive and the costs can increase quickly if the CRMs are routinely used to check the performance of methods in analytical chemistry. One alternative is the use of Laboratory Reference Materials (LRMs) to reach this goal [5]. The production of (LRMs) is much cheaper than the CRMs. CRMs and LRMs have the same two basic tests (homogeneity and stability) of production, however it must be stressed that an in-house reference material do not replace CRMs, but merely enable CRMs to be used on a less frequent basis [6].

This paper describes the preparation of a soil to be used as a reference material for radionuclide analysis. Soils samples were collected in a high natural radioactivity area in Southeast of Brazil. This soil has about 1 % of Th. The radionuclides of interest are ^{40}K, ^{212}Pb, ^{214}Pb, ^{214}Bi and ^{228}Ac.

The procedure used to prepare this soil is similar to reported by Llauradó [7] but some parameters were experimentally changed, like ground conditions and mixing time.

2. EXPERIMENTAL

2.1 sampling

The soil was collected in Morro do Ferro, Poços de Caldas City, located in Minas Gerais State, Southeast of Brazil. Poços de Caldas Plateau, one of the biggest alkaline intrusions in the world is one of the Brazilian high natural radioactivity areas due to the occurrence of uranium and thorium ore deposits [8].

2.2 Apparatus

An Ortec high-resolution spectrometer with HPGe (ORTEC) with 20.0 % relative efficiency and 1.93 Kev of resolution (FWHM) at 1.33 MeV was used to measure gamma emitters.

A microwave system with eight digestion cavities, DGT 100 PLUS, from Provecto Analítica LTDA, was used to digest soil samples.

A PerkinElmer Model Optima 4100 DV consisting of a radio frequency source working at a power 750-1500 W and a frequency of 40 MHz and a diffraction grating of 374 lines mm^{-1} was used in the determination of homogeneity tests for the minor elements V and Zn.

A PerkinElmer SCIEX ELAN 6000 ICP-MS equipped with spray chamber and cross flow nebulizer was used in determination of homogeneity tests for the minor elements U and Th.

2.3 Preparation of Soil

The soil was slowly air-dried at room temperature. A nylon sieve of 2 mm was used to separate particles bigger than 2 mm that were discarded. Soil particles lower than 2 mm were ground in a Planetary Ball Mill (Type PM 400 of Retsch Gmbh) during sixty minutes using 8 steel balls.

After grinding the fraction that passed in 250 μm sieve was separated. The resulting material was homogenized in a steel mixer of 30 liters for 24 h.

The material used to check the bulk homogenization was removed of five portions from several parts of the mixer. After the test of bulk homogeneity the prepared material was bottled in 250 ml polyethylene bottle, taking 200 g of soil. 10 bottles were selected to the final homogeneity.

The temperatures chosen for the stability studies were 20 °C and 40 °C [7,11]. A high-resolution spectrometer HPGe with 20.0 % relative efficiency was used to measure gamma emitters, undertaking 100 and 10 g of sample. The soil was measured directly, after the radiochemical equilibrium was reached inside the measurement container.

2.4 Gamma Spectrometry

The method used for γ determination was the same utilized in the routine analysis of environmental samples that have proved precision and accuracy in intercomparisons programs [2,3,4]. The energies utilized to perform gamma spectrometry can be seen in the table 1. Others energies were also used to check the values obtained in γ spectrometry.

Table 1 Radionuclide energy used in gamma spectrometry

Radionuclide	Energy (KeV)
^{212}Pb	300.09
^{214}Pb	351,92
^{214}Bi	609,32
^{228}Ac	911,21
^{40}K	1460,80

The soil activity was measured directly, after the radiochemical equilibrium was reached inside the measurement container. A standardized cocktail solution of gamma emitter radionuclides prepared by the National Metrology Laboratory of Radiation Ionizing of IRD was used for the calibration of the efficiency of the HPGe detector.

2.5 Bulk homogeneity test

The bulk homogeneity test was mainly performed for γ emitters. For some minor elements like U, Th, V and Zn the homogeneity was performed by ICP-MS and ICP-AES. The γ emitters (^{40}K, ^{212}Pb, ^{214}Pb, ^{214}Bi and ^{228}Ac) were analyzed undertaking 100 g of sample. To perform the analysis of the minor elements V and Zn, 1000 mg from each soil portion was digested [9] by microwave oven and analyzed by ICP-AES technique.

2.6 Final homogeneity and stability test

After the bottling process 10 bottles, from the total of 50, were selected to the final homogeneity test [10]. The Between-bottle homogeneity was determined in duplicate for each of 10 bottles [7]. To calculate the within-bottle homogeneity it was selected one bottle and 10 replicates were taken. It was used the mass of 100 g to test the

between-bottle homogeneity and 10 g to test the within-bottle homogeneity. The bottles were the same used for homogeneity studies. Five bottles were kept in an oven at 40 ± 2 °C and five bottles stored at room temperature in the laboratory (20 ± 3 °C).

All γ emitters were measured at room temperature, considering both temperatures of test and the followings times after bottling: zero, one and six months.

After testing the bulk homogeneity, the bottling was undertaken. The soil content of each 250 ml polyethylene bottle was 200 g.

3. RESULTS

3.1 Bulk homogeneity test

The coefficient of variance (CV) of the activity from each γ emitters was obtained for single determinations of five portions. All values of CV were under 10 % (1,96-4,94), which are in the same order of magnitude as those of the measurement technique that used the RM AIEA-327.

The CV obtained for the ICP-AES analysis to the elements V and Zn were respectively 5.4 and 4.6 %. The elements U and Th presented values of CV respectively 3.6 and 2.0 % when analyzed by ICP-MS. The results indicated that the bulk material was homogeneous, therefore the bottling was processed.

3.2 Final homogeneity and stability test

The final soil homogeneity was performed considering the CVs of radionuclides determinations from two groups: between-bottle and within-bottle. Table 2 shows the prepared soil activity, the RM soil (AIEA 327) activity (used as technique) and the between-and within-bottle CVs.

Table 2: Radionuclide Activity, between-bottle cv, within bottle cv, technique cv and F test.

Radio nuclide	Activity (Bq/Kg)	between-bottle cv(%)	within-bottle cv(%)	Tec. cv (%)	F_{calc}
^{40}K	4814 ± 113	2.3	4.4	4.9	3.7
^{214}Bi	472 ± 14	3.0	3.4	7.5	1.3
^{214}Pb	434 ± 8	1.8	3.0	6.9	2.8
^{212}Pb	52188 ± 992	1.9	2.3	6.5	1.5
^{228}Ac	50236 ± 249	0.5	1.0	7.2	4.0

An F-test was used to test the significant difference between between-bottle and within-bottle [12]. For the studied conditions F(9,9) the critical value is 4,026 for P=0.05. It means that if there is no significant difference value between the data series, the obtained values should be lower than the critical value. From the Table 2, it can be observed that there is no significant difference between-bottle and within-bottle test.

The results of tests taking between- and within-bottle stability are shown by Figs 1 and 2. The ratios between the

activity at a given temperature (20 or 40 $^{\circ}$C) and the initial activity measured at room temperature (t_{zero}) at 1 and 6 months for each radionuclide are shown by the graphs.

We can consider that the activity concentration of all radionuclides remained constant, once they presented a ratio close to 1, during the period of time studied. Analysis of variance (ANOVA) from results also showed no significant differences when the contribution of each factor (temperature, time and bottle) was analyzed using the sum of squares method.

The Fischer's least significant difference (LSD) test was applied and the results showed that all elements presented just one homogeneous group for each factor.

Fig. 2   Activity ratio at a given temperature with respect to initial activity at different times for between-bottle stability studies.
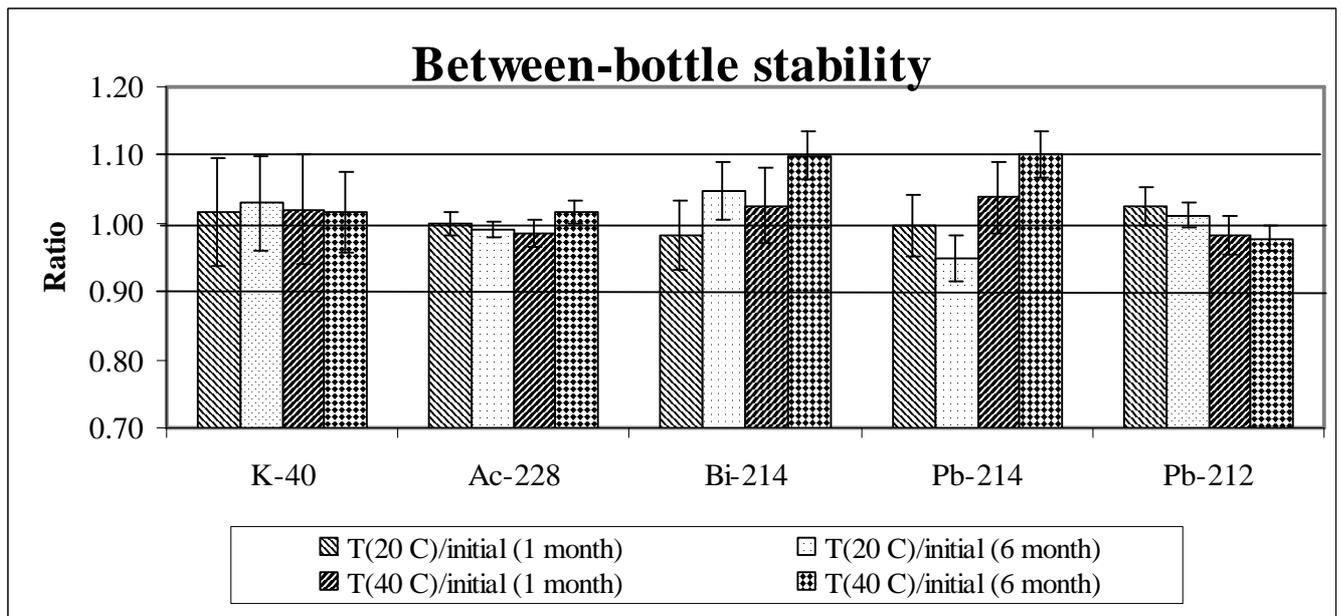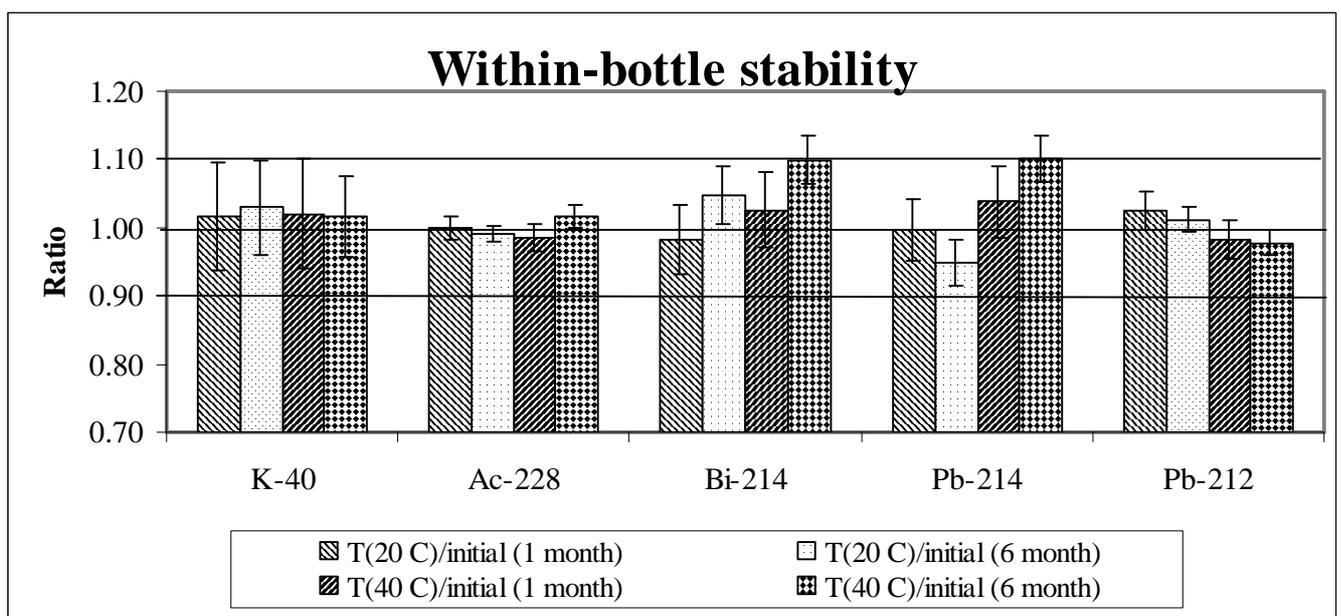

Fig. 3 Activity ratio at a given temperature with respect to initial activity at different times for within-bottle stability studies.

4. CONCLUSIONS

The Reference Material prepared is stable at 20 and 40 °C related to the radionuclides activity measured during the studied period.

No significant differences were observed in between-bottle and within-bottle homogeneity tests, showing that the material was homogeneous for the radionuclides tested [40]K, [214]Bi, [214]Pb, [212]Pb, and [228]Ac.

We concluded that the prepared material can be used in intercomparisons programs. This soil can be also used as raw material to prepare spike sample to simulate environmental specimen of low activities.

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