THE TESTING OF A RADIONUCLIDE IN SOIL SAMPLES FOR USE IN INTERCOMPARISON PROGRAM

A.F. Clain[1], *A.M.G.F. Azeredo*[1], *M.J.C.S. Bragança*[1], *L. Tauhata*[1]

[1]*Instituto de Radioproteção e Dosimetria, Rio de Janeiro, Brasil, almir@ird.gov.br, adelaide@ird.gov.br, maura@ird.gov.br, tauhata@ird.gov.br*

Abstract: – Soil samples were produced to the determination of the activity of radionuclides. After the preparation the samples were then tested. The results of ^{137}Cs activity in soil and statistical tests showed that the prepared reference material was homogeneous enough to be used in intercomparison exercises.

Keywords: soil, radionuclides, intercomparison.

1. INTRODUCTION

Intercomparison exercises for radiochemical laboratories in Brazil are coordinated by the Radioprotection and Dosimetry Institute (IRD) through the National Intercomparison Program (PNI) of radionuclides assays in environmental samples [1, 2, 3]. The PNI was created in 1989 and began operating in 1991. The aim of PNI is to evaluate the performance of national laboratories in the determination of radionuclides in samples of low activity in different matrices such as water, soil, vegetation and air filters.

The main laboratories participating in this program are involved in environmental control of radionuclide activity and monitoring the radioactivity of nuclear plants. This Program provides environmental samples to participant laboratories in intercomparison exercises. The main matrices are water, soil, air filters and sediment. Hence, it is necessary the continuous development of production in order to obtain several kinds of matrices. The PNI produces radionuclides in water, while the other matrices are purchased from outside suppliers and provided to the laboratories.

Nowadays there are about 20 participant laboratories in the PNI program. From 1991 to 2007 there were carried out 6939 tests. Water is the most widely used matrix for analysis (66%). The table1 shows the intercomparison program offered to participant laboratories.

These matrices can be collected in contaminated areas or can be produced artificially by a process named spike sample.

To find a contaminated area containing all the representative radionuclides is not an easy task; therefore, it was chosen to produce these samples (soil, air filter and sediment) by the spiked sample method.

To produce homogeneous simulated samples from radionuclides in water is not particularly difficult. Solid matrices like soil, air filters and sediment present problems to achieve homogeneity due their intrinsic forms. To produce reference material (RM) or certified reference material (CRM), it is necessary to follow the recommendations of some guides [4, 5, 6, 7].

Table 1: Intercomparison Program in water matrix

Intercomparison Study	Determination	Activity Bq/L
Gamma	^{60}Co , ^{65}Zn, ^{106}Ru, ^{133}Ba, ^{134}Cs, ^{137}Cs	<20
Alfa and beta total	^{241}Am e ^{137}Cs	<5
Tritium	^{3}H	<500
Strontium	^{90}Sr	<5
Uranium and Radium	U_{nat}, ^{226}Ra e ^{228}Ra	<5
Lead	^{210}Pb	<5
Thorium	^{232}Th	<0,5

Two methods of soil preparation by spiked sample with a radionuclide solution were tested.

The first (whole material method) is to make one spike in a big container with the whole material and later to remove sub-samples.

The second (individual method) is firstly to remove the sub-samples from the whole material and then to conduct individual spikes for each sample. Shakashiro et al [8] have prepared a sample of soil with eight radionuclides. In this preparation, Shakashiro used the individual method. After the preparation, the samples were used in intercomparison program [9} and the results showed good concordance with the reference value.

This paper describes the tests carried out during the preparation of a soil to be used in radionuclide intercomparison exercises. An inert sandy soil was artificially contaminated with a radionuclide solution of ^{137}Cs.

SAMPLE PREPARATION

Soil Test

Two methods were performed to evaluate the preparation of radionuclides in soil. The first was named the "whole material method" and the other the "individual method". Both test methods were made on the same homogenized matrix. In the first method, a certain mass of the sample was contaminated with ^{137}Cs and then this sample was divided in sub samples. In the second method, the same mass used in the first method was split into sub samples, afterwards each sub sample was contaminated with the same amount of radionuclide contained in sub samples from the first method. Sample sets were evaluated for homogeneity and radionuclide content.

2 kg of a low background soil was dried in an oven at 50˚C , milled in a planetary mill during 30 minutes with 4 stainless steel ball and sieved to a size smaller than 250 µm. Figures 1, 2 e 3 show the main equipment used in the sample preparation:

Fig. 1. Planetary Mill

In the first method, 400 g of the prepared soil was mixed in a plastic beaker with 500 ml of methanol. The obtained slurry was homogenized by manual stirring during five minutes and then 530 Bq of 137Cs was added. The resulting solution was then further homogenized by manual stirring during ten minutes. The solution was transferred to a plastic tray and dried in an oven at 40˚C overnight. Ten sub-samples of 40 g were taken and placed in appropriate containers for gamma spectrometry. The samples activity was measured in a gamma spectrometry system over 3 hours, taking the average of 3 measurements. The activity added via the spike was calculated to produce 1325 Bq/kg of dried soil. Figures 4 and 5 show the flowchart of soil preparation.

Fig. 2 "V" Mixer

Fig. 3. Sieve System

In the second experiment, ten samples of 40 g from the prepared soil were placed in a plastic beaker, and 50 ml methanol was added directly to each beaker. The slurry in each beaker was homogenized by manual stirring during five minutes and then 53 Bq was added of ^{137}Cs. The resulting solution was homogenized by manual stirring during ten minutes. The solutions were dried in the same preparation container in an oven at 40°C overnight. The samples were transferred to suitable containers for gamma spectrometry and analyzed by gamma spectrometry in the same condition as that in whole method. As in the first experiment the activity in the individual method was calculated as 1325 Bq/kg of dried soil.

All samples were counted in the same conditions using a low background HPGe system from Ortec Inc. with 20.0 % relative efficiency and 1.93 keV resolution (FWHM) at 1.33 MeV. The optimized counting time was 180 min.

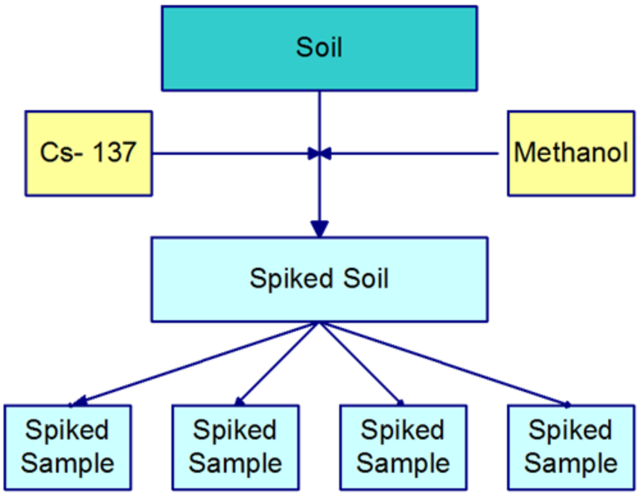

Fig. 4. Flowchart of soil whole method preparation

Table 2 shows the sample activity in Bq/Kg in 40 g of material.

Table 2: Soil activities in Bq/Kg in 40 g of soil

Whole material method		Individual spike method	
Sub-samples	10	Samples	10
Mass	40 g	Mass	40 g
Average Activ.	1214	Average Activ.	1187
Std. Dev.	45	Std. Dev.	35
Std Dev. %	3.7	Std Dev. %	2.9

A t test [10] was applied to verify if there was significant difference between the averages of the activities. The accuracy of the methods was performed trough the t test of student. In such test the average (x_1 and x_2) difference between the methods are checked, considering also the standard deviation.

Equatons 1 and 2 are used to calculate de t value.

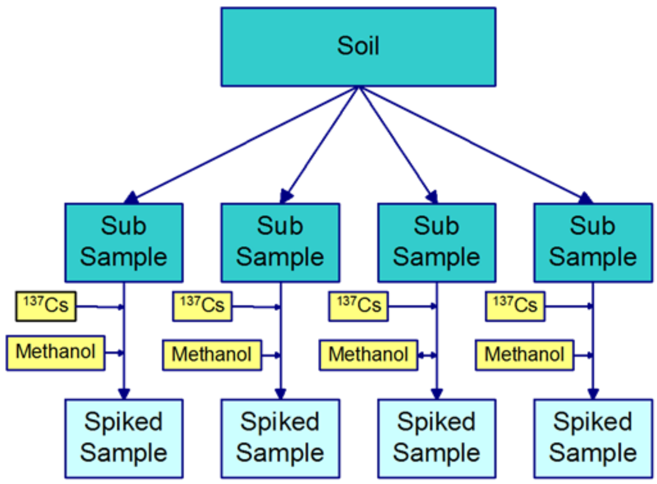

Fig. 5 Flowchart of soil individual method preparation

$$S_c^2 = \{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2\}/(n_1 + n_2 - 2) \qquad (1)$$

$$t = (x_1 + x_2)/S_c \sqrt{\left(\frac{1}{n_1} + \frac{1}{n_2}\right)} \qquad (2)$$

Where

S^2_c = combined variance

n_1= Number of data from method 1
n_2= Number of data from method 2

S^2_1 = Variance from method 1
S^2_2 = Variance from method 2

x_1= average from method 1
x_2= average from method 2

It was found a t value of 1,5 and the critical value is 2.1. Once the found value is smaller than the critical value there is no significant difference between the averages for a 95 % confidence limit.

An F test was used to compare the precision of the methods. The result of the F- test for the comparison of standard deviations showed the value of 1.65.

The critical value is 4.026. Once there is no expectation of finding a method more precise than other, we use a bicauldal table to extract the F value.

It is possible to conclude that the two methods have no significant precision differences for a 95 % confidence limit. The equation 3 shows the formula to calculate the F value.

$$F = S_1^2 / S_2^2 \qquad (3)$$

Where:
S^2_1 = Variance from method 1
S^2_2 = Variance from method 2

The highest value of S^2_1 and S^2_2 is always placed in the numerator.

Figure 6 shows the sample activity in both methods of preparation.

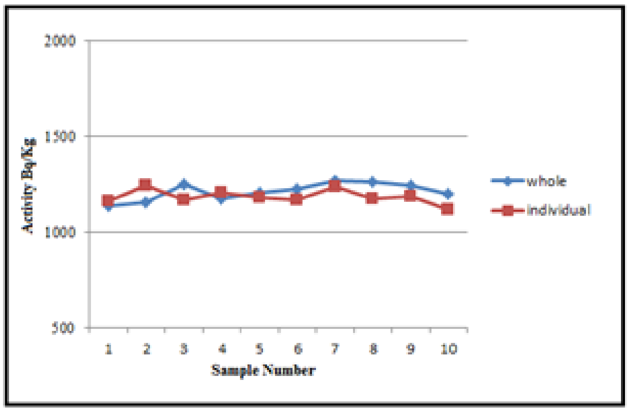

Fig. 6 Sample Activity in both method of preparation

If we consider the value of 1325 Bq/Kg of ^{137}Cs as the "theoretical value" of the soil activity concentration, we can say that the "whole material method" showed accuracy of 92 % and the "individual spike method" showed accuracy of 90 %. This loss can be caused by several factors: the radionuclide solution may not be fully absorbed; loss of the radionuclide during evaporation; absorption of radionuclide by the recipient wall or, most probably, due to the uncertainties of the technique used to analyze the radionuclide activity. The reference value to be used in intercomparison tests, in that case would be the value determined by the Reference Laboratory, like was used by Shakashiro [9].

The choice of a specific method to produce spike soil depends on the amount of available sample. If there is a small sample size is preferable to use the whole method but otherwise the individual method is recommended due to safety and practices conditions. Because of this, the second method (individual) will be applied in future work

More realistic soil samples, such as those used in agriculture containing radionuclides with different behaviors than ^{137}Cs must also be tested.

CONCLUSION

Analyses of ^{137}Cs activity in soil and the F test showed that the prepared reference material was homogeneous enough to be used in intercomparison exercises.

Both test methods can be used to prepare samples of ^{137}Cs in soil for intercomparison programs, as there were no significant differences between the uncertainties of the methods and between the average values of activity for the two methods of sample preparation. The key deciding factor between the two methods is the total mass of reference sample to be prepared.

Tests of stability related to the temperature and to the time of preparation must be performed in the next preparation

AKNOWLEDMENTS

We are thankful to Octávio Luiz T. Filho from the SERIN/IRD for the γ spectrometry analysis .

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