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Methodology for preparing a reference sample in the air filter matrix

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ABSTRACT

Proficiency tests are widely used to evaluate the analytical capacity of laboratories as well as part of the accreditation processes. The National Intercomparison Program (PNI) is a Proficiency Test that uses radioactive reference materials in soil, vegetation, water and air filters. This work discusses the ideal composition of radionuclides to be used in air filters to be produced by LNMRI (Laboratório Nacional de Metrologia das Radiações Ionizantes) as reference material for PNI.

Five cocktails, each composed of a distinct set of gamma-emmiting radionuclides in the energy range of 30 to 2000 keV, were prepared. Each cocktail was distributed in three glass fiber air filters using a pantograph by the pycnometer technique, thus contaminating each filter with 19 (nineteen) drops. As a result fifteen (15) air filter samples were obtained, with the objective of homogeneous distribution of the droplets at the sites determined by the geometry chosen without the need for marking in the filters, in order to choose the best composition to be used in the preparation of reference material.

Keywords: **Reference Material, Air filter, Radionuclide Metrology, Pantograph.**

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1. INTRODUCTION

There are some nuclear installations in Brazil with the possibility of accidents that could compromise the environment. Air quality monitoring is important for public health protection. For this monitoring some laboratories use air filters as a sample to determine radionuclides present in the air. Laboratories that perform such monitoring should have experience and credibility in their determinations. For this purpose, laboratories should participate in proficiency testing not only to evaluate laboratory performance but also to validate methods and reference samples. Interlaboratory radiochemical comparison exercises in Brazil are coordinated by the Instituto de Radioproteção e Dosimetria (IRD) through the National Intercomparison Program for radionuclides in environmental samples (PNI) [1] [2] and [3]. Twice a year, this program sends to costumers radionuclide samples in various matrices such as water, soil, sediment and air filter. There is a need to meet national demand for reference materials (matrices: soil, vegetation and air filter) in order to avoid importation by eliminating the delay and customs disruption as well as the high cost associated with these materials. In Brazil reference materials are produced by various institutions, INMETRO (NMI) [4] and accredited laboratories [5], but in the area of radioactive materials this production is practically zero. This material to be developed will contribute as a tool for method validation and equipment calibration, routine air analysis work and environmental control programs.

To make the filters, several gamma-emitting radionuclides with energies in the range between 30 and 2000 keV were chosen. In order to facilitate uniform distribution of radionuclides in the filter, five standard solutions (radionuclide mixers) were prepared for use in artificial contamination (Spiked Sample technique) at certain filter positions with the aid of a pantograph [6]. The purpose of pantograph use is to add the solution to the filter at certain points without having to make markings on the pen filter.

The objective of this work is to study which gamma-emitting radionuclides should compose the air filter measured in gamma spectrometry without interference from summation effects, X-γ sum effect or spectral interferences. The technique used was the “Spiked Sample” withpantograph assistance. The composition with the least interference will be used to prepare an air filter (reference material) to be made available in the National Intercomparison Program – PNI.

In addition, this paper describes the methodology employed to prepare reference material in the air filter matrix containing radionuclides for use in the National Intercomparison Program.

2. MATERIALS AND METHODS

2.1. Choice of Geometries

The simulated air filters chosen were produced with a 47 mm diameter circular fiberglass with an active diameter of 34 mm, as shown in Figure 1, because this is the geometry commonly used for air monitoring in laboratories performing such analysis. Each filter was packed in aplastic petri dish60mm diameter. For each cocktail, three air filters were prepared.

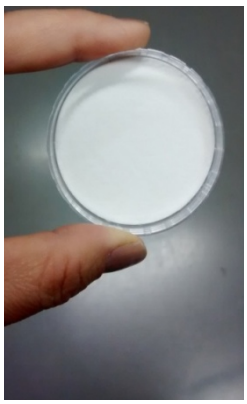

Figure 1: *Simulated air filter.*

The hexagonal geometry was selected for drop deposition because the dispersion in this geometry is equivalent to a uniform active circle [6]. Figure 2 shows the geometry used.

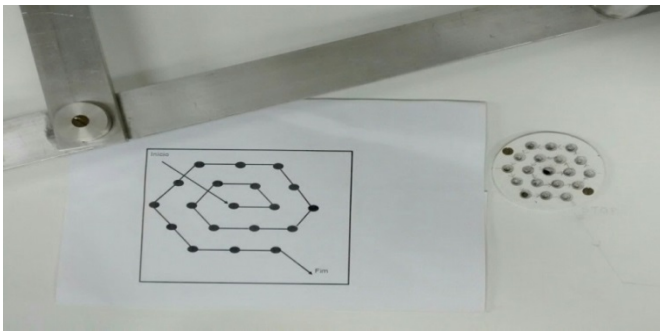

Figure 2: *Geometry used for solution deposition in air filters.*

2.2. Choise of radionuclides

For the preparation of the cocktails, some radionuclides were chosen for the energy of each gamma emission covering the range from 30 to 2000 keV and aiming at a study of the sum effect, X - γ sum and spectral interferences. Table 1 shows the approximate activities chosen for the composition of each filter type.

Table 1. Composition chosen for each type of air filter prepared.

	TOTALACTIVITY (Bq)								
Filter	**^{137}Cs**	**^{60}Co**	**^{54}Mn**	**^{241}Am**	**^{152}Eu**	**^{57}Co**	**^{134}Cs**	**^{133}Ba**	**^{65}Zn**
A	70	50	40	01	---	---	---	---	---
B	90	60	---	---	35	20	---	---	---
C	90	120	---	---	70	03	35	---	---
D	50	20	40	1.5	---	---	---	50	---
E	45	35	40	1.5	---	---	---	---	15
Energy* (keV)	604.7	1173.2 1332.5	834.8	59.5	121.7 344.2	122.0	604.7	80.99 356.0	1115.5

* main energies considered of each radionuclide for the cocktail preparation [7].

2.3. Cocktails preparation

The cocktails were prepared gravimetrically by differential weighing, using the pycnometer method [8] and [9] on a Mettler Toledo model XP-56 micro-analytical balance. The activities of each cocktail and their associated uncertainties are described in Table 2, dated 16 July 2018. The radionuclide stock solutions used in the cocktail composition were calibrated by the Radionuclide Metrology / LNMRI laboratory.

Table 2. Composition of each prepared cocktail.

ACTIVITY CONCENTRATION (Bq/g) – Reference date: 16 July 2018									
Cocktail	**^{137}Cs**	**^{60}Co**	**^{54}Mn**	**^{241}Am**	**^{152}Eu**	**^{57}Co**	**^{134}Cs**	**^{133}Ba**	**^{65}Zn**
69L18	369.068	213.957	203.766	6.532	---	---	---	---	---
70 L18	503.625	294.093	---	---	166.478	104.817	---	---	---
71 L18	502.887	572.530	---	---	430.697	16.300	180.568	---	---
72 L18	270.180	85.432	219.676	7.509	---	---	---	326.421	---
73 L18	236.206	265.111	209.999	8.430	---	---	---	---	94.41
Uncertainty U (%)	2.7	0.88	1.2	1.6	1.7	1.6	1.8	1.0	1.6

2.4. Filter preparation

Cocktails were added to each filter gravimetrically by differential weighing using the pycnometer method [8] and [9] on a Mettler Toledo model AX-205. Each cocktail was distributed in three filters with 19 (nineteen) drops (each drop with approximate mass of 0.01g), totaling about 0.190g of the solution in each filter, using a pantograph, as shown in figure 3, where the geometry used for Deposition of each drop of solution is shown in Figure 2. Each filter was positioned on a plate fixed below the solution addition site. The deposition was performed with a pycnometer from the central point following the spiral deposition scheme until the 19th drop, as shown in figure 2. The hexagonal geometry was chosen for the deposition of the drops because the dispersion in this geometry is equivalent to a uniform active circle [6].

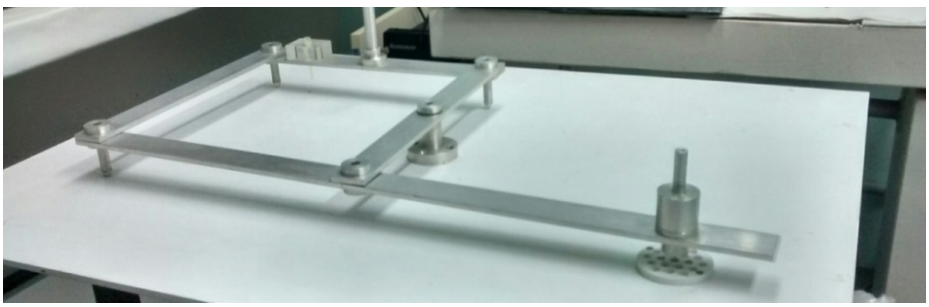

Figure 3: *Pantograph*

The pantograph is an instrument composed of four rulers arranged in the form of an articulated parallelogram that allows reproducing mechanically geometry equal to the original one, however, being used in this case to allow the deposition of the drops in a specific place following the chosen geometry pattern, according to the diagram shown in figure 2.

2.5. Gamma spectrometry analysis

In the determination of Activity, an efficiency curve is used associating the number of counts recorded for each energy with the number of radiations emitted by the sample in this energy per unit of time, according to equation 1.

$$A_i = \frac{S}{\varepsilon_i . P_{xi} . t} \quad (1)$$

Where:

A_i Source activity at the time of measurement

S peak net area

$P_{x,\gamma}$ X or gamma emission intensity for this energy

$\mathcal{E}_i$ detector efficiency for Ei energy radiation

T counting time

The detector system consisted of a low background HPGe detector with resolution of 2 keV FWHM at 1.33 MeV and relative efficiency 30 %. The coaxial detector is operated with an energy range that includes all the radionuclides used in the preparation of cocktails: 200-1400 keV. Each filter was measured for 60000 seconds. The peak area evaluation was carried out using the Genie 2000 software. The standards filters and the air filter samples were placed on the top of the γ-detector.

Standard sources of the mixture of radionuclides used for spiking the filters with precisely known activities were used to obtain the efficiency response of the detector over the stated energy

range of measurement. The activity for each radionuclide was obtained by means of counting rates and in interest absorption peak E given by the Equation 1.

3. RESULTS AND DISCUSSION

3.1. Reproducibility in the deposited mass

In the weighing of the first two types of filters, static sources were observed in the gloves and edge of the filter holder, causing the droplet deposited by the pycnometer to be attracted causing the deposition of more than one drop at some points. From the third type of filter, the pycnometer capillary tip was cut to reduce static interference. Thus, in the type C, D and E filters, the added masses presented a lower rate of variation.

$$A_d = m.A_r \quad (2)$$

where:

A_d = Radionuclide Activity deposited in the filter

m = cocktail mass deposited on filters

Ar = radionuclide activity in Bq

Table 3. Radionuclide activity (Bq) deposited on air filters.

ACTIVITY (Bq) – Reference date: July 16, 2019										
Type	**Filter Nº**	**^{137}Cs**	**^{60}Co**	**^{54}Mn**	**^{241}Am**	**^{152}Eu**	**^{57}Co**	**^{134}Cs**	**^{133}Ba**	**^{65}Zn**
A	**02F18**	64.542	37.417	35.635	1.618	---	---	---	---	---
	03F18	86.528	50.162	47.773	1.531	---	---	---	---	---
	04F18	44.749	25.142	24.707	0.792	---	---	---	---	---
B	**05F18**	120.361	70.285	---	---	39.787	25.050	---	---	---
	06F18	134.498	78.540	---	---	44.460	27.992	---	---	---
	07F18	108.038	63.089	---	---	35.713	22.485	---	---	---
C	**09F18**	93.824	106.817	---		80.355	3.041	33.688	---	---
	10F18	94.452	107.532	---	---	80.893	3.061	33.914	---	---
	12F18	94.482	107.567	---	---	80.919	3.062	33.25	---	---
D	**13F18**	53.868	17.033	43.799	1.497	---	---	---	65.082	---
	14F18	50.289	15.901	40.888	1.398	---	---	---	60.757	---
	15F18	51.769	16.370	42.092	1.439	---	---	---	62.545	---
E	**17F18**	44.213	49.623	39.308	1.578	---	---	---	---	17.752
	19F18	43.034	48.301	38.260	1.536	---	---	---	---	17.279
	20F18	45.243	50.779	40.223	1.615	---	---	---	---	18.166

In order to improve the reproducibility of drops position and mass, special attention will be required to the following items:

a) Control laboratory humidity (55-80% RH);

b) Control the laboratory temperature (19-21 ºC), avoiding sunlight in the pycnometer;

c) Press the body of the pycnometer with reproducible pressure and speed (same operator);

d) Electrically ground the pantograph avoiding the collection of electrostatic charge at different points of deposition and in the drops themselves;

e) Avoid air bubbles in the pycnometer capillary.

The filters prepared in this work will be submitted to the interlaboratory comparison coordinated by LNMRI to define the best radionuclide configuration to be applied in the production of the reference material. The comparison will be made between three (3) laboratories of proven competence in germanium detector gamma spectrometry analysis.

To choose the best composition, it was considered:

- availability of standards in Radionuclide Metrology

- radionuclides that may be present in the atmosphere from accidents or tests with nuclear artifacts
- gamma energies and intensities of each radionuclide to cover the range from 30 to 2000 keV
- ease of identification and quantification by laboratories (analysis result)

3.2. Choosing the ideal composition for the filters

To choose the best composition to be used in the filters, one filter of each composition was analyzed in gamma spectrometry with a HPGe detector .

The filters selected for analysis were: 03F18, 06F18, 10F18, 14F18 and 19F18. The results of the measurements on the filters are shown in Tables 4, 5, 6, 7 and 8. The difference between the reference value and the average of the 3 measurements are reported in each table and the calculation of this difference is given by the equation 3.

$$D\ (\%) = \frac{(R_v - A_v)}{R_v} x100 \quad (3)$$

where:

D (%) = Difference in %

R_v = Reference value

A_v = Average value

Table 4. Results of measurements in Filter 03F18.

Nuclide	Reference value (Bq)	Analysis 1 (Bq)	Analysis 2 (Bq)	Analysis 3 (Bq)	Average	Difference (%)
Cs-137	86.528	81.06 ± 4.1	81.44± 4.2	80.2 ± 4.1	80.90	6.50
Co-60	50.162	49.02 ± 2.5	48.53 ± 2.5	43.78 ± 2.2	47.11	6.08
Mn-54	47.773	35.27 ± 1.9	35.21 ± 1.9	34.93 ± 1.8	35.14	26.45
Am-241	1.531	1.34 ± 0.07	1.38 ± 0.08	1.28 ± 0.07	1.33	12.91

Table 5. Results of measurements in Filter 06F18.

Nuclide	Reference value (Bq)	Analysis 1 (Bq)	Analysis 2 (Bq)	Analysis 3 (Bq)	Media	Difference (%)
Cs-137	134.498	128.8 ± 6.8	128.3 ± 6.6	130.2 ± 6.7	129.10	4.01
Co-60	78.540	77.2 ± 3.9	75.8 ± 3.8	76.94 ± 3.9	76.65	2.41
Eu-152	44.460	38.16 ± 2.0	34.74 ± 2.0	40.61 ± 2.1	37.84	14.90
Co-57	27.992	8.32 ± 3.3	8.57 ± 3.4	8.18 ± 3.2	8.36	70.15

Table 6. Results of measurements in Filter 10F18.

Nuclide	Reference value (Bq)	Analysis 1 (Bq)	Analysis 2 (Bq)	Analysis 3 (Bq)	Media	Difference (%)
Cs-137	94.452	91.58 ± 4.7	92.14 ± 4.7	91.48 ± 4.7	91.73	2.88
Co-60	107.532	108.1 ± 5.5	107.3 ± 5.4	107 ± 5.4	107.47	0.06
Cs-134	33.914	32.42 ± 1.7	32.99 ± 1.7	32.91 ± 1.7	32.77	3.36
Eu-152	80.893	71.49 ± 3.6	74.02 ± 3.7	73.61 ± 3.7	73.04	9.71
Co-57	3.061	0.75 ± 0.30	0.98 ± 0.39	0.99 ± 0.39	0.91	70.38

Table 7. Results of measurements in Filter 14F18

Nuclide	Reference value (Bq)	Analysis 1 (Bq)	Analysis 2 (Bq)	Analysis 3 (Bq)	Media	Difference (%)
Cs-137	50.289	49.07 ± 2.5	48.91 ± 2.5	49.15 ± 2.5	49.04	2.48
Co-60	15.901	15.68 ± 0.80	16.12 ± 0.80	15.85 ± 0.8	15.88	0.11
Mn-54	40.888	30.87 ± 1.6	31.54 ± 1.7	31.06 ± 1.6	31.16	23.80
Am-241	1.398	1.59 ± 0.08	1.65 ± 0.09	1.64 ± 0.09	1.63	-16.36
Ba-133	60.757	40.47 ± 3.2	40.17 ± 3.2	40.36 ± 3.2	40.33	33.62

Table 8. Results of measurements in Filter 19F18

Nuclide	Reference value (Bq)	Analysis 1 (Bq)	Analysis 2 (Bq)	Analysis 3 (Bq)	Media	Difference (%)
Cs-137	43.034	41.59 ± 2.1	41.82 ± 2.1	42.8 ± 2.2	42.07	2.24
Co-60	48.301	47.29 ± 2.4	48.01 ± 2.4	48.25 ±2.4	47.85	0.93
Mn-54	38.260	29.14 ± 1.5	29.48 ± 1.6	29.4 ± 1.5	29.34	23.31
Am-241	1.536	1.47 ± 0.08	1.36 ± 0.08	1.41± 0.08	1.41	7.99
Zn-65	17.279	18.33 ± 1.0	17.95± 1.01	18.72 ± 1.0	18.33	-6.10

In the filters that were present ^{57}Co and ^{152}Eu, there was difficulty in identifying and determining the activity of^{57}Co, because the photopeak of 122.061 keV of ^{57}Co is very close to the 121.7817 keV of ^{152}Eu, the photopeaks overlapped, not allowing separation.

It is verified that:

- ^{60}Co,^{134}Cs and^{137}Cs are radionuclides of easy identification and quantification.

- Ba 133 and Mn54 are radionuclide that are easy to determine, but Mn54 is not always available in laboratory stock.

- ^{65}Zn, despite not presenting difficulty to be quantified, will not be used because the ^{134}Cs has energy lines that coincide with those of the ^{65}Zn and with better quantified.

- ^{152}Eu for presenting many photopeaks and for interfering in the identification of the ^{57}Co will not be used. However, ^{57}Co will be used because it presents a very intense photopeak in the region of 122 keV.

- ^{134}Cs, in addition to presenting good identification and quantification, has several photopeaks along the spectrum can be used to replace several radionuclides.

- ^{241}Am is a radionuclide that has γ ray around 59 keV and can be used to cover the spectrum band at low energy.

4. CONCLUSIONS

By artificially contaminating 15 (fifteen) air filters with 05 (five) different radionuclide compositions, it has been found that the deposition of reproductive amounts is possible provided that static effect interference is minimized.

The methodology used proved to be effective and will be applied in the production of larger quantities of air filters, so that they are grouped in batches, with approximate activities and masses to be submitted to interlaboratory comparison, thus defining the reference value for each one lot by the average of the activities deposited in the filters.

So, it follows that the best composition to use in the filters will be: ^{57}Co,^{60}Co,^{134}Cs,^{137}Cs and ^{241}Am.

It is concluded that the result was satisfactory since it was possible to assemble a composition capable of meeting the need of laboratories for monitoring the air that did not cause spectral interferences or sum effects with a well-distributed range of energy along the spectrum, facilitating the use of the filter as a reference material for surveying the efficiency curve in laboratories that use the gamma spectrometry method.

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