

ESTABLISHING ADEQUATE CONDITIONS FOR MERCURY DETERMINATION IN ENVIRONMENTAL SAMPLES BY INAA

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ABSTRACT

Mercury (Hg) is a toxic element released into the environment mainly by anthropic activities. Consequently, the improvement for Hg determination in environmental samples is of great interest. Instrumental Neutron Activation Analysis (INAA) is considered an adequate method to determine several elements. However, Hg determination by INAA is often hampered by its volatility, which causes losses. The aim of this study was to establish adequate irradiation conditions for Hg determination in environmental samples by INAA. The following parameters were evaluated: irradiation time, container for irradiation and spectral gamma ray interferences. For the study, aliquots of certified reference materials (CRMs) and tree bark samples were irradiated together with Hg synthetic standard at the IEA-R1 nuclear research reactor. Gamma ray activities of ^{197}Hg and ^{203}Hg were measured in a spectrometer coupled to a HGe detector. Results obtained indicated that polyethylene capsules or envelopes can be used as container for sample irradiation and the Hg impurities in these containers were negligible. Irradiation time of one hour was adequate for Hg determination and in long irradiations of 8 h problems of spectral interference of ^{198}Au and ^{75}Se were observed. In addition, Hg loss during the irradiation of 1 h and after irradiation was not observed. Quality control of Hg results, obtained in the CRMs analyses using one hour of irradiation, indicated good precision and accuracy with $|Z \text{ score}| < 2$. The experimental conditions established in this study were applied to tree bark samples. Detection limits for Hg of these analyses were between 0.14 and 1.9 $\mu\text{g g}^{-1}$.

1. INTRODUCTION

Mercury (Hg) is a toxic element that causes adverse effects on human health and on the environment, arousing much concern everywhere due to its volatility, persistence and bioaccumulation [1]. Its toxicity depends on its chemical form, concentration, route of exposure and the exposed individual's vulnerability [2]. Mercury is emitted into the atmosphere by various anthropic activities, such as coal-fired power plants, mining activities, waste incineration and industrial processes used in foundries and cement production [3]. Consequently, it is of great interest to improve analytical methods for the quantification of this element in environmental samples.

Instrumental neutron activation analysis (INAA) is considered an advantageous technique for elemental determination of environmental contaminants, since it is a non-destructive technique, that requires minimal manipulation of the sample and provides low detection limits [4,5]. However, some elements are not determined with good accuracy by this technique, as in the case of mercury.

In the analysis of Hg by INAA, two radioisotopes that can be measured for its quantification are formed: ^{197}Hg (77.34 keV with half-life of 64.16 hours) and ^{203}Hg (279.20 keV with half-

life of 46.61 days) [6]. However, the main difficulty in the determination of Hg by INAA is the loss of this element during irradiation, caused by thermal heating [7]. The use of quartz ampoules as irradiation container would avoid the Hg loss [8], but it is not adequate because of the difficulty in transferring the irradiated sample from the ampoule to a counting vessel. In addition, the ampoule becomes quite radioactive due to the activation of the sodium present in it.

The aim of this study was to establish adequate conditions for Hg determination in environmental samples by INAA. In order to obtain reliable results, the following experimental parameters were evaluated: irradiation time, type of container for sample irradiation and the problem of the spectral interferences. For this study, environmental certified reference materials and tree bark samples, used as environmental biomonitor, were analyzed.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Certified reference materials

For quality control in relation to the precision and accuracy of the results, certified reference materials (CRMs) INCT M-4 CormTis Cormorant Tissue provided by Institute of Nuclear Chemistry and Technology, IAEA-085 Methylmercury, Total Mercury and Other Trace Elements in Human Hair provided by International Atomic Energy Agency, NRC DOLT-3 Dogfish Liver Certified Reference Material for Trace Metals provided by National Research Council Canada and BCR 186 Trace Elements in Lyophilised Pig Kidney provided by Community Bureau of Reference were analyzed.

Percentages of residual humidity of these CRMs were determined in order to obtain the results on dry basis. For this determination, approximately 250 mg of each material were dried in a Universal oven at a temperature of 85 °C, for 24 hours. The percentages of humidity obtained in this drying process were 6.06 % for CRM INCT M-4 Cormorant Tissue, 6.65 % for IAEA-085 Human Hair, 14.5% for NCR DOLT-3 Dogfish Liver and 5.71 % for BCR 186 Pig Kidney.

2.1.2. Environmental samples

Tree bark samples of the species *Poincianella pluviosa* (Sibipiruna) and *Tipuana tipu* (Tipuana) were collected in several sites of São Paulo Metropolitan Region (SP/Brazil). The collection was carried out at a height from 1.5 to 2.5 m from topsoil using a stainless steel knife. When the bark was wet, it was previously dried at 40 °C using an oven with forced air circulation. For the analyses, the samples were carefully cleaned using a dental brush with soft nylon bristles in order to remove the foreign materials and then the surface layer of the tree bark, with a thickness less than 3 mm, was grated using a titanium grater. Finally, the

samples were ground to a fine powder using a vibratory micro mill with an agate mortar (Vibratory Micro Mill Pulverisette 0, FRITSCH), and then placed in plastic vials that were stored in a desiccator.

Percentages of residual humidity of these powder bark samples, determined as described for CRMs, varied from 4.88 to 12.5 %.

2.2. Procedure for Neutron Activation Analysis

2.2.1. Preparation of synthetic standard of mercury

Certified standard solution of mercury acquired from Spex CertiPrep USA was used to prepare synthetic standard. From the stock standard solution, a diluted solution with concentration of $136.54 \mu\text{g mL}^{-1}$ was prepared. To avoid Hg loss in the synthetic standard, thioacetamide solution was also used. Thioacetamide minimizes Hg losses by volatilization, since the sulfur present in its structure reacts with Hg, leading to the formation of HgS [9,10].

A 7.83 mg mL^{-1} thioacetamide solution was prepared by dissolving 195.70 mg of thioacetamide p.a. from Merck with purified water, and diluting to 25 mL.

Aliquots of 50 μL of thioacetamide solution were pipetted on each small sheet of n°. 40 Whatman filter paper with the size 1.5 cm x 6.0 cm. The sheets were placed in a desiccator for drying the aliquots at room temperature. Then, aliquots 50 μL of diluted Hg solution were pipetted on these sheets, which remained again in a desiccator for drying at room temperature. The sheets were folded and placed in plastic envelopes. The plastic (polyethylene) foils used to prepare these envelopes were previously cleaned using diluted nitric acid solution and purified water, and finally drying at room temperature. The micropipette used was previously checked in relation to its calibration.

To prepare Hg standard in the type W polyethylene capsule (Vrije Univesiteit, Amsterdam, The Netherlands), a small sheet of N°. 40 Whatman filter paper was cut and placed inside the capsule. Then, 50 μL of thioacetamide solution were pipetted on the small sheet placed inside the capsule, which remained in a desiccator for drying at room temperature. After that, 50 μL of Hg diluted standard solution were pipetted on this sheet, which remained again in a desiccator for drying at room temperature.

The Hg synthetic standards were kept in a refrigerator until its use in the analyses.

2.2.2. Irradiation, measurement and calculations

Aliquots of each tree bark sample or certified reference material were weighted (150 to 200 mg) in polyethylene envelopes. Each envelope containing the sample or standard was wrapped with aluminum foil. This set of samples and standard was placed in an aluminum irradiation device called “rabbit”. Irradiation was performed at the IEA-R1 nuclear research

reactor for 1 or 8 hours, under a thermal neutron flux varying from $4.2 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ to $4.6 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$.

In the case of irradiations using polyethylene capsules, aliquots (150-200 mg) of each material were weighed in the capsules, occupying about 2/3 of the total volume of the capsule. Each capsule containing sample or standard was wrapped with aluminum foil and then the set of samples and standard was placed into the “rabbit”.

After adequate decay time of 1 day, for samples irradiated for 1 h, and of 3 days, for samples irradiated for 8 h, samples and standard were placed individually in stainless steel planchets for gamma ray activity measurements. In the case of irradiations using polyethylene capsules, samples and standard were placed individually in plastic counting tubes.

The induced gamma ray activity measurements were carried out using a hyperpure germanium detector from Canberra (model GC3020) connected to a digital spectrum analyzer (model DSA 1000). The system used had a resolution (FWHM) of 0.90 keV for 121.97 keV peak of ^{57}Co and of 1.70 keV for 1332.49 keV peak of ^{60}Co . The analysis of gamma spectra was performed using the computer program Genie 2000, 3.1 version, also from Canberra. The photopeaks of two radioisotopes of Hg were measured at different decay times: 77.34 keV of ^{197}Hg ($t_{1/2} = 64.16 \text{ h}$) and 279.20 keV of ^{203}Hg ($t_{1/2} = 46.61 \text{ d}$). The counting times varied from 1800 to 5400 s for the standard, and from 3600 to 36000 s for the samples, depending on their activities. The calculations for obtaining Hg mass fraction were performed by comparative method [11].

2.3. Treatment of data

To evaluate the mass fraction results of Hg in the CRMs in relation to their accuracy and precision, the arithmetic mean of the results, standard deviation, relative standard deviation, relative error and standardized difference (Z score) were calculated.

In addition, detection limits and quantification limits of Hg were obtained for the analyzed environmental samples of tree barks.

2.3.1. Relative standard deviation

The precision of the results was evaluated according to Wood [12], who considers that this parameter is related to the level of concentration (or mass fraction) of the analyte in the sample and it is defined by the Horwitz equation [13] given by:

$$\text{RSD} = 2^{(1-0.5 \log c)} \quad (1)$$

Where RSD is the value of Horwitz and c is the analyte's mass fraction. The method is considered accurate when it presents levels of variations within the acceptable for each level of mass fraction calculated using equation (1).

2.3.2. Standardized difference or Z score

To evaluate the accuracy of the CRMs results, Z score values were calculated using Equation 2, where X_{lab} is the mass fraction obtained in the laboratory, X_{ref} , the mass fraction of the certificate and SD_{mod} , the modified standard deviation, obtained by Equation 3 [14].

$$Z \text{ score} = \frac{X_{lab} + X_{ref}}{SD_{mod}} \quad (2)$$

$$SD_{mod} = \sqrt{SD^2 + u_{Xref}^2} \quad (3)$$

Where SD is the standard deviation of the measurements performed in the laboratory and u_{Xref} is the combined uncertainty of the reference value of the certificate. The result is classified as satisfactory or unsatisfactory according to the following criteria [14]:

If $|Z \text{ score}| \leq 2$, the result is considered satisfactory;
If $2 < |Z \text{ score}| < 3$, the result is considered uncertain;
If $|Z \text{ score}| \geq 3$, the result is considered unsatisfactory.

2.3.3. Detection limits and quantification limits

Detection limits and quantification limits were calculated using Currie's criterion [15], which defines the detection limit (DLT) and the quantification limit (QLT) as:

$$DLT = 3.29 \frac{\sqrt{BG}}{LT} \quad (4)$$

$$QLT = 10 \frac{\sqrt{BG}}{LT} \quad (5)$$

Where DLT and QLT are, respectively, detection limit and quantification limit in terms of counting rates, BG is the background and LT is the counting time. Once the DLT and QLT values were obtained, the detection limits (DL) and quantification limits (QL) in terms of the element mass fraction were obtained by the comparative method.

2.4. Preliminary Assays to Establish Adequate Conditions for Hg Determination

2.4.1. Analysis of Hg impurities in the polyethylene envelopes and in the N°. 40 Whatman filter paper sheets

In order to evaluate the presence of Hg in the polyethylene envelopes used for sample irradiation, empty envelopes were analyzed using the same experimental conditions used in the sample analyses.

The same procedure used for determination of Hg in the polyethylene envelopes was applied for the analysis of the N°. 40 Whatman filter paper sheets, used as support in the preparation of synthetic standard. For this study, filter paper samples were cut in the same size as the sheets used for preparing the synthetic standard.

2.4.2. Irradiation using different polyethylene containers for Hg determination

To choose the most adequate container for irradiation in the Hg determination, aliquots of the CRM IAEA-085 Human Hair and Hg synthetic standard were irradiated for 1 h in polyethylene capsules and in polyethylene envelopes, in order to evaluate if there is Hg loss. Mercury losses during the irradiation were evaluated by comparing the Hg mass fractions results obtained in the analyses of the CRM and the certified value. To evaluate Hg loss after the irradiation, gamma ray activities of the Hg standards were measured at different decay times and the counting rates obtained were corrected to zero decay time, according to the law of radioactive decay (Equation 6) [16].

$$A = A_0 e^{\frac{-\ln 2}{t_{1/2}} t} \quad (6)$$

Where A and A₀ are the counting rates for decay times t and t = 0, respectively and t_{1/2} is the half-life.

2.4.3. Selection of irradiation time

Aliquots of the CRM IAEA-085 Human Hair and Hg synthetic standard placed in polyethylene envelopes were irradiated for 1 and 8 h and the gamma ray activities were measured at different decay times. In order to evaluate the Hg loss after irradiation, the counting rates of Hg standard obtained for different decay time were corrected for zero decay time. The irradiated Hg standard was kept in the counting room at temperature of 20 °C throughout the period in which the counts were performed. Mercury losses during the irradiation were evaluated by comparing the Hg mass fractions results obtained in the analyses of the CRM and the certified value.

3. RESULTS AND DISCUSSION

3.1. Determination of Hg Impurities in the Polyethylene Envelopes and in the Filter Paper Sheets

Mercury impurities in the polyethylene envelopes used in the irradiations were not detected, and detection limits of 0.007 and 0.10 µg per envelope were obtained by measuring ¹⁹⁷Hg and ²⁰³Hg, respectively.

The determination of Hg impurity in the N^o. 40 Whatman filter paper sheet (used in the preparation of synthetic standard) indicated that this element is present at very low mass fractions. In the analysis of a filter paper sheet, measuring 1.5 cm x 6.0 cm and weighting 0.12030 g, Hg mass fraction of $0.0702 \pm 0.0056 \mu\text{g g}^{-1}$ or a quantity of 0.0084 μg per sheet was obtained. Since the Hg mass in the synthetic standard is 6.8 μg , the presence of this element in the filter paper sheet was considered negligible.

3.2. Irradiation using Different Kinds of Polyethylene Containers for Hg Determination

This study was carried out in order to choose a most adequate container for sample irradiation, avoiding Hg loss by volatilization.

The Hg loss in the envelope and in the capsule during 1 h of irradiation was verified by the analysis of aliquots of the CRM IAEA-085 Human Hair, which has a certified value of Hg mass fraction of $23.2 \pm 0.8 \mu\text{g g}^{-1}$ [17]. By measuring ^{197}Hg and ^{203}Hg for different decay times, results of Hg mass fraction were obtained and they varied from 23.23 ± 0.11 to $26.75 \pm 0.40 \mu\text{g g}^{-1}$, for sample irradiated in polyethylene capsule, and from 23.58 ± 0.14 to $25.536 \pm 0.087 \mu\text{g g}^{-1}$, when polyethylene envelope was used. These results indicate that there were no Hg losses during the irradiations from both containers, since the obtained results for mass fraction are very close to the certified value.

The Hg loss after irradiation was also verified by measuring synthetic standard of Hg for different decay times. The counting rates obtained were corrected for the same decay time ($t = 0$) from the measurements obtained in different decay times. Tables 1 and 2 show the obtained results for Hg standard irradiated in polyethylene capsule and in polyethylene envelope, respectively. Counting rates with their respective uncertainties were obtained for the photopeaks of 77.34 keV of ^{197}Hg and 279.20 keV of ^{203}Hg .

Results of Table 1 show that for the Hg standard irradiated in capsule, the values of the counting rates for the two photopeaks remained approximately constant until about 12 days of decay. In the case of the standard irradiation in polyethylene envelope (Table 2), the counting rates remained approximately constant until about 14 days of decay. These results indicate that, for decay times of up to 12 days, there was no Hg loss after irradiation either from the capsule or from the envelope.

Based on these results, it was decided to use polyethylene envelopes for sample and standard irradiations for Hg determination due to its ease of acquisition and cheaper cost.

Table 1: Counting rates of Hg synthetic standard corrected (A_0) for decay time $t_0 = 0$. Measurements obtained for different decay times. Irradiation time of 1 h in polyethylene capsule

Decay times, days	^{197}Hg , 77.34 keV	^{203}Hg , 279.20 keV
	A_0 , countings s^{-1}	A_0 , countings s^{-1}
2.0	106.80 ± 0.30	4.889 ± 0.058
4.9	104.81 ± 0.23	4.521 ± 0.030
5.9	108.30 ± 0.27	4.626 ± 0.031
7.0	108.44 ± 0.31	4.611 ± 0.031
8.9	109.77 ± 0.41	4.691 ± 0.031
11.0	108.07 ± 0.75	4.534 ± 0.031
11.9	108.95 ± 0.60	4.601 ± 0.032

Table 2: Counting rates of Hg synthetic standard corrected (A_0) for decay time $t_0 = 0$. Measurements obtained for different decay times. Irradiation time of 1 h in polyethylene envelope

Decay times, days	^{197}Hg , 77.34 keV	^{203}Hg , 279.20 keV
	A_0 , countings s^{-1}	A_0 , countings s^{-1}
1.8	114.20 ± 0.16	6.765 ± 0.043
4.8	116.96 ± 0.25	6.567 ± 0.036
5.7	116.78 ± 0.28	6.397 ± 0.036
6.9	120.15 ± 0.32	6.498 ± 0.036
8.9	120.75 ± 0.42	6.510 ± 0.037
9.9	91.93 ± 0.42	6.278 ± 0.036
13.9	121.39 ± 0.84	6.488 ± 0.038

3.3. Mercury Determination using Different Irradiation Times

The adequate irradiation time for Hg determination without causing its loss was chosen by analyzing the CRM IAEA-085 Human Hair, using irradiation times of 1 and 8 h. Mercury mass fraction obtained with 1 and 8 h of irradiation, by measuring ^{197}Hg and ^{203}Hg for different decay times, presented good agreement with certified value ($23.2 \pm 0.8 \mu\text{g g}^{-1}$) [17]. The results varied from 23.58 ± 0.14 to $25.536 \pm 0.087 \mu\text{g g}^{-1}$, for sample irradiated for 1 h, and from 25.311 ± 0.020 to $25.316 \pm 0.034 \mu\text{g g}^{-1}$, for that irradiated for 8 h. These results indicate that there were no Hg losses during the irradiation, since the obtained values of mass fraction are close to the certified value. However, after decay of ^{24}Na in the sample, the radionuclide ^{75}Se was identified in the CRM IAEA-085 Human Hair irradiated for 8 h, becoming impossible to determine Hg by measuring ^{203}Hg , since the gamma ray energies

emitted by ^{75}Se and by ^{203}Hg are very close to each other (279.93 keV and 279.20 keV, respectively) [6]. Besides using the irradiation of 8 h for CRM IAEA-085 Human Hair, a complex gamma ray spectrum was obtained in the region of low energy with high counting rates at of 68.89 keV and 411.80 keV of ^{198}Au . According to Zmijewsk [8], an important interference in Hg determination by INAA is that of ^{198}Au , whose photopeaks of energies 70.8 and 80.3 keV are not resolved from ^{197}Hg photopeak. The interference of ^{198}Au in the 77.34 keV photopeak of ^{197}Hg could not be verified by determining half-life, since these two radionuclides present very close half-lives (64.16 h for ^{197}Hg and 64.80 h for ^{198}Au) [6].

Table 3 shows the results obtained in the study of Hg loss after irradiation for Hg standard irradiated for 8 h in polyethylene envelope. The counting rates with their respective uncertainties corrected for decay time $t_0 = 0$ were obtained for the photopeaks of 77.34 keV of ^{197}Hg and 279.20 keV of ^{203}Hg . This table shows that the counting rates calculated for zero decay time remained approximately constant until about 14 days of decay, indicating no loss of Hg after irradiation.

Table 3: Counting rates of Hg synthetic standard corrected (A_0) for decay time $t_0 = 0$. Measurements obtained for different decay times. Irradiation time of 8 h in polyethylene envelope

Decay times, days	^{197}Hg , 77.34 keV	^{203}Hg , 279.20 keV
	A_0 , countings s^{-1}	A_0 , countings s^{-1}
3.9	557.20 ± 0.56	32.939 ± 0.099
6.9	716.27 ± 0.86	38.140 ± 0.092
9.1	711.1 ± 1.1	37.266 ± 0.089
10.0	719.0 ± 1.9	37.51 ± 0.21
14.0	722.9 ± 2.2	37.793 ± 0.094

Based on the obtained results, irradiation time of 1 h was chosen, in order to avoid gamma ray spectral interferences from ^{198}Au and ^{75}Se .

3.4. Analyses of Certified Reference Materials and of Environmental Samples

Tables 4 to 7 show the results obtained in the analyses of certified reference materials NCR DOLT-3 Dogfish Liver, BCR 186 Pig Kidney, INCT M-4 Cormorant Tissue and IAEA-085 Human Hair, respectively. In these Tables, results are presented for different decay times used for counting.

For CRMs NCR DOLT-3 Dogfish Liver, BCR 186 Pig Kidney and INCT M-4 Cormorant Tissue, it was observed that determinations performed after 4 days of decay presented higher values of relative standard deviation and relative error, probably due to the high activity of

^{24}Na ($t_{1/2} = 14.96$ h) that masked the less intense activities of ^{197}Hg . Except in these cases, all the parameters evaluated presented satisfactory values for relative standard deviation, relative error and Z score for all the materials in all measurements, with the exception of the measurement of ^{203}Hg after 5 days of decay of the CRM INCT M-4 Cormorant Tissue, which presented high value of relative standard deviation when compared to the 16% value established according to Horwitz for mass fractions in the order of 10^{-6} [12]. For CRMs NCR DOLT-3 Dogfish Liver and BCR 186 Pig Kidney, Hg was not determined by measuring ^{203}Hg , since ^{75}Se was identified in the spectra of these materials.

Mercury was not detected in the tree bark samples analyzed in this study, so detection limits and quantification limits for Hg determinations were calculated by the measurement of ^{197}Hg and ^{203}Hg radionuclides (Table 8). The bark samples analyzed were not collected in regions considered polluted by Hg emission into the atmosphere. According to Martín et al [21], this element is naturally present in the environment at very low concentrations (0.005 to 0.06 ng m^{-3} in air). Results showed in Table 8 indicate that detection limits obtained for ^{197}Hg gamma ray peak are lower than those obtained for ^{203}Hg .

Table 4: Mass fractions of Hg obtained in the CRM NCR DOLT-3 Dogfish Liver by measuring the ^{197}Hg radioisotope. Results obtained for different decay times used for counting

Evaluated parameters ^a	Results obtained in this study, $\mu\text{g g}^{-1}$			Certified value, $\mu\text{g g}^{-1}$
	^{197}Hg , 77.34 keV			
	dt ^b = 4 d	dt = 5 d	dt = 6 d	
X \pm SD (n)	3.14 \pm 0.43 (3)	3.26 \pm 0.15 (3)	3.72 \pm 0.24 (3)	3.37 \pm 0.14 [18]
RSD, %	13.6	4.6	6.6	
RE, %	6.9	3.2	10.3	
Z score	-0.54	-0.64	1.4	

a. X \pm SD: Arithmetic mean and standard deviation; n: number of determinations; RSD: relative standard deviation; RE: relative error;

b. dt = decay time.

Table 5: Mass fractions of Hg obtained in the CRM BCR 186 Pig Kidney by measuring the ^{197}Hg radioisotope. Results obtained for different decay times used for counting

Evaluated parameters ^a	Results obtained in this study, $\mu\text{g g}^{-1}$			Certified value, $\mu\text{g g}^{-1}$
	^{197}Hg , 77.34 keV			
	dt ^b = 4 d	dt = 5 d	dt = 6 d	
X \pm SD (n)	1.55 \pm 0.32 (3)	1.67 \pm 0.15 (3)	1.84 \pm 0.13 (3)	1.97 \pm 0.04 [19]
RSD, %	20.8	9.1	7.0	
RE, %	21.4	14.8	6.5	
Z score	-1.3	-1.9	-0.97	

a. X \pm SD: Arithmetic mean and standard deviation; n: number of determinations; RSD: relative standard deviation; RE: relative error;

b. dt = decay time.

Table 6: Mass fractions of Hg obtained in the CRM INCT M-4 Cormorant Tissue by measuring the ^{197}Hg and ^{203}Hg radioisotopes. Results obtained for different decay times used for counting

Evaluated parameters ^a	Results obtained in this study, $\mu\text{g g}^{-1}$						Certified value, $\mu\text{g g}^{-1}$
	^{197}Hg , 77.34 keV			^{203}Hg , 279.20 keV			
	dt ^b = 4 d	dt = 5 d	dt = 6 d	dt = 4 d	dt = 5 d	dt = 6 d	
X \pm SD (n)	1.89 \pm 0.24 (4)	2.05 \pm 0.11 (4)	2.13 \pm 0.11(4)	1.82 \pm 0.33 (4)	2.10 \pm 0.34 (4)	2.30 \pm 0.23 (4)	2.20 \pm 0.14 [20]
RSD, %	12.6	5.2	5.1	18.1	16.1	10.0	
RE, %	14.2	6.7	3.1	17.2	4.6	4.3	
Z score	1.2	1.1	0.53	1.1	0.30	-0.40	

a. X \pm SD: Arithmetic mean and standard deviation; n: number of determinations; RSD: relative standard deviation; RE: relative error.

b. dt = decay time.

Table 7: Mass fractions of Hg obtained in the CRM IAEA-085 Human Hair by measuring the ^{197}Hg and ^{203}Hg radioisotopes. Results obtained for different decay times used for counting

Evaluated parameters ^a	Results obtained in this study, $\mu\text{g g}^{-1}$						Certified value, $\mu\text{g g}^{-1}$
	^{197}Hg , 77.34 keV			^{203}Hg , 279.20 keV			
	dt ^b = 1 d	dt = 2 d	dt = 5 d	dt = 1 d	dt = 2 d	dt = 5 d	
X \pm SD (n)	24.1 \pm 1.4 (4)	23.8 \pm 2.1 (4)	24.7 \pm 2.7 (4)	24.9 \pm 1.8 (4)	24.9 \pm 2.4 (4)	25.0 \pm 1.9 (4)	23.2 \pm 0.8 [17]
RSD, %	5.6	8.8	11.1	7.3	9.5	7.6	
RE, %	4.1	2.5	6.5	7.2	7.2	7.9	
Z score	-0.27	-0.15	-0.36	-0.45	-0.41	-0.49	

a. X \pm SD: Arithmetic mean and standard deviation; n: number of determinations; RSD: relative standard deviation; RE: relative error.

b. dt = decay time.

Table 8: Detection limits (DL) and quantification limits (QL) of Hg obtained in the analysis of the tree bark samples

Sample code ^a	Radioisotope	DL, $\mu\text{g g}^{-1}$	QL, $\mu\text{g g}^{-1}$
A1	^{197}Hg	0.07	0.22
	^{203}Hg	0.7	2.1
A2	^{197}Hg	0.08	0.24
	^{203}Hg	0.8	2.3
A3	^{197}Hg	0.14	0.42
	^{203}Hg	1.9	5.8
A4	^{197}Hg	0.1	0.3
	^{203}Hg	1.6	4.8
A5	^{197}Hg	0.07	0.22
	^{203}Hg	1.0	3.0
A6	^{197}Hg	0.1	0.3
	^{203}Hg	1.4	4.3

- a. Samples coded A1 to A5 are from *Tipuana tipu* (Tipuana) specie. and A6, from *Poincianella pluviosa* (Sibipiruna) specie.

3. CONCLUSIONS

From the results obtained in the analyses of polyethylene envelope and of the N°. 40 Whatman filter paper sheet, it can be concluded that Hg is present in these materials at very low levels and it was considered negligible in the analyses.

Results obtained using different containers for irradiation demonstrated that polyethylene capsules and polyethylene envelopes can be used for Hg determination by INAA. Both containers showed no Hg loss. In this study, polyethylene envelope was chosen due to its ease of acquisition and cheaper cost.

Irradiation time of 1 h was chosen due to the problem of gamma ray spectral interference of ^{198}Au and ^{75}Se radionuclides. In addition, high activities of ^{24}Na , formed by the longer irradiation time, may affect the results of Hg determinations. The high activity of ^{24}Na masked the less intense activities of ^{197}Hg . The use of decay time of 6 d, in general, presented more precise and accurate results.

The results obtained for certified reference materials indicated good agreement with the certificate values, demonstrating the accuracy of the data. Results obtained also presented good precision, evaluated by the relative standard deviation values, and were considered satisfactory by Z score obtained values ($|Z \text{ score}| < 2$). The exception was for Hg determination in the analysis of CRM INCT M-4 Cormorant Tissue using decay time of 5 d.

Mercury was not detected in tree bark samples. The detection limits obtained for tree bark analysis varied from 0.07 and 1.9 $\mu\text{g g}^{-1}$, and the quantification limits were between 0.22 and 5.8 $\mu\text{g g}^{-1}$. Results obtained for Hg determination in tree barks indicated that there is no emission source of this element in the region where they were collected.

The findings of this study demonstrated the possibility of Hg determination by applying INAA in environmental samples.

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REFERENCES

1. J. Yang, Y. Zhao, J. Zhang, C. Zheng, "Removal of elemental mercury from flue gas by recyclable CuCl_2 modified magnetospheres catalyst from fly ash. Part 1. Catalyst characterization and performance evaluation," *Fuel*, **v. 164**, pp.419-428 (2016).
2. G. A. Drasch, *Handbook on metals in clinical and analytical chemistry*, Marcel Dekker, Inc., New York, USA (1994).
3. Z. Špirić, I. Vučković, T. Stafilov, V. Kušan, K. Bačeva, "Biomonitoring of air pollution with mercury in Croatia by using moss species and CV-AAS," *Environmental Monitoring and Assessment*, **v. 186**, n. 7, pp.4357-4366 (2014).
4. P. S. Bedregal, P. A. Mendoza, M. S. Ubillus, I. M. Cohen, E. H. Montoya, "The k_0 and relative INAA methods to determine elements in entire archaeological pottery objects," *Journal of Radioanalytical and Nuclear Chemistry*, **v. 300**, n. 2, pp.673-678 (2014).
5. S. M. Almeida, C. A. Ramos, A. M. Marques, A. V. Silva, M. C. Freitas, M. M. Farinha, M. Reis, A. P. Marques, "Use of INAA and PIXE for multipollutant air quality assessment and management," *Journal of Radioanalytical and Nuclear Chemistry*, **v. 294**, n. 3, pp.343-347 (2012).
6. IAEA, INTERNATIONAL ATOMIC ENERGY AGENCY. *Practical aspects of operating a neutron activation analysis laboratory*. Viena: IAEA, (IAEA – TECDOC – 564) (1990).
7. D. L. Anderson, "Use of l-cysteine for minimization of inorganic Hg loss during thermal neutron irradiation," *Journal of Radioanalytical and Nuclear Chemistry*, **v. 282**, n. 1, pp.11-14 (2009).
8. W. Zmijewska, "Activation analysis of mercury in environmental samples," *Journal of Radioanalytical Chemistry*, **v. 35**, pp.389-418 (1977).
9. T. Takeuchi, M. Shinogi,; I. Mori, "Volatilization losses of mercury in neutron activation analysis," *Journal of Radioanalytical Chemistry*, **v. 53**, pp.81-88 (1979).
10. J. W. Patterson, R. Passino, *Metals speciation separation and recovery* (Vol. 1), CRC Press, Chicago, USA (1987).
11. D. de Soete, R. Gilbels, J. Hoste, *Neutron activation analysis*, Wiley-Interscience, New York (1972).
12. R. Wood, "How to validate analytical methods," *Trends in Analytical Chemistry*, **v. 18**, pp.624-632 (1999).

13. W. Horwitz, R. Albert, "The Horwitz ratio (HorRat): A useful index of method performance with respect to precision," *Journal of AOAC International*, v. **89**, n. 4, pp.1095-1109 (2006).
14. P. Konieczka, J. Namiesnik, *Quality assurance and quality control in the analytical chemical laboratory: a practical approach*, CRC Press, Boca Raton, USA (2016).
15. L.A. Currie, "International recommendations offered on analytical detection and quantification concepts and nomenclature," *Analytica Chimica Acta*, v. **391**, pp.127-134 (1999).
16. G. Friedlander, J. W. Kennedy, J. M. Miller, *Nuclear and radiochemistry*, John Wiley & Sons, London (1964).
17. IAEA. International Atomic Energy Agency, Reference sheet, IAEA-085 Methylmercury, Total Mercury and Other Trace Elements in Human Hair (2000).
18. NCR. National Research Council Canada, Certificate of analysis, DOLT-3 Dogfish Liver Certified Reference Material for Trace Metals (2002).
19. BCR. Community Bureau of Reference, Certificate of analysis, BCR 186 Trace elements in lyophilized pig kidney (1986).
20. INCT. Institute of Nuclear Chemistry and Technology, Certificate of Analysis, Polish Certified Reference Material MODAS-4 Cormorant Tissue, M-1 CormTis (2015).
21. J. R. Martín, N. Nanos, J. Miranda, G. Carbonell, L. Gil, "Volcanic mercury in *Pinus canariensis*", *Naturwissenschaften*, v. **100**, pp.739-747 (2013).