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Investigating the antimony determination in environmental samples by NAA

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Abstract In recent years, environmental concerns regarding antimony have grown considerably due to anthropogenic processes that have resulted in increasing concentration of Sb in the environment, and also because of its impacts and possible adverse effects to living organisms. Several techniques have been used, to obtain reliable results for Sb, since Sb is present at low level concentration, requiring analytical instrumentation with low detection limits. The neutron activation analysis (NAA) technique has a high metrological level for the determination of several elements in different matrices. However, Sb determination in environmental and biological samples presents some analytical difficulties due to its low concentrations and gamma ray spectrum interferences. The objective of this research was to study on Sb determination in environmental reference materials by NAA. Ten environmental reference materials were selected and analyzed using long period irradiation at IEA-R1 research nuclear reactor. The induced gamma activities of ^{122}Sb and ^{124}Sb were measured. Relative errors of the results demonstrated that the accuracy depends mainly on Sb radioisotope measured, the decay time for counting and the sample composition.

Keywords Antimony · Certified reference materials · Environmental · NAA

Introduction

Antimony is an element present in trace levels in environmental and biological samples. For many years, Sb was not considered as an element of great importance from the environmental point of view and its study was omitted, probably due to its low abundance in nature from and its compounds are poorly soluble [1]. In Earth's crust its concentration varies from 0.2 to 0.5 mg/Kg.

In recent years, environmental concerns regarding antimony have grown considerably due to anthropogenic processes that have resulted in increasing concentration of Sb in the environment. Due to its environmental impact and its possible adverse effects to the organisms, Sb and its compounds are on the list in US Environmental Protection Agency and of European Union as pollutants of the high priority interest [2].

Presently, Sb presents a growing application in the semiconductor industry, and at the metallurgical industries this element has been added in alloys and used to produce fireproof materials, ceramics, glass and as pigment [3, 4]. Its oxides and sulfides are found in rubber products and it is used as dye, color pigment as well as a flame retardant. Besides antimony oxides currently are used as catalyst for the poly-condensation and to produce poly (terephthalate) (PET) used in the production of bottles. Consequently Sb migration from the bottles to the beverage has been widely evaluated [5].

In addition, antimony is used as a therapeutic agent against various tropical protozoal diseases, such as leishmaniasis, schistosomiasis and ascariasis, although lately it has been replaced by other agents [6]. In the nuclear field, ^{124}Sb and ^{125}Sb radioisotopes are frequently used in the leak test of pipes, in neutron activation analysis (NAA) and also in nuclear medicine [1].

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Several analytical techniques have been suggested, to be used, to obtain reliable Sb results, since its concentrations are low, requiring analytical instrumentation with low detection limits. The method of NAA presents a high metrological level for the determination of several elements in different kind of matrices [7–10]. Nevertheless, the determination of this element in environmental and biological samples presents some analytical difficulties due its low concentrations and gamma ray spectrum interferences, in particular of ^{76}As radioisotope that emits gamma rays with energies of 559.10 and 563.23 keV very close to 564.24 keV of ^{122}Sb.

In this study, the accuracy of Sb determination results obtained by NAA in certified environmental reference materials was evaluated and interference problems found in these analyses are discussed.

Experimental

Materials

Ten reference materials selected for Sb determination were of biological and geological matrices produced by the following institutions: National Institute of Standards and Technology (NIST), USA, International Atomic Energy Agency (IAEA), Austria, Institute of Nuclear Chemistry and Technology (INCT), Poland and by the European Community Bureau of Reference (BCR), Belgian.

NAA procedure

Aliquots of approximately 180 mg of each sample were irradiated together with the synthetic standard of Sb in sealed polyethylene bags previously cleaned using diluted nitric acid solution and MilliQ purified water. Sb synthetic standard was prepared using a diluted solution of this element that was prepared using a certified solution of Sb, purchased from Spex Certripet, USA. Samples and Sb standard (mass = 50 μg) were wrapped separately in aluminum foil and irradiated together within sealed aluminum container suitable for irradiation inside the reactor core. The samples and standard were irradiated under a thermal neutron flux of about 5×10^{12} n cm^2 s^{-1} for a period of 8 h for geological materials and of 16 h for biological materials in the IEA-R1 nuclear research reactor of the Nuclear and Energy Research Institute, IPEN -CNEN/SP.

The counting system consisted of a 2018GC hyperpure Ge detector coupled to a digital spectrum analyzer (DAS 100), both from Canberra. The resolution (FWHM) of the system was 1.0 keV for the 122 keV peak of ^{57}Co and 1.78 keV for 1.332 keV peak of ^{60}Co. Samples and standard were measured twice for different decay times. The first measurement was performed after 7 to 9 day of decay time, and using counting times of 3,600 s for the standard and of 36,000 s for the samples. The second measurement was performed after from 13 to 16 days of decay time, and using counting time of 5,400 and 50,000 s for the standard and samples, respectively.

Samples and standards were measured in the same geometry and the distance from sample to detector was adjusted so that the dead time was less than 12%. The software Genie 2000 version 3.1 from Canberra was used for data acquisition and spectral analysis, producing a table with the detected energies and their respective counts and its uncertainty. The radioisotopes were identified by its half-lives and gamma rays energies and the concentrations of elements were calculated by the comparative method, using the in-house built ESPECTRO program.

To evaluate the interference of ^{76}As radioisotope in the determination of Sb, synthetic As standard (As mass = 1.5 mg) was also irradiated together with reference material samples and Sb synthetic standard.

Concentrations of Sb in the materials were calculated from the counting data obtained for the peaks of 564 keV gamma ray energy of ^{122}Sb ($t_{1/2} = 2.7$ day) and 1,692 keV gamma ray energy of ^{124}Sb ($t_{1/2} = 60.2$ day). To express the Sb results on dry weight basis, approximately 200 mg of certified reference materials were dried at 85 °C for 24 h for moisture determination.

Results and discussion

The analytical data obtained from duplicate determinations are presented in Tables 1 and 2 together with the values of certificates. The uncertainties of the results are composed of two components. The first one is associated to the counting statistics provided by the software. The second is associated to the experimental procedure adopted in this work, which was overestimated in 10% of the experimental value, which is frequently referred to as a usual value in the literature [11–13]. The accurate determination of that last component is under study and will be refined in the future. The relative errors for Sb concentrations and Z-score values [14] were calculated from mean and standard deviation of measured and certified values.

Table 1 shows that in the first determination, by measuring 564 keV photopeak after a decay time of 7 day, for the certified reference materials of INCT-MPH2 mixed polish herbs, INCT- TL-1 tea leaves, Sl-1 trace and minor elements in lake sediment, CTA VTL-2 Virginia tobacco leaves and BCR 679 trace elements in white cabbage, the data were good agreement with the certified values with ranging from 0.76 to 13.5% of relative errors and | Z score | smaller than 1.0. In this condition, the 1692 keV photopeak

Table 1 Concentrations of Sb (mg kg^{-1}), relative errors and *Z*-score values obtained in the first determination of the certified reference material analyses

Reference materials	Gamma ray energy (keV) measured	This work						Values of the certificates
		Average decay time			Average decay time			
		7 days			13 days			
		C ± Ic	RE (%)	Z-score	C ± Ic	RE (%)	Z-score	
NIST SRM 1515 apple leaves	564	0.023 ± 0,006	–	–	0.30 ± 0.01	–	–	[0.013]
	1,692	<0.04	–	–	nd	–	–	
NIST SRM 1633b constituents elements in coal fly ash	564	4.67 ± 0.05	–		**6.05 ± 0.11**	–	–	[6]
	1,692	4.69 ± 0.21	–	–	4.3 ± 0.4	–	–	
INCT MPH-2 mixed polish herbs	564	0.068 ± 0,001	4.6	0.3	**0.0730 ± 0.0021**	12.3	0.06	0.0655 ± 0.0091
	1,692	0.070 ± 0.020	7.7	0.2	**0.07 ± 0.01**	7.7	0.5	
INCT- TL-1 tea leaves	564	0.050 ± 0.001	–	–	0.304 ± 0.004	–	–	[0.050]
	1,692	nd	–	–	0.038 ± 0.004	–	–	
NIST SRM 1573a tomato leaves	564	nd	–	–	0.08 ± 0.01	26.9	1.5	0.063 ± 0.006
	1,692	nd	–	–	0.08 ± 0.01	26.9	1.5	
IAEA SL-1trace and Minor elements in lake sediment	564	**1.3 ± 0.02**	0.8	−0.1	2.01 ± 0,36	53.5	1.7	[1.31 (1.19–1.43)]); *n* = 15, *P*= 0.05
	1,692	1.10 ± 0.14	16.3	−1.1	1.01 ± 0.05	22.9	−0.7	
IAEA-140/TM trace elements and Methyl mercury in seaweed (focus sp)	564	nd	–	–	**0.09 ± 0.05**	13.6	−0.06	0.103 (0.081–0.125) *n* = 12, *P* = 0.05
	1,692	nd	–	–	**0.09 ± 0.01**	12.6	−0.1	
IAEA 336 trace and minor elements in lichen	564	0.090 ± 0.001	23.1	1.7	0.091 ± 0.004	24.6	1.1	0.073 (0.063–0.083); *n* = 12; *P* = 0.05
	1,692	0.060 ± 0.020	17.8	−0.6	**0.08 ± 0.01**	9.6	0.4	
BCR 679 trace element on white cabbage	564	**0.019 ± 0.003**	7.7	−0.4	0.025 ± 0.004	21.3	0.9	0.0206 ± .0014
	1,692	<0.5	–	–	**0.021 ± 0.003**	1.9	−0.02	
CTA VTL-2 Virginia tobacco leaves	564	0.210 ± 0.002	32.8	−4.1	**0.328 ± 0.004**	5.1	0.6	0.312 ± 0.025
	1,692	**0.27 ± 0.02**	13.5	−1.3	**0.3 ± 0.1**	1.3	−0.1	

Results that presented good agreement with the values of the certificates are written in bold

Detection limit calculated according to Currie criterion [15]

C ± *Ic* Concentration with uncertainty value, *RE* Relative error,–indicates not calculated, *nd* indicates not identified, numbers between square brackets indicate informative values, *n* and *P* are numbers of determinations and significance level, respectively

of ^{124}Sb was not detected because of the low activity of ^{124}Sb photopeak is masked by high activities of other radionuclides.

When the measurements were carried out with 13 days of decay time, the certified reference materials of INCT-MPH2, IAEA-140/TM trace elements and methyl mercury in seaweed (focus sp) and CTA VTL-2 were presented most accurate results for both photopeaks of Sb used in this study. For the materials IAEA 336 trace and minor elements in lichen, NIST SRM 1633b constituents elements in coal fly ash and BCR 679, the best results were found using the 1692 keV photopeak of ^{124}Sb, with relative errors ranging from 1.3 to 13.6 and |Z score | smaller than 1.0, indicating that these results are within the range values of the certified values at the confidence level of 68% [14].

In the second determination (Table 2), using a decay time of 9 days for counting, for the references materials CTA VTL-2 and IAEA 336, the consistent results with the values of their certificates were obtained using both photopeaks, different from the results obtained in the first determination which measurement was performed after 7 day of decay time. The difference of 2 days for decay time, allowed to the detection of ^{122}Sb photopeak with reduced interference of 559 keV photopeak of ^{76}As. Also in the first measurement, good results were obtained for INCT-MPH2 mixed polish herbs and BCR 679 when the 564 keV peak of ^{122}Sb was used. Radioisotopes of ^{124}Sb were not detected due its low activity and interference caused by the high activity of other radionuclides such as ^{82}Br.

As can be seen in Table 2, after 15 days of decay time, good results were obtained for the reference materials of INCT-MPH2, NIST SRM 1573a tomato leaves, IAEA-140/TM, CTA VTL-2. The relative errors were lower than 7.7 and |Z score | values were smaller than 1.0.

Table 2 Concentrations of Sb (mg kg^{-1}), relative errors and *Z*-score obtained in the second determination of the certified reference materials analyses

Reference materials	Gamma ray energy (keV) measured	This work						Values of the certificates
		Average decay time			Average decay time			
		9 days			16 days			
		C ± Ic	RE (%)	Z-score	C ± Ic	RE (%)	Z-score	
NIST SRM 1515 apple leaves	564	**0.013 ± 0.003**	–	–	0.021 ± 0.005	–	–	[0.013]
	1,692	nd	–	–	<0.04	–	–	
NIST SRM 1633b constituents elements in coal fly ash	564	4.5 ± 0.1	–	–	5.2 ± 0.1	–	–	[6]
	1,692	4.7 ± 0.2	–	–	4.2 ± 0.1	–	–	
INCT MPH-2 mixed polish herbs	564	**0.060 ± 0.001**	8.6	−0.6	0.074 ± 0.001	13.8	0.7	0.0655 ± 0.0091
	1,692	0.081 ± 0.001	24.6	1.3	0.070 ± 0.003	7.7	0.5	
INCT- TL-1 tea leaves	564	0.08 ± 0.01	–	–	0.530 ± 0.001	–	–	[0.050]
	1,692	0.04 ± 0.01	–	–	0.05 ± 0.01	–	–	
NIST SRM 1573a tomato leaves	564	nd	–	–	0.06 ± 0.01	4.8	0.0	0.063 ± 0.006
	1,692	nd	–	–	0.07 ± 0.01	6.3	0.4	
IAEA SL-1 trace and minor elements in lake sediment	564	1.1 ± 0.1	19.1	−1.4	2.70 ± 0.01	103.8	8.2	[1.31 (1.19- 1.43)]); $n = 15$, $P = 0.05$
	1,692	**1.3 ± 0.1**	2.3	−0.2	0.12 ± 0.03	90.8	9.6	
IAEA-140/TM trace elements and Methyl mercury in seaweed (Focus sp)	564	0.065 ± 0.001	37.1	–0.5	0.127 ± 0.004	23.3	0.07	0.103 (0.081–0.125) $n = 12$, $P = 0.05$
	1,692	nd	–	–	0.10 ± 0.01	3.9	0.1	
IAEA 336 trace and minor elements in lichen	564	**0.07 ± 0.01**	1.0	0.06	0.06 ± 0,01	16.4	−1.1	0.073 (0.063–0.083); $n = 12$; $P = 0.05$
	1,692	**0.07 ± 0.01**	1.4	0.1	0.06 ± 0.01	12.3	−0.8	
BCR 679 Trace element on white cabbage	564	**0.022 ± 0.004**	6.8	0.3	<0.11	–	–	0.0206 ± 0.0014
	1,692	<0.14	–	–	<0.08	–	–	
CTA VTL-2 Virginia tobacco leaves	564	**0.321 ± 0.004**	2.9	−0.3	0.37 ± 0.01	19.6	2.3	0.312 ± 0.025
	1,692	**0.31 ± 0.02**	0.6	0.06	0.30 ± 0.01	3.8	−0.4	

Results that presented good agreement with the values of the certificates are written in bold

Detection limit calculated according to Currie criterion [15]

C ± *Ic* Concentration with uncertainty value, *RE* Relative error, – indicates not calculated, *nd* indicates not identified, numbers between square brackets indicate informative values, *n* and *P* are numbers of determinations and significance level, respectively

For the reference material, NIST SRM 1633b there is no certified values for Sb. Results close to the informative values were obtained when both ^{122}Sb and ^{124}Sb peaks were used.

In the first determination, when 7 days of decay time was used, the obtained values do not agree with the certificate ones, due to the interference of the gamma-ray lines of ^{76}As. In this case the intensity of the 559 keV peak of ^{76}As was about 40 times higher than the peak intensity of the 564 keV peak of ^{122}Sb. When this ratio of intensities is lower than 40, the result obtained is in fact a stacking between the peaks of 559 and 563 keV, which could lead to a "false" signal for the peak of 564 keV, thus explaining the high relative errors found. The results were also indicated a significant improvement in the results for the same certified reference materials for the counting carried out with 15 days of decay, where the results were in agreement with the certified values.

Conclusion

The results indicated the possibility of using neutron activation analysis in the determination of Sb in environmental samples, depending on the Sb content in the material, under a thermal neutron flux of about 5 × 10^{12} n cm^{-2} s^{-1} for a period of 8 h for geological materials and of 16 h for biological materials with first measurement performed after 7–9 days of decay time and second measurement performed after from 13 to 16 days of decay time. The most accurate results in the determination of antimony using the radioisotope ^{122}Sb were obtained when the counting is performed after about 9 days of decay time, while for ^{124}Sb measurement, a decay time of 15 days was adequate to obtain more accurate results. These findings showed that the accuracy of Sb determination is strongly dependent on the decay time for the counting and on the radioisotope measured. Results also demonstrated that the significant interference of ^{76}As in the Sb determination by measuring of the 564 keV peak was dependent on the ratio between As and Sb concentrations in the sample.

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