Study on Determination of Antimony in Environmental Samples by Neutron Activation Analysis

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There is an increasing interest in the determination of antimony in environmental samples since this element is cumulative and potentially toxic at very low concentrations. Moreover, the quantification of antimony presents difficulties due to its low concentrations in the samples and to the interference problem in the analyses. In this study, neutron activation analysis procedure was established in order to obtain reliable results for Sb determination in environmental samples. For this study ten reference materials were analyzed. Aliquots of these materials and synthetic standard of Sb were irradiated at the IEA- R1 nuclear reactor under a thermal neutron flux of about $5x10^{12}$ n cm^{-2} s^{-1} for 8 or 16 hours. The induced gamma activities of ^{122}Sb and ^{124}Sb were measured using a hyperpure Ge detector. Antimony concentrations were calculated by comparative method and the uncertainties of the results were estimated using statistical counting errors of the sample and standard. Relative errors calculated demonstrated that the accuracy of the results depends on the Sb radioisotope measured and the decay time for counting.

Keywords: antimony, reference materials, neutron activation analysis, interference

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INTRODUCTION

Antimony is a chemical element with symbol Sb, 5A family and 51 atomic number in the periodic table [1]. This element with atomic weight of 121.75 u, fusion point of 630ºC and boiling point of 1380ºC is composed of a nonmetal isotopes 121 and 123 in the proportions of 57.25% and 42.7% respectively[2]. The Sb may exist in multiple oxidation states (III, 0, III and V), but is mainly found in two states (III and V) in environmental, biological and geological samples[3]. The main routes of entry are the water cycle and atmosphere through the burning of coal[2]. Maximum emission level in any industrial process is 50 mg/m^3 of air and the ambient exposure limit in work places is 0.05 mg/m^3.

In aquatic environment, Sb is present as the result of weathering of rocks and soil through the disposal of effluents from mining and smelting. The typical concentration of dissolved Sb in unpolluted waters is less than 1 mg/L, however, in close proximity to anthropogenic sources, concentrations can be found in up to 100 times the natural level. The guide of the European community in the policy concerning the quality of water intended for human consumption in 2001 sets a maximum limit of 10 mg Sb/L

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not to be exceeded for drinking water. As for sediments and soils, the Sb concentration is in the order of a few µg/g and the highest concentrations are directly related to anthropogenic sources, especially near foundries[4]. For food, there are several different limits acceptable for this element due to the difference in the amount of Sb available in soils and waters in distinct countries.

Antimony was already known to the ancients since this element could be mixed with many other metals. This element was used for the purification of gold, silver and copper until the 18th century [3]. Currently, Sb is used in large scale as a retardant additive. Their oxides and sulfides are found in rubber products and used as dye and color pigment. Antimony oxides are also used to slow the plastics photolysis and in the form of antimony trichloride, it is used as a pigment to degenerate Fe, Zn and Sn. The antimony trifluoride is used as a mordant in the textile industry. 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[3].

In addition, antimony is used as a therapeutic agent against various tropical protozoal diseases, such as leishmaniasis, schistosomiasis and ascariasis, although in recent years it has been replaced by other agents[5]. Presently, the concern on Sb determination has grown considerably due to the anthropogenic processes that increase concentrations in the environment. Due to its environmental impact and its possible adverse effects to the organisms, Sb and its compounds are on the list of U.S Environmental Protection Agency (USEPA) and the European Union (EU) as pollutants of the high priority interest [6]. Chronic exposure by inhalation of this element can cause pneucomoconiosis diseases associated to obstructive pulmonary disease, cardiac abnormalities, increased blood pressure, abdominal pain, ulcers, skin and eye irritation [7].

Several techniques have been suggested, in recent decades, to obtain reliable results of Sb, since its concentrations are present at low levels, requiring analytical instrumentation with low detection limits. The neutron activation analysis technique has a high metrological level for the determination of several elements in different matrices. However, the Sb determination in environmental and biological samples present some analytical difficulties due its low concentrations and gamma ray spectrum interferences. Within this context, the objective of this research was study on antimony determination in environmental reference materials by neutron activation analisis (NAA).

EXPERIMENTAL

Ten reference materials with different Sb concentrations were selected to evaluate the quality of their results in relation to the accuracy. Biological and geological reference materials produced by the 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), Europe, were analyzed.

The experimental procedure for Sb determination was to irradiate about 180 mg of each sample together with the synthetic standard of Sb in sealed polyethylene bags previously cleaned using diluted nitric acid solution and MilliQ purified water. Samples and standards were wrapped separately in aluminum foil and irradiated together inside sealed aluminum containers suitable for irradiation inside the reactor core. To express these results on dry weight bases, approximately 200 mg of each certified reference material were dried at 85ºC for 24 hours for moisture determination. The samples and standard were irradiated under thermal neutron flux of about $5x10^{12}$ cm^2 s^{-1} for a period of 8 or 16 hours in the IEA-R1 nuclear research reactor of the Nuclear and Energy Research Institute, IPEN -CNEN/SP.

Two sets of measurements were carried out for the samples and standard. The first measurement was performed about seven days of decay time, and using counting times of 3.600 s for the standard and 36.000 s for the samples. The second measurement was performed after approximately 15 days of decay time, and using counting time of 5.400 and 50.000 s for the standard and samples, respectively. 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 standards were measured in the same geometry and the distance from sample to detector was chosen so that the percentage of dead time was less than 12%. The software Genie 2000 from Canberra was used for data acquisition and spectral processing. The radioisotopes were identified by the half-lives and gamma rays energies and the concentrations of elements were calculated by the comparative method, using the SPECTRUM program.

To evaluate the interference of ^{76}As in the determination of Sb, synthetic As stardard (mass=1500 ng) was irradiated along with samples of reference material and synthetic stardard of Sb.

Concentrations of Sb in certified reference materials were calculated from the counting data obtained after approximately 7 and 15 days of decay times and the photopeaks used were 564 keV of ^{122}Sb ($t_{1/2}$=2.7 d) and 1692 keV of ^{124}Sb ($t_{1/2}$=60.2 d).

RESULTS

In Table 1 and 2 the results obtained in two determinations and the values of the certificates are presented for comparison. The uncertainties presented in this table were calculated assuming errors in the statistical counts of both sample and standard, and the percentage of relative errors and Z-score values were also calculated for materials with certified Sb concentrations values.

The best results of Sb were obtained in the analysis of certified reference materials, INCT-MPH2 Mixed Polish Herbs, SRM 1573a Tomato Leaves, Sl-1 Trace and Minor Elements in Lake Sediment, IAEA-140/TM Trace Elements and Methyl mercury in Seaweed (Focus sp), IAEA 336 Trace and Minor Elements in Lichen, Trace Elements in White Cabbage and CTA VTL-2 Virginia Tobacco Leaves whose results showed percentages of relative error ranging from 0.76 to 13.6 and | Z score | smaller than 1.0, in first determination, and relative error ranging from 0.6 to 8.6 and | Z score | smaller than 1.0 in second determination, indicating that these results are within the range of values of the certificate to a confidence level of 68% [8].

TABLE 1. Concentrations of Sb (mg kg^{-1}), relative error and Z-score obtained in the analysis in first determination of certified reference materials

Reference materials	Gamma ray energy (keV)	Decay Time 7 days		Zscore	Decay Time 15 days		Values of Certificates
		C ± Ic	RE (%)		C ± Ic	RE (%)	
NIST SRM 1515 Apple Leaves	564	0.023± 0.006	- (*)	-	0,030±0.006	-	[0.013]**
	1692	< 0.040 (****)	-	-	nd	-	
NIST SRM 1633b Constituents Elements in Coal Fly Ash	564	4.67±0.03	-		**6.05±0.09**	-	[6]
	1692	4.69±0.20	-	-	4.31±00.12	-	
INCT MPH-2 Mixed Polish Herbs	564	**0.0680±0.0007**	4.6	0.33	**0.073±0.002**	12.3	0.0655±0.0091
	1692	**0.07±0.02**	7.7	0.23	**0.070±0.005**	7.7	
INCT- TL-1 Tea Leaves	564	**0.0493±0.0008**	-	-	0.304±0.002	-	[0.050]
	1692	nd	-	-	0.038±0.004	-	
NIST SRM 1573a Tomato Leaves	564	nd	-	-	0.08±0.01	26.9	0.063±0.006
	1692	nd	-	-	0.08±0.01	26.9	
IAEA SL-1Trace and Minor Elements in Lake Sediment	564	**1.30±0.01**	0.76	-0.08	2.01±0.03	53.48	[1.31(1.19-1.43)]); n=15, p=0.05 (***)
	1692	1.10±0.14	16.3	-1.14	1.01±0.05	22.9	
IAEA-140/TM Trace Elements and Methyl mercury in Seaweed (Focus sp)	564	nd	-	-	**0.089±0.05**	13.6	0.103(0.081-0.125) n=12, p=0.05
	1692	nd	-	-	**0.09±0.01**	12.6	
IAEA 336 Trace and Minor Elements in Lichen	564	0.0899±0.0009	23.1	1.68	0.091±0.004	24.6	0.073(0.063-0.083); n=12; p=0.05
	1692	0.06±0.02	17.8	-0.58	**0.08±0.01**	9.6	
BCR 679 Trace Element on White Cabbage	564	**0.019±0.003**	7.7	-0,40	0.025±0.004	21.3	0.0206±.0014
	1692	< 0.51	-	-	**0.021±0.003**	1.9	
CTA VTL-2 Virginia Tobacco Leaves	564	0.2096±0.0009	32.8	-4.09	**0.328±0.003**	5.1	0.312±0.025
	1692	0.27±0.02	13.5	-1.31	**0.308±0.008**	1.3	

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. **** Detection limit value calculated according to Currie criterion [9].

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

TABLE 2. Concentrations of Sb (mg kg^{-1}), relative error and Z-score obtained in the analysis in second determination of certified reference materials

Reference materials	Gamma ray energy (keV)	Decay Time 7 days			Decay Time 15 days		Values of Certificates
		C ± Ic	RE (%)	Zscore	C ± Ic	RE (%)	
NIST SRM 1515 Apple Leaves	564	**0.013±0.003**	-	-	0.021±0.005	-	[0.013]**
	1692	nd	-	-	< 0.040	-	
NIST SRM 1633b Constituents Elements in Coal Fly Ash	564	4.49±0.04	-	-	5.20±0.05	-	[6]
	1692	4.75±0.19	-	-	4.25±0.11	-	
INCT MPH-2 Mixed Polish Herbs	564	**0.0594±0.0007**	8.6	-0.61	0.074±0.001	13.8	0.0655±0.0091
	1692	0.081±0.0008	24.6	1.32	**0.070±0.003**	7.7	
INCT- TL-1 Tea Leaves	564	0.0848±0.008	-	-	0.530±0.005	-	[0.050]
	1692	0.04±0.01	-	-	0.046±0.005	-	
NIST SRM 1573a Tomato Leaves	564	nd	-	-	0.06±0.01	4.8	0.063±0.006
	1692	nd	-	-	**0.067±0.009**	6.3	
IAEA SL-1Trace and Minor Elements in Lake Sediment	564	1.06±0.13	19.1	-1.41	2.67±0.08	103.8	[1.31(1.19-1.43)]); n=15, p=0.05 (***)
	1692	**1.28±0.13**	2.3	-0.17	0.12±0.03	90.8	
IAEA-140/TM Trace Elements and Methyl mercury in Seaweed (Focus sp)	564	0.0648±0.0007	37.1	-0.55	0.127±0.004	23.3	0.103(0.081-0.125) n=12, p=0.05
	1692	nd			**0.099±0.008**	3.9	
IAEA 336 Trace and Minor Elements in Lichen	564	**0.0737±0.007**	1.0	0.06	0.061±0.005	16.4	0.073(0.063-0.083); n=12; p=0.05
	1692	**0.074±0.007**	1.4	0.08	0.064±0.005	12.3	
BCR 679 Trace Element on White Cabbage	564	**0.022±0.004**	6.8	0.29	< 0.11	-	0.0206±.0014
	1692	< 0.14	-	-	< 0.08	-	
CTA VTL-2 Virginia Tobacco Leaves	564	**0.321±0.002**	2.9	-0.28	0.373±0.008	19.6	0.312±0.025
	1692	**0.31±0.02**	0.6	0.06	**0.30±0.01**	3.8	

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. **** Detection limit value calculated according to Currie criterion [9].

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

For the reference material SRM-1515 Apple Leaves, INCT-TL-1 Tea Leaves, IAEA-SL-1 Trace and Minor Elements in Lake Sediment and CTA-VTL-2 Virginia Tobacco Leaves and the material BCR-679 Trace Elements in White Cabbage their results agreed with the certificate values when the 564 keV peak of ^{122}Sb was used and measurements made after 7 days of decay. In the second session of measurement carried out approximately 15 days of decay time and using 564 keV peak of ^{122}Sb, the concentrations of Sb obtained for these materials were discrepant when compared with the certified values, with very high relative errors. In view these results, other potential interferences were evaluated, in addition to ^{76}As, through the analysis of the energies of the photopeaks, half-life and concentration in these certified reference materials.

Other radioisotopes that could interfere in the ^{122}Sb peak of 564 keV are ^{134}Cs, ^{152}Eu, both with longer half lives and concentration levels higher than those of Sb, and ^{194m2}Ir, that was definitely identified in this study, through the determination its half-life and identification of its several gamma-ray peaks. Concentrations of these interfering elements in the reference materials and nuclear characteristics of these radioisotopes are presented in Table 3.

TABLE 3. Concentration of Cs, Eu and Ir (mg kg^{-1}) from the certificates of reference materials and nuclear characteristics (half life, gamma ray energies, isotopic abundance and cross section) of radioisotopes

Reference Material	**Cs**	**Eu**	**Ir**
IAEA SL-1Trace and Minor Elements in Lake Sediment	6.1-7.9	1.1-2.1	np
INCT- TL-1 Tea Leaves	3.61 ± 0.37	49.9 ± 9.4	np
NIST SRM 1515 Apple Leaves	np	0.2	np
CTA VTL-2 Virginia Tobacco Leaves	0.515 ± 0.046	0.033	np
Half-life	^{134}**Cs** = 2.0648 y	^{152}**Eu** = 13.537 y	^{194m2}**Ir** = 171 d
Gamma Ray Energy (keV)	^{134}**Cs** = 569	^{152}**Eu** = 564	^{194m2}**Ir** = 562
Isotopic Abundance (%)	^{134}**Cs**=100	^{152}**Eu**=0,489	^{194m2}**Ir** =35
Cross Section (barns)	^{134}**Cs**=30.3±1.1	^{152}**Eu**=9.200±100	^{194m2}**Ir** =111±5

*np indicates value not provided by producers

The study demonstrated that the presence of Cs, Eu and Ir in the certified reference materials raises analytical difficulties in the determination of Sb, due to overlapping peaks in the same region as the 564 keV peak of ^{122}Sb, which presents lower intensity, therefore masking the Sb peak, leading to obtain sara with very high relative errors, or even completely preventing its determination.

In an attempt to evaluate the possibility to quantify the possible interferences and subtract their values to obtain the concentration of Sb, linear regression of the Sb peaks was attempted. For this, spectra were converted to ASCII format using the Cambio program and Gnuplot was used for the regression fits. The best fits in first determination found for the materials SRM-1515 Apple Leaves, IAEA-SL-1 Trace and Minor Elements in Lake Sediment had five peaks and parabolic background. In the second determination, the best fit for Lake Sediment had six peaks and also parabolic background. For the materials CTA - VTL-2 Viriginia Tobacco Leaves and INCT-TL-1 Tea Leaves, in first determination, the best fit had three peaks and also parabolic background. In second determination, VTL-2 Viriginia Tobacco Leaves was unable to be fitted due to spectral interferences.

Due to ^{76}As interference the results of the materials CTA - VTL-2 Viriginia Tobacco Leaves, IAEA-140/TM Trace Elements and Methylmercury in Seaweed (Focus sp), IAEA-336 Trace and Minor Elements in Lichen and SRM-1633b Constituent Elements in Coal Fly Ash presented a good agreement for the results of the second measurement. In the second counting, after 15 days decay, in none of the materials, the ^{76}As peak was detected, due to its relatively short half-life of 26.32 hours or because of its low content in the material. In materials SRM 1515 Apple Leaves and SRM-1573a Tomato Leaves, ^{76}As peak was not detected due to spectral interferences of high activity of ^{24}Na or their low levels in the samples.

CONCLUSION

The results indicated the possibility of using neutron activation analysis in the determination of Sb in environmental samples of the reference materials. The best results in the determination of antimony using the radioisotope ^{122}Sb were obtained when the counting is performed with 7 days of decay time and 15 days of decay for ^{124}Sb measurement. The findings show that this accuracy of the determination depends on the decay time used for the counting and the radioisotope considered. It was also verified that three other interfering radioisotopes (^{134}Cs, ^{152}Eu and 1^{94m2}Eu) undermine the determination of the 564 keV peak when counting the samples are carried out after 15 days of decay.

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REFERENCES

1. P. W. Atkins and L. L. Jones, “Antimônio”, in *Princípios de química: questionamento a vida moderna e o meio ambiente*, edited by Companhia Editora Bookman, Porto Alegre, 2001, **01**, pp.873.
2. K. Bencze; H.G. Seiler; A. Sigela; H. Sigel. “Antimony”, in *Handbook on Metals in Climical and Analytical Chemistry*, edited by Marcel Dekker, New York, 1994, pp. 227-236.
3. M. Filella; N. Balzile; Y.W. Chen. Antimony in the environment: a review focused on natural waters. *Earth Sci Rev*, 2002, **57**, pp. 125-176.
4. T. Asami; M. Kubota; Saito, S. Simultaneous determination of antimony and bismuth in soil by continuous hydride generation-atomic absorption spectrometry. *Water Air Soil Pollut*, 1992, **62**, pp. 349-355,.
5. M. Krachle; M. Burow; H. Emons. Development and evaluation of an analytical procedure for the determination of antimony in plant materials by hydride generation atomic absorption spectrometry. *Analyst*, 1999,**124**, pp. 777 - 782.
6. United States Environmental Protection Agency-USEPA. Toxics Release Inventory. Washington, DC, USA. 1999. Doc. 745-R-00-007.
7. Agency for Toxic Substances and Disease Registry - ATSDR. Public Health Assessment Guidance Manual, Public Health Service, US Dept. of Health and Human Services, Atlanta, GA, 1992.
8. P. Bode, “Principles of Instrumental Neutron Activation Analysis”, in *Instrumental and organizational aspects of a neutron activation analysis laboratory*, edited by Interfaculty University of Delft, Netherlands, 1996, **01**, pp.23-42.
9. L.A. Currie. Limits for qualitative detection and quantitative determination. *Analytical Chemistry*. **40**, n. 3, pp. 586-593, 1968.