2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-05-2**

RAPID AND ACCURATE DETERMINATION OF BARIUM BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Maria José A. Armelin[1], Anderson R. Trevizam[2], Vera A. Maihara[1] and Mitiko Saiki[1]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes, 2242
05508-000 São Paulo, SP
marmelin@ipen.br, vmaihara@ipen.br, mitiko@ipen.br

[2] Universidade Estadual do Centro Oeste - UNICENTRO
Rua Camargo Vilela de Sá, 03
85040-080 Guarapuava, PR
aanrt@hotmail.com

ABSTRACT

Barium is an alkaline earth metal naturally present in soils. When available at a high level in the soil it can cause toxicity to plants and animals. Not all the barium is readily available to living organisms. Inorganic and organic barium compounds can be presented as soluble or insoluble forms in the soil. The soluble form of BaS is extremely toxic to humans, animals and plants. Researchers have noted a decrease of K absorption in the plant when Ba concentrations are increased and a change in overall plant growth. In case of animals, Ba tends to be concentrated in the bones which may compete with calcium, although only about 2% barium ingested in dietary is absorbed by the body. Another effect is that the Ba can interfere with the availability of sulfur in the soil due to the sulphate formation of low solubility. Barium and some other elements are considered palioclimatic proxies. For some researchers, barite is perhaps the most appropriate indicator of paleoproductivity because of a high resistance to dissolution. As explained about the barium effects in various situations, it was considered important to study the more appropriated experimental conditions for determination of this element by INAA. Conditions established for this analysis were: a) Irradiation time, 15 and 40 seconds, under thermal flux neutron about 4 x 10^{12} n cm^{-2} s^{-1}, for determining barium in geological and biological matrices, respectively; b) Decay time, approximately of 4 minutes; c) Counting time of 30 minutes; d) Radionuclide measured ^{139}Ba. The quality of Ba results was evaluated from the analysis of certified reference materials. The performance of the method was satisfactory, according to the criterion of E_n score. Results obtained in this study indicate INAA is a good alternative for Ba determination in geological and biological samples.

1. INTRODUCTION

Barium is an alkaline earth metal naturally present in soils. When available at a high level in the soil it can cause toxicity to plants and animals. Not all the Ba is readily available to living organisms. Barium is present in different forms in the soil: soluble, insoluble, inorganic and organic. The soluble form of BaS is extremely toxic to humans, animals and plants [1]. Suwa et al. [1] investigated the phytotoxicity of Ba (at 100, 1000 and 5000 µM Ba) in soybean plants, under hydroponic culture conditions. It was noticed a decrease in the absorption of K in the plant at all concentrations tested and change in overall plant growth. In case of animals, barium tends to be concentrated in the bones which may compete with calcium, although only about 2% barium ingested in dietary is absorbed by the body [2]. Another effect is that

the barium can interfere with the availability of sulfur in the soil due to the sulphate formation of low solubility [3,4].

Barium and some other elements are considered palioclimatic proxies. For some researchers [5,6], Barite is perhaps the most appropriate indicator of paleoproductivity because of a high resistance to dissolution.

In view of the importance of knowing the barium concentration in different matrices, the objective of this study was to establish a most suitable experimental conditions for the determination of this element by Instrumental Neutron Activation Analysis (INAA) [7, 8], and its application for the Ba analysis in biological and geological samples.

The analytical parameters that were considered to evaluate the performance of the method were: sensitivity, detection limit and accuracy. Within this context it was also considered how quickly to obtain the results. The accuracy was assessed by analysis of various biological and geological reference materials. Further the method was applied in the analyses of a soya flour sample, used for nutrition of domestic animals, and a sample of marine sediment.

2. EXPERIMENTAL

2.1. Samples Analyzed

The samples used in the experiment were the following certified reference materials, 1) Biologial materials: NIST SRM 1515 Apple Leaves, INCT – MPH-2 Mixed Polish Herbs, NIST SRM 1547 Peach Leaves, NIST SRM 1573a Tomato Leaves with Ba concentrations ranged from 32.5 to 124 μg g^{-1}; 2) Geological materials: NIST SRM 2704 Buffalo River Sediment and IAEA – Soil-7, where the barium concentrations were of 414 and 159 μg g^{-1}, respectively. These materials were used to demonstrate the applicability of INAA for determining barium concentration.

The following samples with unknown content barium were analyzed: soya flour, from of Southeast Embrapa Cattle, São Carlos-SP, used in the nutrition of domestic animals and, marine sediment provided by the Oceanographic Institute of São Paulo University (IO/USP). These samples were with granulometry suitable for analysis.

As biological materials tend to absorb moisture, aliquot of approximately 200 mg of each biological material was placed in an oven at 100°C for 24 hours. The moisture content obtained via this procedure was used to correct for dry weight.

2.2. Instrumental Neutron Activation Analysis (INAA)

Aliquots of approximately 130 mg of the biological material and about 50 mg of geological materials were transferred to polyethylene bags, which had been cleaned by leaching with a diluted HNO_3 (1:5) and purified water.

Barium certified standard solution (Spex Certiprep) was used to prepare the standard. Aliquots (25 µL) were transferred to small sheets of analytical filter paper (Whatman Nº 42). After its drying, these sheets were placed into polyethylene bags.

Irradiations were carried out at the IEA-R1 nuclear research reactor of IPEN-CNEN/SP through a pneumatic transfer system. The thermal neutron flux utilized was about 4×10^{12} n cm^{-2} s^{-1}. Sample and Ba standard were irradiated together in a polyethylene container for 40 s, in case of biological matrices, and 15 s in case of geological ones. After a decay time of 4 min the ^{139}Ba was measured in the standard, for 5 min, and in the sample for 25 min. The nuclear characteristics of reaction (n,ɣ) for forming the ^{139}Ba are shown in Table 1. The equipment used to measure the gamma-radiation was a model GX2020 hyperpure Ge detector, coupled to a model 1510 Integrated Signal Processor and MCA System 100, both from Canberra. The detector used had a resolution (FWHM) of 0.9 keV for 122 keV gamma rays of ^{57}Co and 1.9 keV for 1332 keV gamma-ray of ^{60}Co.

Table 1: Nuclear characteristics of reaction (n,ɣ) for forming the ^{139}Ba [9]

	Parameters						
	Stable isotope	Isotopic abundance	Nuclear reaction	Cross section	Isotope produced	Half - life	Energy ɣ
Unit	-	%	-	Millibarns	-	min	keV
Description	^{138}Ba	71.66	(n,ɣ)	380.00	^{139}Ba	82.90	165.85

3. RESULTS AND DISCUSSION

3.1. Sensitivity and Detection Limit

Barium sensitivity and detection limit of INAA obtained, under the experimental conditions applied in this study, are shown in Table 2. The detection limit was determined according to the IUPAC definition [10], the background radiation and the time of measurement are considered. The value of the background radiation was obtained directly from data issued in the gamma spectrum of the sample, for the photopeak of barium. In this case, the time of irradiation, decay and measurement as well as, interference situation and Compton continuum of gamma ray energies can influence the values of detection limit. For this reason, the values shown in Table 2 vary with different materials.

Table 2. Barium sensitivity and detection limit of INAA

Type of Matrices	Sensitivity (Signal[a] μg^{-1})	Detection Limit[b] ($\mu g\ g^{-1}$)
Biological	0.3	4 – 13
Geological	0.1	22 – 35
a.Signal=counts per second (cps) for INAA; b.Range for detection limits of the materials analyzed		

3.1. Barium Concentrations Obtained for the Certified Reference Materials

The method validation was carried out from the analysis of various biological and geological reference materials. Table 3 shows the obtained and certified values of barium concentration, as well the results of E_n score, for each material. The criterion for performance evaluation of the method considering E_n score is as follows:

If $|E_n| \leq 1$ the performance of the method is satisfactory
If $|E_n| > 1$ the performance of the method is unsatisfactory

Based on E_n values presented in Table 3, the performance of INAA for determining barium was quite satisfactory.

Table 3. Obtained and certified values for the reference materials

Reference Material	Ba concentration in μg g^{-1}		
	Obtained[a]	Certified[b]	E_n Score[d]
NIST - 1515 Apple Leaves	49.4 ± 5.6	49 ± 2	0.06
INCT – MPH-2 Mixed Polish Herbs	36.5 ± 3.9	32.5 ± 2.5	0.86
NIST – 1547 Peach Leaves	124.5 ± 11.4	124 ± 4	0.04
NIST – 1573a Tomato Leaves	65.6 ± 5.4	63[c]	0.34
NIST – 2704 Buffalo River sediment	488.7 ± 93.7	414 ± 12	0.79
IAEA – Soil-7	176.7 ± 33.4	159[c]	0.50

a. mean values and confidence interval at 95 % for n = 5;
b. certified values with its expanded uncertainties informed in the certificate;
c. uncertainties calculated using the modified Horwitz equation, $\sigma = 0.02c^{0.8495}$, if $1.2 \times 10^{-7} \leq c \leq 0.138$ [11,12] from the "informative value" supplied by the producer.
d. E_n score was calculated from the following equation: $E_n = (x_{obt} - x_{ref})/\sqrt{u_{obt}^2 + u_{ref}^2}$ [13].

Barium concentrations obtained in a sample of soya flour and a sample of marine sediment are shown in Table 4. Each value is the result of one determination with its uncertainty evaluated using statistical counting errors. The uncertainty of statistical counting is affected by the low sensitivity of the method and by the low concentration of barium, especially in the sample of soya flour.

Table 4. Barium concentrations (μg g^{-1}) in soya flour and marine sediment, with its uncertainties in parentheses

Determ. N°	Soy flour		Marine sediment	
1	8.8	(1.4)	517	(59)
2	11.0	(1.9)	590	(70)
3	11.1	(1.9)	455	(50)

Based on the following considerations: a) value of prevention to barium in soil is 150 $mg.kg^{-1}$, according to the criteria of CONAMA-2009 [14]; b) the results of Table 3; c) the experimental conditions applied in this study, INAA can be considered an efficient and rapid method for the determination of barium in biological and geological matrices.

4. CONCLUSION

The results obtained in the present study indicated that INAA proved to be a good alternative for Ba determination in geological and biological samples, in a wide range of concentration. Besides this, it is also possible to obtain Ba concentration results in approximately 40 minutes.

ACKNOWLEDGMENTS

The authors wish to thank CNEN, CNPq and FAPESP from Brazil for financial support.

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