NEUTRON ACTIVATION ANALYSIS APPLIED TO THE DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES AT IPEN-CNEN/SP

A.M.G. FIGUEIREDO; D.I.T. FÁVARO; C. GONÇALVES, R. P. PAIVA
Instituto de Pesquisas Energéticas e Nucleares - CNEN/SP
Caixa Postal 11049 - CEP 05422-970 - São Paulo - SP - Brasil

INTRODUCTION

Neutron activation analysis (NAA) is particularly useful for environmental studies. It affords low detection limits for many elements, providing accurate and precise results. Its main advantages are: high specificity, few sources of systematic errors, multi-element capability, absence or minimization of the blank and analysis of samples up to a few grams.

NAA is particularly useful for trace and ultra-trace analysis and, in the purely instrumental mode, allows the determination of about 30 elements in environmental samples (Salbu and Steinnes, 1992; Kolesov, 1995). Multi-element analysis of compartments of the ecosystem as soils, rocks, sediments, plants and airbone particulate matter can provide informations for environmental problems (Presley et al., 1980, Markert and Wtorova, 1992).

Researches concerning environmental geochemistry are very recent at the Radiochemistry Division of IPEN-CNEN/SP. INAA was applied to the determination of As, Cr, Hg, Sb and Zn. in sediments of São João de Meriti estuary, in Guanabara bay system (Figueiredo et al., 1994) and in sediments from the region of Serra do Navio, Amapá (Fávaro et al., 1995). INAA was also employed to the detemination of rare earth elements in soil and plants of the alkaline-ultramafic complex of Salitre (Ceccantini et al., 1995). The reliable results obtained provided valuable informations about the geochemical behaviour of the analysed elements in the studied ecosystems.

The aim of the present work is to present the possibilities of INAA at IPEN-CNEN/SP for the determination of several trace elements in environmental samples. For this purpose, the results obtained for reference materials of sediment, plant, soil and air particulates are presented, and the precision, accuracy and detection limits of the method are evaluated.

EXPERIMENTAL

Standard solutions of the analysed elements were prepared by using specpure reagents. A convenient aliquot of each standard solution was pipetted onto a 1 cm^2 piece of Whatman No. 40 filter-paper, evaporated to dryness and packed in a polyethylene vial. In the particular case of Hg, a solution of thioacetamide (2 mg/mL) was first pipetted onto the filter-paper, to avoid volatilization of Hg during irradiation. The certified reference materials JB-1 (GSJ), GS-N and BE-N (IWG) were used as secondary standards.

The reference materials analysed were: Buffalo River Sediment (NIST 2704), Citrus Leaves (NIST 1572), Soil-7 (AIEA) and Urban Particulate Matter (NBS 1648). The reference materials were not submitted to any pre-treatment, since they were already powdered.

Irradiation was carried out at the IEA-R1 nuclear reactor of the IPEN-CNEN/SP. Aliquots of 100-200 mg of the reference materials were weighed in pre-cleaned polyethylene vials and placed, with the chemical standards, inside aluminium irradiation vessels, for long irradiations (8 to 16 hours), or in polyethylene vessels, for short irradiation (1 to 30 min). Samples and standards were irradiated at a thermal neutron flux of about 10^{12} n cm^{-2} s^{-1}.

The measurements of the induced gamma-ray activity were carried out in an hyper-pure Ge detector (EG&G ORTEC), connected to a multichannel analyser and to a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma ray of ^{60}Co. The gamma ray spectra were processed by using the program VISPECT, developed at IPEN by Piccot (1989), from Saclay, France. This program locates peak positions and calculate gamma ray energies and net areas.

Two series of counting were performed, the first one about five days after irradiation, and the second one after a cooling time of about 15 days. The counting times were of about 2 hours in the first series and about 10 hours in the second one

RESULTS

The results obtained for the reference materials analysed and also the certified values and the detection limits for the analytical conditions employed, are presented at Table 1. The reproducibility of the method was tested by replicate analysis, and the errors associated with the data represent one standard deviation.

For Buffalo River Sediment, Soil-7 and Urban Particulate Matter, the obtained data agreeded with the certified values, showing relative errors between 0 to 10%, and good precision (average standard deviation less than 15%).

For the reference material Citrus Leaves, the results obtained showed good agreement with certified values (relative errors from 0 to 15%) and good precision (less tan 20%). In the case of Lu, the data presented less precision due to the very low concentration of this elements in the analysed samples.

It can be seen that the detection limits achieved are adequate to determine trace elements in the analysed matrices, most of them less than 1 $\mu g\ g^{-1}$. For some elements, the detection limit changed according to the sample, which is due to spectral interferences of elements present in the matrix.

The results obtained showed appropriate accuracy and precision of the method for multi-element analysis, indicating good possibilities for environmental studies.

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Results obtained for the reference materials Buffalo River Sediment (NIST 2704), Citrus Leaves (NIST 1572), Soil 7 (AIEA) and Urban Particulate Matter (NBS 1648) ($\mu g\ g^{-1}$). Number of determinations (n) = 4. DL = Detection Limit

Element	Buffalo River Sedim. This work	Certified Values (NIST, 1990)	DL ($\mu g\ g^{-1}$)	Citrus Leaves This Work	Certified Values (NIST, 1982)	DL ($\mu g\ g^{-1}$)	Soil 7 This Work	Certified Values (AIEA, 1990)	DL ($\mu g\ g^{-1}$)	Urban Part. Matter This Work	Certified values (NBS, 1972)	DL ($\mu g\ g^{-1}$)
As	23.2 ± 0.8	23.4 ± 0.8	1.4	3.02 ± 0.02	3.1 ± 0.3	0.021	13.7 ± 0.8	13.4 ± 0.8	0.33	114.5 ± 0.7	115 ± 10	0.4
Ca (%)	---	2.60± 0.03	---	3.21 ± 0.18	3.15 ± 0.1	180	---	---	---	5.54 ± 0.37	---	3300
Cd	---	3.45±0.22	---	---	---	---	---	---	---	75 ± 5	75 ± 7	7
Co	12.5±0.1	14.0±0.6	0.02	---	---	---	8.2 ± 0.3	8.9±0.8	0.09	17.4 ± 1.1	(18)	0.2
Cr	135 ± 1	135 ± 5	1.9	0.74 ± 0.05	0.8 ± 0.2	0.11	63 ± 2	60±12	0.90	370 ± 24	403 ± 12	2.5
Fe (%)	3.76±0.07	4.11±0.10	23	90 ±2($\mu g\ g^{-1}$)	90 ± 10	2.2	2.6 ± 0.2	2.57	85	3.76 ± 0.08	3.91 ± 0.10	200
Hg	1.44 ±0.09	1.47± 0.07	0.32	0.07 ± 0.01	0.08 ± 0.02	0.05	---	0.04	---	---	---	---
Mn	---	555±19	---	---	---	---	---	631± 22	---	778 ± 68	(860)	1.6
Na	5396±81	5470±140	39	156 ± 16	160 ± 20	0.36	---	2400	---	4000 ± 200	4250 ± 20	121
Rb	91± 4	100	5.9	4.8 ± 0.3	4.84 ± 0.06	0.3	46 ± 2	51 ± 4	2.6	48 ± 5	(52)	8
Sb	3.77 ±0.06	3.79 ±0.15	0.082	46 ±3(ng g^{-1})	(40)	0.005	1.63 ± 0.07	1.7 ± 0.2	0.14	44.5 ± 1.5	(45)	1.5
Sc	10.8±0.01	12	0.027	---	---	---	8.04 ± 0.09	8.3 ± 0.1	0.012	6.4 ± 0.2	(7)	0.1
Se	---	1.12±0.05		---	---	---	---	0.4	---	31 ± 2	27 ± 1	1.5
Th				---	---	---	---	8.2 ± 1.1	---	6.4 ± 0.5	(7.4)	0.2
V				---	---	---	---	66 ± 7	---	128 ± 7	140 ± 3	4
Zn	476 ± 5	438 ± 12	0.3	28.3 ± 0.3	29 ± 2	0.14	---	104 ± 6	---	4600 ± 200	4760 ± 140	13
La	23.4±0.3	(29)	0.06	0.16 ± 0.01	0.19	0.003	29.3 ± 0.6	28 ± 1	0.15	33.4 ± 0.4	(42)	0.2
Ce	---	(72)	---	0.31 ± 0.03	0.28	0.02	---	61 ± 7	---	42 ± 4	(55)	0.8
Nd	20.0±0.9	---	6	0.15 ± 0.03	(0.16)	0.08	33 ± 3	30 ± 6	1.7	---	---	---
Sm	4.9±0.1	6.7	0.014	0.060± 0.009	(0.052)	0.0009	5.1 ± 0.1	5.1± 0.3	0.013	3.9 ± 0.5	(4.4)	0.02
Eu	1.25±0.01	(1.3)	0.097	0.010± 0.001	0.009	0.0007	---	1.0 ± 0.2	---	0.80 ± 0.05	(0.8)	0.08
Tb	0.90±0.02	---	0.23	0.010± 0.001	0.010	0.0040	0.66 ± 0.05	0.6 ± 0.2	0.10	---	---	---
Yb	2.91±0.03	(2.8)	0.15	0.024± 0.003	0.027	0.0045	2.37 ± 0.08	2.4 ± 0.4	0.054	---	---	---
Lu	0.58±0.01	(0.6)	0.015	0.003± 0.001	0.004	0.0006	---	(0.3)	---	---	---	---