NEUTRON ACTIVATION ANALYSIS APPLIED TO THE DETERMINATION OF HEAVY METALS AND OTHER ELEMENTS OF INTEREST IN SEDIMENTS FROM SEPETIBA BAY, RIO DE JANEIRO, BRAZIL.

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ABSTRACT

Neutron activation analysis was applied to the determination of As, Co, Cr, Fe, Hf, Rb, Sb, Sc, Se, Zn and rare earths La, Ce, Nd, Sm, Eu, Tb , Yb and Lu in a mangrove core sediment from Sepetiba bay, Rio de Janeiro, Brazil. Analysis of the reference material Buffalo River Sediment showed the accuracy and precision of the method. The results obtained for Cr, Fe and Zn were compared to previous values presented for this region.

INTRODUCTION

Nowadays, pollution of aquatic systems by heavy metals and other elements from industries and other activities of modern human life, results in a modification of natural geochemistry cycle of these elements, increasing their dispersion in the environment. The study of coastal areas affected by the discharge of wastes, mainly estuaries of tropical region, have become of great interest, due to their high degree of degradation and the little knowledge of these areas. The analysis of sediments has been widely used to assess the quality of aquatic environments concerning heavy metals concentration.

Sepetiba bay is a 519 km^2 semi-enclosed bay, 60 km SE from the city of Rio de Janeiro, Brazil. During the last years, it has been submitted to an increasing industrial growth, that provides the bay with high loads of pollutants, specially heavy metals. Although several studies concerning heavy metal distribution have been done in Sepetiba bay in recent years [1,2], few information are available about the behavior and concentration of other elements. Neutron activation analysis is a powerful tool to provide information about trace elements levels, due to its high accuracy and sensitivity. It has the advantage of not requiring the chemical dissolution of the sample and of using only few miligrams for analysis (100 to 500 mg).

Neutron activation analysis was applied to the determination of the metals (Co, Cr, Fe, Hf, Rb, Sc, Zn), rare earths (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu), non-metals and semi-metals (As, Sb and Se), in core sediments of Sepetiba bay. The accuracy and precision of the method employed were evaluated by the analysis of the reference material Buffalo River Sediment (NIST SRM-2704).

MATERIAL AND METHODS

Sampling

One 30 cm sediment core was collected in an intertidal zone, between the trees, in a fringe mangrove area, in the NE coast of Sepetiba bay. The core was sliced each 3 cm in the field and stored at 4^0 C. The fine grain fraction (< 63μm) was separated by wet sieving and dried for neutron activation analysis.

Neutron Activation Analysis

About 100 mg of the samples and of Buffalo River reference material were accurately weighed in pre-cleaned polyethylene bags. Aliquots of standard solutions of the analyzed elements were pipetted onto pieces of Whatman filter paper. Samples and standards were irradiated for 16 hours at the IEA-R1 nuclear reactor, under a thermal neutron flux of 10^{12} n $cm^{-2}s^{-1}$. After irradiation, samples and standards were allowed to decay from about 5 days up to 15 days.

The gamma-ray activities were measured in a gamma spectrometer consisting of a hyperpure Ge detector (CANBERRA model GX20190). The multichannel analyser was a 8192 channel Canberra S-100

plug-in-card in a PC computer. Gamma-ray spectra were processed by using a in-house gamma-ray software which locates peak positions and calculates the energies and net areas.

RESULTS AND DISCUSSION

The results obtained for the Buffalo River Sediment reference material and also the certified values and detection limits are presented in Table 1. The reproducibility of the method was verified by replicate analysis, and the errors associated with the data represent one standard deviation. The obtained data agreed with the certified values, showing relative errors between 0 to 10% and good precision (average standard deviation less than 15%). It can be seen that the detection limits achieved are adequate to determine trace elements in the analyzed samples.

Table 2 shows the results obtained for the analysis of sediment samples from Sepetiba bay. These are preliminary results from one sampling site and other samples are being analyzed in order to get more information about this region. It can be observed that there is no significative difference in the concentration values with depth for the elements As Sb, Rb, and Sc. The rare earth elements, Hf and Zn present decreasing concentrations with depth. The average values presented by Leitão Filho et al [1], for Cr and Fe in bottom sediments from Sepetiba bay, agreed with the results obtained in the present work (Cr=56.8 $\mu g\ g^{-1}$; Fe=4.0%). For Zn, the average value (588.8 $\mu g\ g^{-1}$) was higher than our value (Zn $\cong$ 300$\mu g\ g^{-1}$). Dornelles [2] analyzed Cr and Zn in bottom sediments from different sites of Sepetiba bay, and found a concentration range of 3.4 to 52.3 $\mu g\ g^{-1}$ for Cr, and of 21.8 to 970.0 $\mu g\ g^{-1}$ for Zn. There is no information about the concentration of the other elements analyzed and the presented values are a contribution to the study of behavior and distribution of trace elements in the Sepetiba bay.

Table 1. Results obtained ($\mu g\ g^{-1}$) for the reference material Buffalo River Sediment (NIST 2704). (DL = Detection Limit).

Element	Buffalo River Sedim.	Certified Values	DL ($\mu g\ g^{-1}$)	Element	Buffalo River Sedim.	Certified Values	DL ($\mu g\ g^{-1}$)
As	23.2 ± 0.8	23.4 ± 0.8	1.4	La	23.4±0.3	(29)	0.06
Co	12.5±0.1	14.0±0.6	0.02	Ce	—	(72)	—
Cr	135 ± 1	135 ± 5	1.9	Nd	20.0±0.9	—	6
Fe (%)	3.76±0.07	4.11±0.10	23	Sm	4.9±0.1	6.7	0.014
Hg	1.44 ±0.09	1.47± 0.07	0.32	Eu	1.25±0.01	(1.3)	0.097
Rb	91± 4	100	5.9	Tb	0.90±0.02	---	0.23
Sb	3.77 ±0.06	3.79 ±0.15	0.082	Yb	2.91±0.03	(2.8)	0.15
Sc	10.8±0.01	12	0.027	Lu	0.58±0.01	(0.6)	0.015
Zn	476 ± 5	438 ± 12	0.3				

REFERENCES

[1] Leitão Filho, C.M.; Silva Filho, E.V.; Wasserman, J.C.; Patchineelam, S.R. (1995). Anais do V Congresso Brasileiro de Geoquímica / III Congresso de Geoquímica dos Países de Lingua Portuguesa, Niterói, R.J. (em CD ROM)

[2] Dornelles, L.M.A. (1997). Actas X Semana de Geoquímica / IV Congresso de Geoquímica dos Países de Língua Portuguesa, Braga, Portugal, 435-438.

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Element	TA	TB	TC	TD	TE	TF	TG	TH	TI	TJ
As	11.0 ± 0.3	16.7 ± 0.5	12.0 ± 0.7	9.4 ± 0.1	16.8 ± 0.1	11.5 ± 0.1	12.5 ± 0.5	13.6 ± 0.5	8.9 ± 0.7	11.4 ± 0.4
Ce	284 ± 1	243 ± 1	212 ± 1	214 ± 2	195 ± 5	189 ± 2	137 ± 3	129 ± 3	169 ± 2	187 ± 2
Co	9.6 ± 0.1	10..3 ± 0.1	9.76 ± 0.04	9.01 ± 0.03	10.53 ± 0.04	10.18 ± 0.04	9.5 ± 0.8	10 ± 1	9.2 ± 1.8	11.7 ± 0.1
Cr	60.5 ± 0.3	65.1 ± 0.3	63.2 ± 0.2	59.1 ± 0.3	57.8 ± 0.9	55.4 ± 0.9	53 ± 5	62 ± 6	65 ± 9	71 ± 7
Eu	1.74 ± 0.09	1.8 ± 0.1	1.59 ± 0.01	1.9 ± 0.4	1.5 ± 0.1	1.5 ± 0.1	1.35 ± 0.08	1.37 ± 0.08	1.52 ± 0.05	1.6 ± 0.1
Fe (%)	3.87 ± 0.01	4.41 ± 0.01	4.10 ± 0.01	3.80 ± 0.01	4.43 ± 0.01	4.1 ± 0.1	3.7 ± 0.5	4.0 ± 0.6	4.13± 0.01	4.30 ± 0.04
Hf	42.6 ± 0.9	30 ± 2	25 ± 2	30 ± 2	22.7 ± 0.1	22.3 ± 0.1	18.0 ± 0.3	14.5 ± 0.4	15.6 ± 0.9	16 ± 1
La	109 ± 1	95.3 ± 0.7	84.0± 0.1	75.7 ± 0.6	75 ± 8	63 ± 9	50 ± 5	48 ± 6	54 ± 9	64 ± 5
Lu	1.16 ± 0.02	0.72 ± 0.01	0.69 ± 0.02	0.73 ± 0.02	0.72 ± 0.01	0.43 ± 0.04	0.54 ± 0.04	0.35 ± 0.01	0.43 ± 0.09	0.45 ± 0.09
Nd	—	—	—	—	52 ± 3	42 ± 2	40 ± 2	36 ± 2	33 ± 3	44 ± 3
Rb	87 ± 1	93 ± 1	91 ± 1	—	100 ± 5	91 ± 6	92 ± 4	99.0 ±0.5	92 ± 5	107 ± 6
Sb	0.48 ± 0.03	0.47 ±0.03	0.45 ± 0.03	0.38 ± 0.01	—	0.46 ± 0.03	0.50 ± 0.01	—	0.45 ± 0.04	0.46 ± 0.04
Sc	11.1 ± 0.1	11.2 ± 0.1	11.6 ± 0.2	—	11.2 ± 0.8	10.9 ± 0.8	10.2 ± 0.9	11 ± 1	12 ± 1	13 ± 2
Se	1.31 ± 0.08	1.12 ± 0.08	1.18 ± 0.08	1.09 ± 0.07	1.2 ± 0.1	1.16 ± 0.09	1.3 ± 0.3	1.3 ± 0.3	2.0 ± 0.3	—
Sm	17.8 ± 0.2	15.6 ± 0.2	13.3 ± 0.2	12.4 ± 0.5	10.3 ± 0.9	9.0 ± 0.9	10.0 ±0.2	6.4 ± 0.6	10 ± 1	10 ± 1
Tb	—	—	—	—	1.20± 0.02	1.21± 0.02	0.97± 0.02	0.96± 0.02	1.13± 0.08	1.00± 0.08
Yb	5.5 ± 0.3	3.2 ± 0.3	3.0 ± 0.1	3.5 ± 0.1	3.5 ± 0.2	3.3 ± 0.1	2.8 ± 0.2	2.7 ± 0.2	2.5 ± 0.1	2.4 ± 0.1
Zn	262 ± 1	296 ± 1	308 ± 1	189 ± 1	255 ± 1	267 ± 1	109 ± 6	133 ± 8	223 ± 33	156 ± 23

Table 2. Concentration of heavy metals and other trace elements in sediment samples from Sepetiba bay, Rio de Janeiro by neutron activation analysis (μ g g^{-1})