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INAA of trace elements in biological materials using the SLOWPOKE-2 reactor in Jamaica

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The biological standard reference materials Orchard Leaves SRM 1571 and Oyster Tissue SRM 1566a was analysed by instrumental neutron activation analysis (INAA) at the International Centre for Environmental and Nuclear Sciences, Jamaica at (ICEN) and at the Instituto de Pesquisas Energeticas e Nucleares (IPEN-CNEN/SP), Brazil. The comparison of the results with those obtained with the more powerful reactor are used to evaluate the possibilities of INAA for the analysis of biological samples at ICENS. The detection limits, the precision and accuracy of the results obtained in both laboratories are compared. The advantages and disadvantages of the different irradiation facilities are discussed. Some results obtained for Jamaican biological samples are also presented.

Introduction

SLOWPOKE reactors have been widely used for the analysis of geological samples by INAA, giving accurate results for several trace elements in rocks and soils.[1,2] In Jamaica, INAA with a SLOWPOKE-2 reactor has been extensively used at the International Centre for Environmental and Nuclear Sciences (ICENS) for multipurpose geochemical surveys of soils, sediments and rocks.[3]

Currently, there is an increasing interest in obtaining information on trace elements in plant, animal and human tissues to support nutrition and health-related studies. More and more researchers use different species of plants and animals as biomonitors for environmental pollution, providing important information for control and evaluation of environmental problems.

Although substantial work has been done on epiphytic plants in Jamaica,[4] little is known about trace metals in the biological materials of the country. This study represents a beginning of biomonitoring the environmental status in Jamaica using INAA.

In this study, the trace element concentrations in plant (Orchard Leaves SRM 1571) and animal (Oyster Tissue SRM 1566a) standard reference materials were determined by INAA using the irradiation facilities at ICENS, Jamaica, and at the Instituto de Pesquisas Energeticas e Nucleares (IPEN-CNEN/SP), Brazil. The aim of the study was to compare the results of INAA using the SLOWPOKE-2 reactor in Jamaica with those obtained with the higher flux reactor in Brazil.

As an application example, three typical biological materials from Jamaica, yellow yam, an epiphytic plant *Tillandsia recuvrata* and freshwater snails *Melanoides tuberculata* were analysed at ICENS. Yam was chosen because it is a common food in Jamaica, while the epiphytic plants and the freshwater snails are suitable for biomonitoring of the atmospheric and freshwater environment in Jamaica.

Experimental

Samples and standards preparation

The yellow yam sample was peeled, oven dried at 45 °C for 72 hours and ground using agate mortar. The epiphytic *Tillandsia recuvrata* was rinsed with distilled water for less than 15 seconds to remove the adhering dust, dried at 45 °C and ground using liquid nitrogen. The snails were frozen at –23 °C to facilitate the separation of the shells. The soft tissue was then oven dried at 45 °C and ground.

Approximately 200 mg of sample was accurately weighed and sealed in pre-cleaned double polyethylene bags for short and long irradiations at IPEN. At ICENS, short irradiations were carried out using 400 mg of sample sealed in double polyethylene bags, while for long irradiations approximately 1000 mg of sample was packed in 1.5cc polyethylene capsules to obtain improved counting statistics, since the irradiation time at SLOWPOKE-2 in Jamaica was limited to 4 hours.

The standard reference materials were dried for 2 hours at 85 °C for moisture determination and prepared in the same way as the samples. Single and multi-element comparator standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No. 41 filter paper, which were packed in 25×25 mm polyethylene bags for irradiation.

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Irradiation and counting

ICENS: The standard reference materials and artificial standards were placed in polyethylene capsules for irradiation. The SLOWPOKE-2 reactor in Jamaica has only 3 in-core irradiation sites, with each in-core site being able to accommodate 2 capsules, allowing a set of 6 samples to be irradiated each time. For the determination of the short-lived radioisotopes, a five minute irradiation, at a neutron flux of $5 \cdot 10^{11}$ n·cm^{-2}·s^{-1} was used. After a decay time of approximately five minutes, samples and standards were counted for five minutes on a EG&G Ortec Gamma X hyperpure Ge detector, with a resolution of 1.90 keV for the peak of 1332 keV of ^{60}Co, with a 15% efficiency. For the determination of the long-lived radioisotopes, samples and standards were irradiated for 4 hours, at a neutron flux of $1 \cdot 10^{12}$ n·cm^{-2}·s^{-1}. After decay times of 4 days and 10 days, the samples were measured for 2 and up to 10 hours, respectively on a Canberra Reverse Electrode Ge detector, with a resolution of 1.90 keV for the peak of 1332 keV of ^{60}Co.

IPEN: Standard reference materials were irradiated together with the comparator standards, in the IEA-R1m reactor, for 3 minutes, at a neutron flux of $5 \cdot 10^{11}$ n·cm^{-2}·s^{-1}, and for 8 hours at a neutron flux of $5 \cdot 10^{12}$ n·cm^{-2}·s^{-1}. For the short irradiation, after a decay time of approximately five minutes, samples were counted for about five minutes. For long irradiation, two series of counting were made: the first after a decay of about 5 days and the second after about 15 days. The time of counting was about 3 h (first count) and 5 to 10 h (second count). The gamma-ray spectrometer used was a GEM 20190 EG&G Ortec POP TOP hyperpure detector and associated electronics, with a resolution of 1.90 keV for the peak of 1332 keV of ^{60}Co.

Data processing

Gamma-ray spectrum analysis and quantification were done using the software packages currently used at both laboratories, and the results were compared. In ICENS, the DOS based EG&G Ortec's OMNIGAM package and the Windows 95 package WinRay[5] were used, while at IPEN the VISPECT package and ESPECTRO programs were used to locate the gamma-ray peaks and calculate the concentrations.

Results and discussion

The results obtained for Orchard Leaves SRM 1571, Bovine Liver SRM and Oyster Tissue SRM, at ICENS and at IPEN, as well as certified and information values are presented in Table 1. It can be seen that the results obtained at ICENS for the analysed elements were, in general, in good agreement with certified or information values (relative errors less than 20%).

Table 1. Results obtained for Orchard Leaves SRM 1571 and Oyster Tissue SRM 1566a (in μg·g^{-1}, except otherwise noted)

Element	Orchard Leaves			Oyster Tissue		
	ICENS	IPEN	Literature values	ICENS	IPEN	Literature values
As, ng·g^{-1}	8.51 ± 0.96	10.3 ± 0.3	10 ± 2	11.9 ± 0.2	11.8 ± 0.2	14.0 ± 1.2
Ba, μg·g^{-1}	37.3 ± 3.8	44 ± 3	(44)	–	–	–
Br, μg·g^{-1}	8.9 ± 0.1	7.10 ± 0.07	(10)	40 ± 1	54.0 ± 0.5	–
Ca, %	2.27 ± 0.07	1.74 ± 0.08	2.09 ± 0.03	0.207 ± 0.054	0.183 ± 0.024	0.196 ± 0.012
Cl, μg·g^{-1}	0.766 ± 0.019	0.657 ± 0.04	(0.690)	8028 ± 182	8146 ± 125	8290 ± 140
Co, μg·g^{-1}	0.162 ± 0.022	0.183 ± 0.02	(0.2)	0.51 ± 0.07	0.604 ± 0.008	0.57 ± 0.11
Cr, μg·g^{-1}	2.3 ± 0.3	2.00 ± 0.002	2.6 ± 0.3	1.57 ± 0.42	1.31 ± 0.04	1.43 ± 0.46
Fe, μg·g^{-1}	236 ± 28	277 ± 7	300 ± 20	609 ± 200	480 ± 10	539 ± 15
K, %	1.45 ± 0.06	1.46 ± 0.09	1.47 ± 0.03	0.740 ± 0.300	0.692 ± 0.097	0.790 ± 0.047
Mg, μg·g^{-1}	0.57 ± 0.07	0.63 ± 0.05	0.62 ± 0.02	1380 ± 246	1219 ± 192	1180 ± 170
Mn, μg·g^{-1}	95 ± 10	85 ± 2	91 ± 4	13.6 ± 1.6	11.5 ± 0.6	12.3 ± 1.5
Mo, μg·g^{-1}	0.25 ± 0.03	0.43 ± 0.06	0.3 ± 0.1	4.74 ± 0.06	5.82 ± 0.07	–
Na, μg·g^{-1}	108 ± 13	76 ± 6	82 ± 6	3940 ± 178	3546 ± 68	4170 ± 130
Rb, μg·g^{-1}	9.7 ± 0.8	11.2 ± 0.4	12 ± 1	2.9 ± 0.8	2.8 ± 0.2	(3)
Sc, μg·g^{-1}	54 ± 3	64 ± 1	–	58 ± 6	55.2 ± 0.5	(60)
Th, μg·g^{-1}	51 ± 5	42 ± 4	64 ± 6	49 ± 8	37.8 ± 2.7	(40)
Zn, μg·g^{-1}	20 ± 2	22.5 ± 0.1	25 ± 3	720 ± 42	748 ± 14	830 ± 57
La, μg·g^{-1}	0.92 ± 0.01	1.00 ± 0.05	(1)	208 ± 24	266 ± 14	(300) ng/g
Ce, μg·g^{-1}	0.80 ± 0.05	1.24 ± 0.08	(0.9)	297 ± 83	344 ± 31	(400) ng/g
Nd, μg·g^{-1}	0.57 ± 0.01	0.62 ± 0.09	(0.57)	–	–	–
Sm, μg·g^{-1}	0.083 ± 0.004	0.12 ± 0.01	(0.1)	51.4 ± 1.4	59 ± 4	60 ng/g
Eu, μg·g^{-1}	0.020 ± 0.007	0.015 ± 0.001	(0.021)	28 ± 11	11.3 ± 0.7	(10)
Yb, μg·g^{-1}	0.024 ± 0.005	0.015 ± 0.001	(0.025)	65 ± 25	–	–
V, μg·g^{-1}	–	–	–	5.4 ± 0.3	4.0 ± 0.2	4.68 ± 0.15

The relative standard deviations obtained at ICENS for Ca, Cr, Fe, K, Rb, Ce and Yb in Oyster Tissue were about two times higher than those in Orchard Leaves. This can be attributed to the oysters matrixes contributing to the higher background levels and poor detection limits. At IPEN, most of the analysed elements were determined with an accuracy and precision better than 15%.

It is important to notice that the elements that give short-lived radioisotopes by neutron activation analysis, such as Cl, Mn and Mg, showed the most accurate results. In fact, the limiting point in a SLOWPOKE-2 reactor is not the neutron flux, but the irradiation time, since SLOWPOKE-2 reactors using high enrichment fuels such as the one at ICENS can not be operated continuously for more than 8 hours at full power.[6] On the other hand, the performance of a SLOWPOKE-2 reactor in short irradiations is similar to IPEN's reactor, since the neutron flux is of the same order of magnitude ($1 \cdot 10^{12}$ n·cm^{-2}·s^{-1}). In addition, SLOWPOKE-2 allows the user to perform very short-lived INAA due to its relatively quick sample transfer.

The main advantages of a SLOWPOKE-2 reactor are the low cost and the very stable neutron flux. The latter allows the use of a semi-absolute neutron activation analysis[7] without a standard being irradiated in the same vial, once the counting conditions for samples and standards are the same. Consequently, a database for standards can be developed, keeping the quality control of the data by irradiating in every set of analysis a standard reference material. At IPEN, due to the variations of the rate of thermal and epithermal neutron flux at the IEA-R1 reactor, the use of comparative neutron activation analysis requires the simultaneous irradiation of a standard in every irradiation vial. So, even if a higher number of radioisotopes could be detected, the quantitative determination depends on the availability of a standard.

The detection limits (3σ) obtained for the different samples analysed by using the ICENS and the IPEN facilities are shown in Table 2. For short irradiations, when the fluxes, irradiation and counting times are of the same order of magnitude, the detection limits obtained at ICENS and IPEN arre similar. The lower detection limits obtained at IPEN for the majority of the analysed elements, such as Br, Co, Cr, Fe, Na, Rb, Th, Zn and REEs are due to the higher rector flux and longer irradiation time. For the elements As, K, Sb and Sc, the better sensitivity obtained at ICENS may be attributed to the larger sample size used in the analysis. Although the detection limits achieved at ICENS are, in general, higher than those obtained at IPEN, they are quite adequate for the analysis of biological samples.

The results obtained for Jamaican biological samples are presented in Table 3. These confirm that toxic elements, such as As, Sb and Cd, and many other elements of interest, can be determined in biological matrixes (plant, snail and foodstuff samples) with the SLOWPOKE-2 reactor, with high sensitivity and good precision. This application opens a new field for investigation since such studies are sparse in tropical environment.

Table 2. Detection limits (in $\mu g \cdot g^{-1}$)

Element	Orchard Leaves	
	ICENS	IPEN
As	0.02	0.17
Ba	7	3.5
Br	0.3	0.057
Ca	410	669
Cl	26	41
Co	0.02	0.002
Cr	0.7	0.17
Fe	80	8.5
K	130	787
Mg	47	72
Mn	0.2	0.25
Mo	0.08	0.06
Na	20	1
Rb	1.5	0.35
Sb	0.007	0.023
Sc	0.007	1.2
Se	0.06	0.03
V, ng/g	76	98
Th	0.02	0.006
Zn	3	0.32
La, ng/g	16	6.5
Ce	0.3	0.12
Nd	0.54	0.37
Sm, ng/g	0.7	2
Eu, ng/g	8	2
Yb, ng/g	12	5

Table 3. INAA results obtained in ICENS for selected biological samples (in $\mu g \cdot g^{-1}$)

Element	*Tillandsia recuvrata*	Yellow Yam	*Melanoides tuberculata*
As	1.43 ± 0.06	0.19 ± 0.02	1.61 ± 0.07
Ba	45 ± 2	–	85 ± 2
Br	18.0 ± 0.2	18.0 ± 0.1	0.39 ± 0.01
Cd	0.8 ± 0.1	7.4 ± 1.0	Nd
Ce	2.2 ± 0.4	1.20 ± 0.06	0.82 ± 0.08
Co	1.61 ± 0.09	0.44 ± 0.02	0.70 ± 0.05
Cr	6.5 ± 0.1	1.9 ± 0.1	2.7 ± 0.9
Cs	0.14 ± 0.02	–	0.05 ± 0.01
Eu	0.08 ± 0.01	0.07 ± 0.01	0.02 ± 0.01
Fe	2329 ± 62	460 ± 14	880 ± 21
Hf	0.21 ± 0.02	0.10 ± 0.01	0.08 ± 0.01
K	1172 ± 114	29724 ± 970	4340 ± 338
La	1.82 ± 0.02	0.92 ± 0.02	0.41 ± 0.04
Na	2510 ± 15	201 ± 2	3296 ± 14
Sb	0.44 ± 0.05	–	0.02 ± 0.03
Sc	0.56 ± 0.08	0.22 ± 0.05	0.08 ± 0.01
Se	0.13 ± 0.06	–	1.3 ± 0.3
Sm	0.19 ± 0.02	0.18 ± 0.01	0.05 ± 0.01
Th	0.28 ± 0.01	0.15 ± 0.01	0.09 ± 0.01
U	0.21 ± 0.01	0.10 ± 0.02	–
Yb	0.10 ± 0.01	–	–
Zn	107 ± 5	43 ± 1	62 ± 3

Conclusions

The INAA results using the SLOWPOKE-2 reactor at ICENS show that more than 20 elements can be determined in biological materials. The ICENS results are comparable with those obtained with the higher flux IPEN reactor.

Jamaica is a small developing country, which is vulnerable to environmental problems associated with development. INAA with a SLOWPOKE-2 reactor is a powerful tool that can provide data on the concentration levels of heavy metals and other elements in biological samples, as a contribution to environmental studies.

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