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Neutron activation analysis at the research reactor center of IPEN/CNEN-SP- biological and environmental applications

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The Research Reactor Center (CRPQ) of IPEN/CNEN-SP operates the IEA-R1 Research Reactor, at a nominal power of 2 MW thermal, on a 64 hour per week continuous cycle. The IEA-R1 is a pool type reactor, moderated and cooled by light water, with graphite as a reflector. One of the main activities of CRPQ is the neutron activation analysis, which is applied to many fields of research, in collaboration with other institutes and universities. The Research Reactor installations are also intensely used for human resources development in the field of radiochemistry and neutron activation analysis, at graduate and post-graduate levels. In the present paper, an overview will be presented of some of the neutron activation analysis research lines that are being developed, comprising environmental and health-related applications.

Introduction

The IEA-R1 research reactor is an open swimming pool type research reactor, operating at a nominal power of 2 MW thermal on a 64 hours a week continuous cycle. It has been working safely since 1957, mostly at 2 MW. Recently, the system was upgraded and installation of other systems were made, such as the emergency water injection system in order to allow the continuous operation at 5 MW in the near future.

The main applications of the IEA-R1 reactor are: radioisotope production for nuclear medicine, agriculture and industry; material testing; nuclear physics; training of reactor operators and, neutron activation analysis (NAA).

Neutron activation analysis has been from the beginning one of the most relevant applications of the reactor and nowadays the Neutron Activation Analysis Laboratory of IPEN(LAN) has a permanent staff of seven PhD researchers, three MScs, two chemistry technicians, one electronics technician and one secretary. Generally, from twenty to twenty-five students, including PhDs, MScs and undergraduate students develop their activities each year at the LAN as part of the courses of the University of São Paulo. Also Post-Graduate Courses are offered, related to applications of radiochemistry and neutron activation analysis. In the last ten years, twenty MSc dissertations and PhD Theses have been finished in these fields.

Neutron activation analysis services are also offered to other research institutes, universities and private companies, mainly chemical industries and mining companies. Another service offered is the determination of dentifrice abrasivity by radiometric method, as requested by multinational industries operating in Brazil.

Several applications of NAA to the analysis of biological samples have been developed or are underway, such as: determination of trace elements, mainly rare-earth elements, in lung samples of coal miners; multielement analysis of bone samples in an osteoporosis study conducted by the IAEA; analysis of mercury, selenium and other trace elements in hair of Brazilian populational groups living in the Amazonic region, as well as multielemental hair analysis of other populational groups living in São Paulo.

In the area of nutritional studies, INAA and also radiochemical separations have been applied to analysis of mineral constituents in diets of University students, industry workers, as well as in diets from nurseries and from patients with chronic renal failure. These are important contributions to studies in trace element deficiencies in the Brazilian population, which have already not sufficiently studied.

Several studies are also being undertaken, in the field of environmental monitoring, utilizing lichens such as the *Canoparmelia texana* as biomonitors, of polluted and non-polluted areas in São Paulo. Also under investigation are the use of *Tradescantia pallida leaves, Solanum lycocarpum* (for rare-earth-elements) and *Tillandsia usneoides*, an epyphitic bromeliad, as environmental biomonitors.

Also in the field of environmental studies, multielemental analyses of sediments and soils from different regions of Brazil have been carried out by INAA, such as: the Sepetiba Bay, in the state of Rio de Janeiro, two localities of the State of Amapá, in the Amazonic region and several others. In the case of the Amazonic region, the studies were focused in the determination of mercury and methyl-mercury, due to the gold exploration activities that have been occurring in the region since the 1980's.

In the present paper, the methodologies utilized and the main conclusions obtained in some of these studies of biological and environmental samples are presented.

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Experimental

Sample collection and preparation

Lung samples were obtained from necropsies of miners working in coal mines located in Criciuma (SC), in Southern Brazil. Control samples were obtained from healthy individuals, in autopsies performed at the Institute of Forensic Medicine of the University of São Paulo. The samples were freeze-dried before analysis and in this process a mean weight loss of 80% occurred. The dried samples were crushed with a teflon pestle and homogenized.[1]

The diets were collected by the duplicate portion method, where the participants provide a duplicate of all foods and meals that they eat, during periods from 3 to 7 days. The main groups studied were: students eating in cafeterias of the University of São Paulo; children staying the whole day in a nursery at the University of São Paulo; a group of patients with chronic renal failure; a group of institutionalized elderly, both living in the city of São Paulo.[2]

Epyphitic lichens like *Canoparmelia texana,* were used as biomonitors of atmospheric pollution in several regions of the State of São Paulo, with different degrees of atmospheric pollution. The lichens were collected at a height of about 1.5 m above the ground, from different kinds of trees, like: palm trees, eucalyptus, rubber tree. The lichens were firstly cleaned by using a pair of tweezers, examining them under an Olympus zoom stereoscopic microscope. Afterwards, they remained immersed in distilled water, in order to remove dust and sand. Next, lichens were placed on a filter paper, freeze-dried and ground manually in an agate mortar, until obtaining a fine powder.[3,4]

Sediment samples were collected in the regions of Serra do Navio and Vila Nova River Basin in the Amapá State, Brazilian Northeastern Amazon, approximately at the latitude of 00° 00'. The samples were collected using the Eckman dredge.[5] All samples (about 1 kg) were stored in polyethylene bags and immediately frozen. In the laboratory, the samples were defrosted and homogenized while still wet and the coarse material (>2 mm) was removed. For sediments the remaining material was sub-fractioned through a 63 μm sieve, obtaining sand (between 2 and 0.063 mm) and mud, which includes silt (between 63 and 2 μm) and clay (<2 μm).

Irradiations

As a general procedure, the powdered samples (100–200 mg) were weighed in polyethylene envelopes, previously cleaned with dilute nitric acid solution.

Since the comparative method of instrumental neutron activation analysis was used, synthetic multielement standards were prepared, by mixing appropriate aliquots of solutions of these elements made from spectroscopically pure elements or compounds, or using SPEX or Perkin-Elmer standard solutions, appropriately diluted. The multielement standards were divided in groups, according to the half-lives of the radioisotopes to be used for analysis. These standards were pipetted in sheets of analytical filter papers for irradiation.

The samples and standards were irradiated at the IEA-R1 Nuclear Research Reactor, under thermal neutron fluxes varying from 10^{11} to 10^{13} $n \cdot cm^{-2} \cdot s^{-1}$. Irradiations from 1 to 5 minutes were performed to analyze Al, Br, Cl, K, Mg, Mn, Na, Ti and V elements.

Suitable reference materials were irradiated together with the samples and synthetic standards, such as: IAEA-336 Lichen, NIST-1572 Citrus Leaves, NIST-1575 Pine Needles, NIES-5 Human Hair, GBW-09101 Human Hair, DORM-1, DOLT-1, IAEA-085 and 086, SRM-1515 Apple Leaves, SRM-1547 Peach Leaves and others.

Irradiations from 8 to 16 hours were carried out, for the determination of As, Ca, Cd, Ce, Cr, Cs, Cu, Co, Eu, Fe, Hg, La, Lu, Mo, Nd, Rb, Sb, Sc, Se, Sm, Tb, Th, Yb, Zn. More detailed INAA procedure has been described elsewhere.[2–5]

Results and discussion

In Table 1 are presented the results obtained for the determination of Sc, Hf, Th, U and rare-earth elements in lung samples from a control group, of non-exposed Brazilian population and of coal miners, who are considered as a critical group, due to their constant exposure to and inhalation of toxic substances. The elements cited were chosen for the present study due to the fact that most Brazilian coal samples have relatively high contents of these elements. It can be observed that the geometric means of all elements were high in the coal miner group and also that there is a variability of elemental concentrations within a single group of individuals. All miners submitted to the present analysis had presented lung disease, according to histopathological studies (coal worker's pneumoconiosis). This fact encourages the development of clinical studies focusing the possible role of the elements determined in the present work in detecting pneumoconiosis.

Table 2 presents the results of the calculated daily intakes of the elements determined by INAA in diet samples from different Brazilian population groups (children, adults, elderly and patients with chronic renal failure), as collected by the duplicate portion method. It can be observed that the diets of some of these groups show deficiency for the essential elements as Ca, Fe, Se and Zn, when their daily intake is compared with the recommended values of RDA. The Ca, Fe and Zn deficiencies in children can impair their growth and development. Studies have also shown that the cognitive development and immune system can be impaired by Zn and Fe defficiency. Iron defficiency is considered a problem of public health in Brazil, because of its low intake in the diet and the low bioavailability, so anaemia is common in the children population.

In Table 3 are presented some of the results obtained for mercury concentrations in soils and sediments of localities in the Amazonic region (State of Amapá). These data were collected as part of a broader study on the hydrogeochemical cycle of mercury in the Amazonic Basin, in which several compartments were studied, including soil, sediments, water, fish and hair of riverside populations.

The levels of Hg found in sediments from the Serra do Navio a non-contaminated region, are higher than several investigated areas in Brazil considered as contaminated, being also 10 times higher than values found for sediments from rivers considered non-contaminated in the Amazonic region (20 $\mu g \cdot kg^{-1}$). Using the Pearson similarity correlation test to the sediment samples, a positive correlation was found between Hg and Fe in sediments, showing that the iron oxides are the main linkage of Hg in this region. These findings, together with work conducted by other authors, suggest that a natural high background of mercury in some parts of Amazonic region exists, which, enhanced by gold exploration activities, could be responsible for high concentrations of mercury found in the hair of populational groups of the region.[6]

Table 4 presents the results obtained for analysis of the lichen *Canoparmelia texana* collected from different sites of the State of São Paulo, from a very clean site (Ibiuna) to sites in the city of São Paulo, with different degrees of pollution. For most elements determined, the elemental concentrations in *Canoparmelia texana* are increasingly higher in the more polluted sites, indicating the viability of this lichen as a biomonitor of atmospheric pollution.

Conclusions

Instrumental neutron activation analysis was succesfully applied by the group of the LAN of the Research Reactor Center of IPEN, to multielemental determinations in many kinds of samples of interest to biological and environmental studies related to several Brazilian populational groups and regions. The main conclusions were:

Lung biopsies from Brazilian coal miners showed very high concentrations of rare-earth elements and this fact encourages the development of clinical studies focusing the possible role of these elements in pneumoconiosis.

Diets of children and elderly showed deficiency for Ca, Fe and Zn and patients with chronic renal failure had reduced intakes of Zn, Se, Fe and Ca.

Sediment samples from Serra do Navio, a region still not contaminated by gold exploration activities, presented high amounts of Hg, possibly derived from natural sources, as already pointed out by other authors, and not only from gold exploration activities.

Table 1. Elements in lung samples from control and coal miner groups (in $\mu g \cdot kg^{-1}$ of dried weight)[1]

Element	Control group* (X_g ×÷ s_g)	Coal miner group* (X_g ×÷ s_g)
Sc	2.56 ×÷ 1.7	93.7 ×÷ 4.1
La	39.0 ×÷ 1.8	354.3 ×÷ 3.6
Ce	159.3 ×÷ 1.4	922 ×÷ 2.9
Nd	122.9 ×÷ 2.1	358 ×÷ 3.5
Sm	3.79 ×÷ 1.3	54.3 ×÷ 4.1
Eu	1.62 ×÷ 1.7	12.4 ×÷ 3.1
Tb	n.d.	17.0 ×÷ 2.9
Yb	n.d.	34.5 ×÷ 4.2
Lu	0.60 ×÷ 2.0	6.1 ×÷ 3.6
Hf	3.23 ×÷ 1.3	35.8 ×÷ 3.5
Th	10.1 ×÷ 1.6	98.1 ×÷ 4.1
U	19.2 ×÷ 4.2	67.0 ×÷ 3.0

* Geometric mean and standard deviation.
n.d.: Not detected.

Table 2. Daily intakes of the essential elements analyzed in the diet samples[2]

Element	Children diet		Adult diet		Elderly diet		Patient group diet	
	Average±SD	Range	Average±SD	Range	Average±SD	Range	Average±SD	Range
Br, mg/d	1.8 ± 0.6	1.0 – 3.7	3.3 ± 1.2	1.2 – 5.8	1.7 ± 0.5	0.8 – 2.5	1.9 ± 0.9	0.9 – 4.3
Ca, mg/d	438 ± 143	241 – 777	636 ± 316	105 – 1275	377 ± 94	171 – 479	353 ± 163	134 – 674
Cl, mg/d	2725 ± 1261	971 – 6258	n.d.	–	1922 ± 494	814 – 2889	n.d.	–
Co, μg/d	10.2 ± 4.1	4.1 – 19.6	40 ± 45	7.3 – 177	10.9 ± 4.7	5.2 – 24.1	15.5 ± 9.7	3.6 – 38.3
Cs, μg/g	16.6 ± 4.4	10.6 – 25.6	36.3 ± 14.5	9.7 – 57	14.9 ± 4.9	8.9 – 26.2	27.8 ± 26	8.3 – 131
Fe, mg/d	5.3 ± 1.0	4.2 – 7.5	19 ± 11	6.6 -49	5.2 ± 1.6	1.9 – 8.7	8.4 ± 4.4	3.1 – 18.2
K, mg/d	1408 ± 340	946 – 2176	3446 ± 1878	800 – 8881	1081 ± 256	582 – 1447	1845 ± 886	819 – 3980
Mn, mg/d	1.5 ± 0.5	0.8- 2.6	n.d.	–	1.1 ± 0.5	0.4 – 2.6	n.d.	–
Na, mg/d	1502 ± 408	872 – 2407	3681 ± 2320	1252–10800	1195 ± 278	525 – 1807	2031 ± 1050	934 – 4267
Rb, mg/d	2.4 ± 0.5	1.6 – 3.1	4.7 ± 2.0	1.3 – 7.0	1.9 ± 0.5	0.8 – 3.0	3.3 ± 1.3	1.2 – 5.8
Se, μg/d	26 ± 7	16 – 40	53 ± 27	15 – 129	30 ± 11	11 – 57	29 ± 15	12 – 71
Sc, ng/d	385 ± 211	206 – 1131	699 ± 278	332 – 1313	390 ± 140	110 – 690	445 ± 262	51 – 1184
Zn, mg/d	4.8 ± 1.1	3.3 – 7.4	11.6 ± 5.1	3.1 – 20.1	3.5 ± 1.1	1.5 – 5.9	6.6 ± 2.9	2.7 – 11.5

Table 3. Results obtained for total Hg (in mg·kg^{-1}) by using RNAA and CVAAS, Al (X-ray fluorescence) and Fe (INAA) analysis in sediments from Serra do Navio and Vila Nova river basin[5]

Location	Sample	Fraction	Al, %	Fe, %	Hg (RNAA)*	Hg (CV-AAS)
SERRA	SDPP0101	Mud	n.d.	9.90	0.46 ± 0.03	n.d.
DO		Sand	1.99	1.60	0.022 ± 0.003	n.d.
NAVIO	SDAP001	Mud	29.3	2.85	0.21 ± 0.01	0.25
		Sand	4.30	1.1	0.041 ± 0.001	0.045
	SDAP002	Mud	n.d.	4.6	0.377 ± 0.005	0.42
	SDAP003	Mud	29.9	3.3	0.19 ± 0.02	0.54
	SDAP004	Mud	32.6	2.9	0.25 ± 0.01	n.d.
VILA	SDVN004	Mud	28.9	2.13	0.27 ± 0.02	0.39
NOVA	SDVN006	Mud	28.7	2.10	0.24 ± 0.01	0.27
RIVER	SDVN001A	Mud	23.4	5.0	2.98 ± 0.04	3.2
BASIN	(20–30 cm)	Sand	5.4	2.1	1.41 ± 0.05	1.40
	SDVN001B	Mud	24.2	1.96	1.03 ± 0.11	1.27
	(10–20 cm)	Sand	10.2	2.20	0.70 ± 0.03	0.71
	SDVN001C	Mud	23.6	2.6	2.0 ± 0.1	2.09
	(0–10 cm)	Sand	4.6	2.35	0.29 ± 0.03	0.35
	SDVN007	Mud	30.5	7.0	1.9 ± 0.1	1.46

n.d.: Not determined.
* Mean of two determinations.

Table 4. Results obtained for *Canoparmelia texana* lichen collected from different sites of the State of São Paulo[4]

Element	Ibiuna, SP	São Paulo, SP (site 1)*	São Paulo, SP (site 2)**
Al, μg·g^{-1}	2747 ± 44	4388 ± 239	7129 ± 137
As, μg·kg^{-1}	411 ± 14	1034 ± 9	1057 ± 14
Br, μg·g^{-1}	39.40 ± 0.07	24.92 ± 0.07	24.85 ± 0.05
Ca, %	4.67 ± 0.08	2.52 ± 0.03	4.13 ± 0.07
Cd, μg·kg^{-1}	456 ± 59	2636 ± 67	3917 ± 209
Cl, μg·g^{-1}	639 ± 14	525 ± 24	284 ± 39
Co, μg·kg^{-1}	219 ± 4	571 ± 20	1063 ± 14
Cr, μg·g^{-1}	2.85 ± 0.05	9.14 ± 0.06	16.4 ± 0.1
Cs, μg·kg^{-1}	117.5 ± 4.1	489 ± 9	1016.4 ± 9.4
Fe, μg·g^{-1}	1033 ± 6	2121 ± 9	4135 ± 21
Hf, μg·kg^{-1}	378 ± 3	522.1 ± 3.5	1464 ± 5
K, μg·g^{-1}	1892 ± 116	1308 ± 21	3849 ± 233
La, μg·g^{-1}	1.454 ± 0.006	4.19 ± 0.01	7.05 ± 0.05
Ce, μg·g^{-1}	3.30 ± 0.02	6.98 ± 0.02	16.58 ± 0.04
Nd, μg·g^{-1}	1.62 ± 1.09	2.96 ± 0.17	6.52 ± 0.21
Sm, μg·g^{-1}	180.7 ± 0.4	456.5 ± 0.4	1055 ± 1
Eu, μg·kg^{-1}	39.4 ± 2.4	98.5 ± 1.7	181 ± 2
Tb, μg·kg^{-1}	20.7 ± 1.9	50.2 ± 2.3	103.6 ± 3.2
Yb, μg·kg^{-1}	53.1 ± 4.1	154.4 ± 5.4	346.6 ± 6.7
Lu, μg·kg^{-1}	10.8 ± 0.4	28.2 ± 1.5	60.1 ± 0.5
Mg, μg·g^{-1}	2513 ± 138	3551 ± 305	3540 ± 437
Mn, μg·g^{-1}	37.8 ± 0.9	140.4 ± 1.3	164.4 ± 1.2
Na, μg·g^{-1}	77.2 ± 0.1	195.8 ± 0.5	422.9 ± 0.5
Rb, μg·g^{-1}	6.0 ± 0.1	7.6 ± 0.1	20.2 ± 0.2
Sb, μg·kg^{-1}	280 ± 6	895 ± 5	2000 ± 10
Sc, μg·kg^{-1}	315 ± 1	604 ± 2	1190 ± 3
Se, μg·kg^{-1}	201 ± 18	403 ± 21	665 ± 24
Th, μg·kg^{-1}	327 ± 2	911 ± 4	1933 ± 5
Ti, μg·g^{-1}	195 ± 39	342 ± 77	510 ± 89
U, μg·kg^{-1}	55.4 ± 5.8	324 ± 2	190.2 ± 8.7
V, μg·g^{-1}	1.53 ± 0.27	13.6 ± 0.7	14.0 ± 0.9
Zn, μg·g^{-1}	137.0 ± 0.5	116.9 ± 0.4	145.7 ± 0.5

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The lichen *Canoparmelia texana* showed to be a useful biomonitor of atmospheric pollution, in different sites of the state of São Paulo.

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