DETERMINATION OF U_{nat}, TH, RARE EARTH AND METALS IN SOIL AROUND IPEN FACILITIES

C.H.R. Saueia[1,2], M.B. Nisti[1] and B.P. Mazzilli[1]

[1]Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP), São Paulo, Brazil
[2] Universidade Nove de Julho, São Paulo, Brazil
chsaueia@ipen.br

Abstract. *The aim of this study is to determine natural radionuclides (U_{nat} and Th), rare earth elements (Ce, Eu, La, Lu, Sm, Tb and Yb) and metals (As, Ba, Co, Cr, Cs, Fe and Sc) in soil samples around Instituto de Pesquisas Energéticas e Nucleares (IPEN) facilities.*

Key words: *metals, natural radionuclides, rare earth elements, soil.*

Introduction: For the assessment of the quality of the soil, it is important to check possible contamination due to anthropogenic influence. The aim of this study is to determine natural radionuclides (U_{nat} and Th), rare earth elements (Ce, Eu, La, Lu, Sm, Tb and Yb) and metals (As, Ba, Co, Cr, Cs, Fe and Sc) in soil samples around Instituto de Pesquisas Energéticas e Nucleares (IPEN) facilities. IPEN is located in the city of São Paulo, Brazil, and comprises several nuclear and radioactive facilities, spread over an area of about 500,000 m² with buildings covering 85,000 m². Among these activities, it is worth to mention the nuclear fuel cycle (beneficiation process) and the thorium nitrate production, which can release to the environment rare earth elements, metals impurities, U and Th.

Materials and Methods: Soil samples were collected at six different locations at IPEN, using a PVC pipe with 7.2 cm of diameter and 15 cm of depth, after cleaning the surface manually. The quantity collected was about 500 g, and each sampling point was analyzed in triplicate. The soil samples were homogenized, dried to constant mass and passed through a sieve of 250 µm.

The determination of the radionuclides, rare earth elements and metals was carried out by Instrumental Neutron Activation Analysis (INAA). The technique consisted of irradiating approximately 150mg of the sample during 8 hours at a neutron flux of 10^{12} n cm^{-2} s^{-1}, at the nuclear research reactor IEA-R1 of IPEN. The induced radioactivity was measured by gamma-spectrometry with a hyper-pure germanium detector, with 25% relative efficiency and resolution of 2.10 keV at 1332 keV. The spectra analyses were made by WinnerGamma program on InterWinner [1]. The concentration of the analyzed elements was determined by comparing the activity obtained in the samples with that obtained with the standard reference material IAEA SL-1 and IAEA SL-3 by the expression (1):

$$C_a^i = \frac{(A_a^i \cdot m_p \cdot C_p^i) \cdot e^{\lambda(ta-tp)}}{A_p^i \cdot m_a} \qquad (1)$$

where: C_a^i = i-element concentration in the sample (µg g^{-1})

C_p^i = i-element concentration in the standard (µg g^{-1})

A_a^i = i-element peak area in the sample (cps)

A_p^i = i-element peak area in the standard (cps)

m_a e m_p = standard and sample weight, respectively (g)

λ = radioisotope decay constant (s^{-1})

t_a - t_p = Difference between sample and standard count time (s).

The determination of the minimum detectable activity (MDA) for INAA was carried out using standard reference material by the expression (2) [2]:

$$MDA = \frac{3 \cdot C_{pR} \cdot \sqrt{Bg}}{T.C} \qquad (2)$$

where: MDA= minimum detectable activity (µg g^{-1})

C_{pR} = concentration of the element in the standard reference material (µg g^{-1})

Bg = background count of the element in the sample (counts)

T = counting time (s)

C = counting in the peak area of the element in the standard reference material (cps)

3 = level between the certified value and the definitive value.

Results and Discussion:

The coordinates of the soil sampling sites are presented in Table 1.

Table 1. Coordinates of the soil sampling sites

Sampling Point	Coordinates
1	23°33'56.66"S,46°44'07.04"O
2	23°33'55.64"S, 46°44'05.63"O
3	23°33'59.69"S, 46°44'15.48"O
4	23°33'46.15"S, 46°44'13.36"O
5	23°33'48.21"S, 46°44'16.35"O
6	23°33'41.26"S, 46°44'28.92"O

The results of natural radionuclides (U_{nat} and Th), rare earth elements (Ce, Eu, La, Lu, Sm, Tb and Yb) and metals (As, Ba, Co, Cr, Cs, Fe and Sc) in soil samples are presented in Table 2.

The standard reference materials IAEA SL-1 and IAEA SL-3 were used to evaluate the accuracy of the methodology, and the results are presented in Figures 1 and 2, respectively.

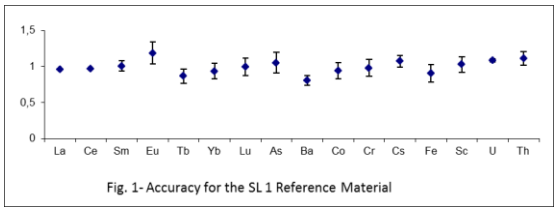

Fig. 1- Accuracy for the SL 1 Reference Material

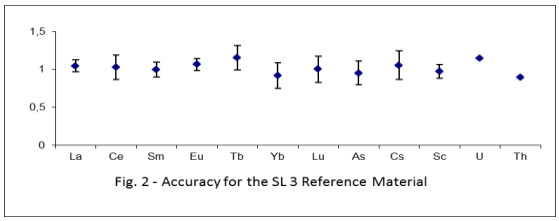

Fig. 2 - Accuracy for the SL 3 Reference Material

Table 2. Results of the natural radionuclides, metals and rare earth concentration (μg g^{-1}) in the soil samples.

	Sampling Point						mean value
Element	1	2	3	4	5	6	
Natural Radionuclides							
U_{nat}	6.15±1.11	5.55±1.03	3.12±0.53	3.73±0.36	3.96±0.41	5.42±0.48	4.65±1.21
Th	28.3±1.2	33.3±1.4	19.5±0.8	46.9±2.1	33.9±1.5	57.4±2.5	36.6±13.6
Metals							
As	9.90±0.92	20.9±1.7	4.00±0.54	8.23±0.72	7.29±0.51	MDA	10.1±6.4
Ba	263±53	MDA	205±52	204±60	396±72	354±68	285±87
Co	4.49±0.29	4.13±0.23	2.61±0.15	8.95±0.48	6.44±0.38	5.94±0.36	5.43±2.20
Cr	61.1±4.7	80.5±5.8	28.3±2.5	76.6±5.2	79.2±5.49	81.9±5.7	68.0±20.8
Cs	2.99±0.53	3.09±0.52	1.75±0.30	4.53±0.41	4.48±0.42	3.95±0.38	3.47±1.07
Fe(*)	4.02±0.06	6.21±0.09	2.30±0.03	6.41±0.11	6.76±0.11	7.47±0.12	5.53±1.96
Sc	13.8±0.5	15.0±0.5	9.66±0.33	22.8±0.82	22.8±0.8	26.5±0.9	18.3±6.5
Rare Earth							
Ce	79.8±4.6	71.0±4.2	77.0±4.9	183±14	132±10	254±19	133±74
Eu	0.64±0.06	0.41±0.04	0.49±0.04	0.85±0.09	0.71±0.08	1.28±0.14	0.73±0.31
La	44.6±1.0	28.4±0.6	58.6±1.3	55.5±1.1	46.8±0.9	95.5±1.8	54.9±22.5
Lu	1.55±0.16	1.22±0.13	0.56±0.06	0.76±0.08	0.61±0.06	0.60±0.06	0.89±0.40
Sm	12.7±0.6	7.44±0.36	16.5±0.8	6.20±0.21	4.32±0.15	7.18±0.25	9.04±4.57
Tb	3.05±1.36	3.02±1.43	1.33±0.63	1.55±0.30	1.66±0.33	1.27±0.36	1.48±0.98
Yb	6.19±0.54	3.53±0.30	2.51±0.22	4.72±0.39	3.97±0.34	3.55±0.31	4.08±1.26

(*) Fe in %.

The relative error ranged from 0.3% (Lu) to 9.5% (Fe) and relative standard deviation from 4.6% (La) to 10.8% (Ba) for standard reference material IAEA SL-1. For the standard reference material IAEA SL-3, the relative error ranged from 1.7% (Yb) to 9.3% (U) and relative standard deviation from 0.35% (Sm) to 10.1% (Th). In general, relative standard deviation and relative error were lower than 10% proving the precision and accuracy of the INAA technique.

The values obtained for the MDA were: U (< 1.32 μg g^{-1}) and Th (< 0.78 μg g^{-1}); Ce (< 5.31 μg g^{-1}) , Eu (< 0.13 μg g^{-1}), La (< 0.8 μg g^{-1}), Lu (< 0.07 μg g^{-1}), Sm (< 0.12 μg g^{-1}), Tb (< 1.5 μg g^{-1}) and Yb (< 0.85 μg g^{-1}); As (< 1.2 μg g^{-1}), Ba (< 82 μg g^{-1}), Co (< 1.3 μg g^{-1}), Cr (< 8.4 μg g^{-1}), Cs (< 1.30 μg g^{-1}), Fe (< 0.18 %) and Sc (< 0.19 μg g^{-1}).

Ruby et al. [3] determined the concentration of U and Th in soil samples used in agriculture and in pristine area of the State of São Paulo. The results obtained range of 0.5 to 5.81 μg g^{-1} and 4.6 to 54.37 μg g^{-1} for U and Th, respectively in agriculture soil; and range of 0.24 to 3.45 μg g^{-1} and 4.19 to 62.42 μg g^{-1} for U and Th, respectively for pristine area.

Peres [4] determined the natural radioactivity concentration in the soil of the State of São Paulo. The results obtained ranged from <1.9 to 16.1 μg g^{-1} for U and from 2 to 20.1 μg g^{-1} for Th.

The State of São Paulo Environmental Agency, Companhia Ambiental do Estado de São Paulo (CETESB) [5] established also reference values for soil quality and values for prevention and intervention in industrial soil. The quality reference level corresponds to a concentration below which the soil is considered clean. Prevention reference level corresponds to a concentration upon which the soil quality can be affected. Intervention reference level is the concentration upon which potential risks to human health exists. The reference values established for CETESB are presented in Table 3**.**

Table 3. Quality, prevention and intervention reference levels in industrial soil (μg g^{-1}).

Metals	Quality reference level	Prevention reference level	Intervention reference level
As	3.5	15	150
Ba	75	150	750
Co	13	25	90
Cr	40	75	400

Conclusion:

The results obtained of U and Th in soil samples around IPEN is in good agreement with the literature.

The concentrations obtained for As and Cr were below the prevention limits established by Cetesb. For the concentration of Ba, the values are above the prevention and below the intervention limits. The concentrations obtained for Co were below the value of the quality reference level.

There are no guiding values for the metals Cs, Fe, Sc and rare earth elements in the soil. The results obtained were compared with the values of the Continental Crust [6]. The concentration of Cs, Fe and Sc obtained in the soil samples around IPEN facilities is of the same order of magnitude of the Continental Crust.

The results obtained for the concentrations of rare earth elements were twice the values of the Continental Crust, with the exception of Eu, which concentration was below the value reported for the Continental Crust.

References

1. InterWinner, “InterWinnerTM 6.0 MCA Emulation, Data Acquisition and Analysis Software for Gamma and Alpha Spectroscopy IW-B32. ORTEC”, Oak Ridge, TN, USA. 2004.
2. L. H. Keith, W. Crummet, J. P. Deegar, R. A. Libby, J. K. Taylor, G. Wenter, “Principles of environmental analysis”, Anal. Chemistry, vol. 55, 1983, pp 2210-2218.
3. E. C. Ruby, A.M. G. Figueiredo, R. P. Modesto, M. M. G. Lemos, “Tório e Urânio em solos agrícolas do Estado de São Paulo”, Proceedings - Congresso Brasileiro de Geoquímica, Diamantina, MG, Brasil, 2013.
4. A. C. Peres, PhD Thesis, Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, SP, Brazil, 2007.
5. CETESB - COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL. “Dispõe sobre a aprovação dos Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo – 2005, em substituição aos Valores Orientadores de 2001, e dá outras providências. Decisão de Diretoria Nº 195-2005-São Paulo”, Brasil, 2005.
6. K. H. Wedepohl, “The composition of the continental crust”, Geochim Cosmochim Acta, vol. 59, 1995, pp. 1217-1232.