2009 International Nuclear Atlantic Conference - INAC 2009
Rio de Janeiro,RJ, Brazil, September27 to October 2, 2009
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-03-8

QUANTIFICATION OF STABLE ELEMENTS IN LIQUID RADIOACTIVE EFFLUENT

Marcelo B. Nisti, Adir J. G. Santos, Marcos A. Hortellani and Jorge E. S. Sarkis

Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
mbnisti@ipen.br

ABSTRACT

The Instituto de Pesquisas Energéticas e Nucleares – IPEN–CNEN/SP possesses a continuous Radioactive Liquid Effluents Monitoring Programme established routinely. At IPEN–CNEN/SP program, each process area liquid effluent discharge point that releases or has potential to release radioactive materials is sampled routinely and analyzed for radioactivity, to subsequent planned release. This paper presents the results obtained by Atomic Absorption Spectrometry Method (AAS), used to 1 L samples of representative radioactive liquid effluents generated at IPEN-CNEN/SP from 2004 to 2008 year. Samples were analyzed for all effluents samples generated in the Centro de Radiofarmácia (CR) and in the Centro do Reator de Pesquisa (CRPq), more contributors to institutional source-term. Effluents samples generated in the others IPEN-CNEN/SP facilities were also analyzed, comprising 38 radioactive liquid effluents samples in the studied range time. The AAS method was investigated for uncertainty using reference materials and calibration curves were plotted. The pre-treatment of the effluent samples included gentle hot plate acid digestion and phase homogenization, for 10 % nitric acid final concentration. The same condition was used for reference materials preparation, assaying the concentration similar to the interval of Brazilian environmental rules for stable elements. The concentrations of the stable elements Ag, Cd, Cr, Fe, Mn, Ni, Pb e Zn were determined. The obtained concentrations were compared to release limits under São Paulo State legislation. Two effluent samples showed values higher than the limits for Zn and Cd elements. The method of AAS discussed presents satisfactory conditions to determine and manage the radioactive liquid effluents for the presented stable species.

1. INTRODUCTION

The Instituto de Pesquisas Energéticas e Nucleares, IPEN–CNEN/SP (Nuclear and Energy Researche Institute) is surrounded by commercial, industrial and residential areas, and it comprises several nuclear and radioactive facilities including a research reactor, two cyclotrons and the radioisotopes and radiopharmaceuticals production plant. Activities related with the nuclear fuel cycle are also developed at the Institute, as well as research in cited fields. IPEN-CNEN/SP is part of Comissão Nacional de Energia Nuclear, CNEN (National Commission for Nuclear Energy). The institute was built 50 years ago, in a remote site in the city of São Paulo, Brazil, but nowadays it is located at an intensely occupied area, after the growth of the city.

Regarding liquid releases, all the radioactive liquid effluents generated at IPEN`s facilities or laboratories are stored and monitored for their respective retention tanks or flasks. Each batch of the effluents generated is representatively sampled and analyzed prior to discharge. Within this programme, liquid effluents are analyzed on a regular basis by using high resolution gamma spectrometry mainly and others techniques as neutron activation analysis, liquid scintillation counting and alpha spectrometry [1]. The total activity together with the total volume of wastewater released by year is consolidated in an annual source-term.

Radiological effluent monitoring results are a major component in determining compliance with applicable dose standards, facing to Brazilian radioprotection regulatory rules, under CNEN policy. Radiological IPEN management philosophy ensures that potential exposures to members of the public and to onsite workers are kept as far below regulatory standards as is reasonably achievable. This philosophy is known as the "as low as reasonably achievable" ALARA concept.

In the 90's of the XX Century and in the beginning of XXI Century decade and beginning of the century XXI the quality systems and the environmental managing were improved, with the objective of reaching the integrated administration. This require the administration of all the parameters which could influence in the economical components and in the company public image, including in the administration the social and environmental responsibility. Figure 1 presents the evolution of the environmental administration, being considered the social and economical component, in the last decades. Actually, the environmental managing legal instruments reach an integration of social and economical factors.

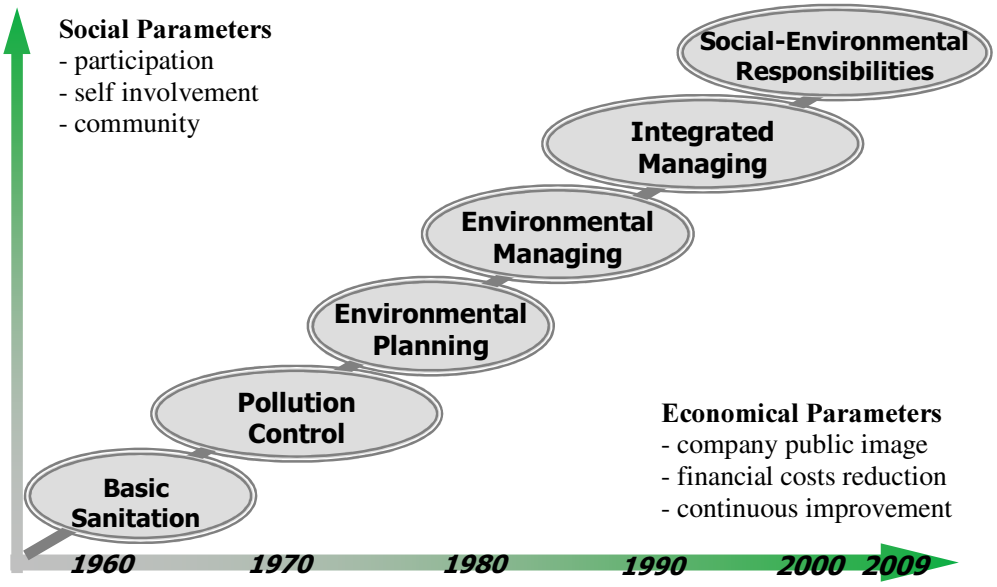

Figure 1. Environmental ambit concerning on productive activity, adapted from [2]

To reach such purpose in the enterprise, it is necessary to manage the environmental parameters under regulation and fiscalization into local and federal bases. In Brazil, in the case of nuclear and radioactive plants, the monitoring effluents plan must consider the radioctive isotopes and nonradioactive or stable chemical species [2]. These constituents must be either monitored or sampled, as applicable, before liquid effluent release.

This paper presents the analytical steps, standards dilution, calibration curves and results of a established methodology used for quantification of nonradioactive chemical elements in radioactive liquid effluents generated at IPEN facilities operation.

2. ATOMIC ABSORPTION SPECTROMETRY METHODOLOGY

The atomic absorption spectrometry (AAS) method was standardized for the determination of the concentrations of stable elements Ag, Cd, Cr, Fe, Mn, Ni, Pb e Zn. The value uncertainty and calibration curves were calculated, as described.

2.1. Operational IPEN-CNEN/SP facilities:

At IPEN, the total activity together with the total volume of wastewater released by year is consolidated in an annual source-term. These procedures accurately determine the types and quantities of radioactive materials being released to the receptor sewerage. Special attention has been given to effluent concentration discharge limits [3, 4, 5].

The Centro de Radiofarmácia (CR – Radioisotopes and Radiopharmaceuticals Production Center) and in the Centro do Reator de Pesquisa (CRPq – Research Reactor (IEA-R1) Center.) centers are the main contributors to institutional source-term at the range time from 2004 to 2006 year [6].

All liquid radioactive effluents samples generated at in the CR and CRPq were analyzed by AAS. Some effluents samples generated in others IPEN facilities were also analyzed, comprising 38 effluent samples generated from 2004 to 2008 march time period [2].

2.2 Radioactive wastewater sample pre-treatment and measurement

Several radioactive liquid effluent generated at IPEN-CNEN/SP facilities were collected and stored for a representative sample of 1.0 ± 0.1 L. Samples were transferred to 30 minutes magnetic agitation and measured the pH with universal indicative paper (pH 0 – 14 range, from colorpHast EMD). Soon afterwards an aliquot of 50 mL was taken using a volumetric glass pipette, it was transferred for a glass beacker cup and submitted to hot-plate heating, under controlled temperature interval 80 to 90^{o}C for 30 minutes. After, 5 mL of HNO_3 37% was added, by using a micropet Gilson P1000. The system was maintained under magnetic agitation even total particulate material dissolution. The obtained final solution was transferred to a polyethylene flask and analyzed by AAS for determination of interest elements [2].

The radioactive liquid effluent stable element concentrations were determined by using a flame way atomic absorption spectrometer, Spectra AA-220, Sequential Fast (Varian), associate to the software SpectrAA, version 5.01, presented in Figure 2.

The methodology calibration was accomplished using a certified material solution, containing Ag, Cd, Cr, Fe, Mn, Ni, Pb, and Zn (Merck and Spex Plasma). The concentrations of 0.1, 0.2, 0.5, 1, 1.25, 1.6, and 2 mg L^{-1} were prepared, in the same conditions used for preparing samples. Three different standard solutions were prepared, being one multi-elementary containing the elements Cd, Fe, Mn, Ni, Pb and Zn, and separate solution for Cr and Ag. The separation of the Cr and Ag of the other elements in the standard calibration solution became necessary, due to the precipitation occurrence after the mixture of those two elements with the other ones.

The standard solutions were prepared by gravimetric technique in analytical balance AL500C (Marte), being used micropet RBC 7993/07 P100 (Labmate-Masterlab) presented in Figure 2.

Figure 2. Atomic absorption spectrometer Spectra AA-220 Fast Sequential and standard gravimetric preparation.

For Cr analysis, it was used compressed air and acetylene with flow of 13.5 and 2.9 L min^{-1}, respectively. The other elements were analyzed Ag, Cd, Fe, Mn, Ni, Pb, and Zn by using compressed air and acetylene with flow of 13.5 and 2.0 L min^{-1}, respectively [7].

For the calculation of the inferior limit of determination, deionized water was used, in the same standards concentration of the analyzed samples, being this assay repeated 7 times, for obtaining of the average and standard deviation [8].

The z-score evaluates the accuracy of the method using certified reference material, using the equation 1 [8].

$$Z=\frac{(X_{lab}-X_{ref})}{S_{ref}} \quad . \qquad (1)$$

Where:
X: concentration value determined;
S: standard deviation;
ref and ***lab***: are indexes that represent results for reference material and laboratory sample.

The evaluation criteria of the z-score parameter is:
$Z \leq 2$ - satisfactory result;
$2 < Z \leq 3$ - questionable result;
$Z > 3$ - unsatisfactory result.

2.3 Results and Discussion

The calibration was accomplished for each concentration point absorbance been assayed and measured three times. The Figure 3 and Figure 4 show the calibration curves and their respective adjustments for each determined stable element (Cd, Pb, Cr, Fe, Mn, Ni, Ag and Zn).

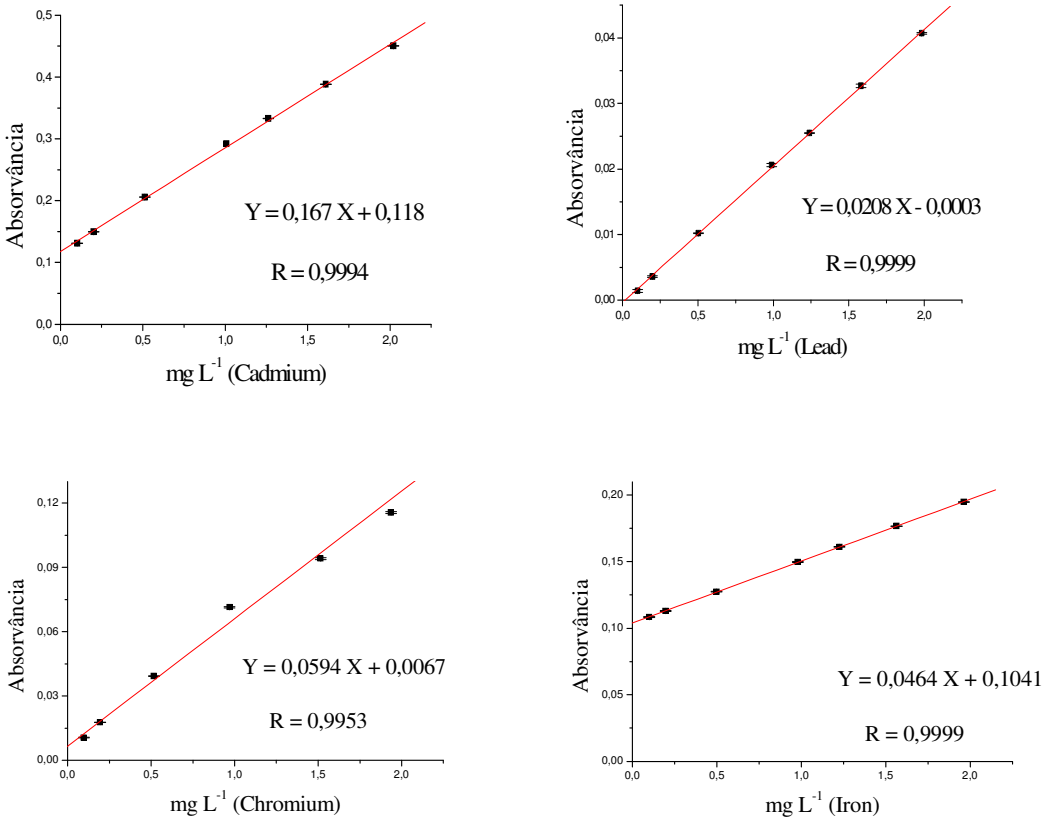

Figure 3. Calibration curve for Cd, Pb, Cr and Fe

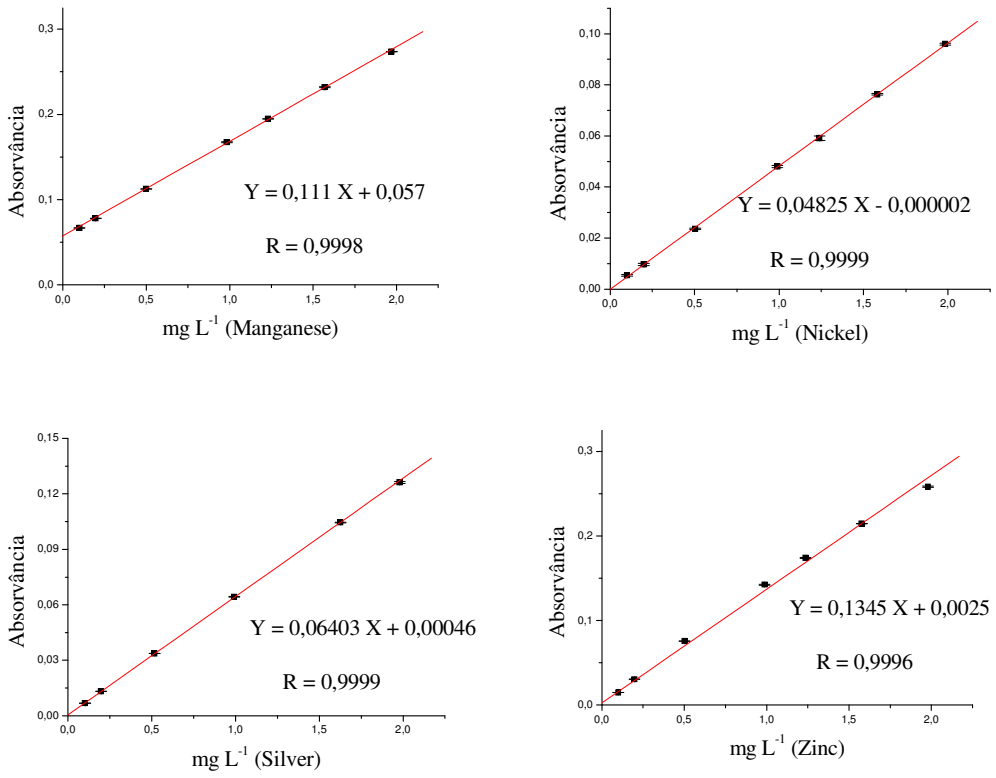

Figure 4. Calibration curve for Mn, Ni, Ag and Zn

The atomic absorption calibration curves verification was carried out using reference materials of code HC617908 and 90376147 (Merck precedence). The averages of three measures of the stable elements were calculated with their respective uncertainties. The concentration values obtained for reference material were inside of the intermediate interval of the calibration curves. Then, was necessary to do dilutions in the standard solutions to obtain calibrated elements values close to 1 mg L^{-1} and the for Manganese in the order of 0.5 mg L^{-1}.

The results for stable elements concentrations and respective uncertainty are presented in the Table 1 and Table 2, for Ag, Cd, Cr, Fe, Mn, Ni, Pb and Zn, analyzed in the generated effluents from facilities of the IPEN-CNEN/SP, from 2004 to 2008.

Table 1: Nonradioactive element concentrations for radioactive liquid effluents from IPEN's facilities

		Fe	Mn	Pb	Ni	Cd	Zn	Ag	Cr
sample code	**Facility**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**
SI-092-04	CCN	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-093-04	CCN	0.69±0.01	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-045-05	CCN	4.42±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.25±0.05	< 0.1	< 0.1
SI-028-07	CCN	0.55±0.01	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-029-07	CCN	0.72±0.01	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-026-06	CMR	< 0.1	< 0.1	< 0.2	< 0.1	205±3	< 0.1	< 0.1	< 0.1
SI-027-06	CMR	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-131-06	CQMA	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0.67±0.05	< 0.1	< 0.1
SI-132-06	CQMA	0.43±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.95±0.05	< 0.1	< 0.1
SI-081-04	CR	1.61±0.01	< 0.1	0.29±0.01	< 0.1	< 0.1	0.46±0.05	< 0.1	< 0.1
SI-098-04	CR	0.29±0.01	< 0.1	0.21±0.01	< 0.1	< 0.1	0.33±0.05	< 0.1	< 0.1
SI-110-04	CR	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0.22±0.05	< 0.1	< 0.1
SI-182-04	CR	0.56±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.28±0.05	< 0.1	< 0.1
SI-100-05	CR	0.20±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.31±0.05	< 0.1	< 0.1
SI-154-05	CR	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-221-05	CR	0.70±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.20±0.05	< 0.1	< 0.1
SI-005-06	CR	0.53±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.17±0.05	< 0.1	< 0.1
SI-049-06	CR	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0.31±0.05	< 0.1	< 0.1
SI-069-06	CR	0.14±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.30±0.05	< 0.1	< 0.1
SI-070-06	CR	0.18±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.23±0.05	< 0.1	< 0.1

Table 2: Nonradioactive element concentrations for radioactive liquid effluents from IPEN's facilities (continuation)

		Fe	Mn	Pb	Ni	Cd	Zn	Ag	Cr
sample code	**facility**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**	**mg L^{-1}**
SI-150-06	CR	0.44±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.11±0.05	< 0.1	< 0.1
SI-094-07	CR	0.85±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.17±0.05	< 0.1	< 0.1
SI-001-07	CRPq	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0.15±0.05	< 0.1	< 0.1
SI-033-08	CRPq	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-034-08	CRPq	0.12±0.01	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-127-06	LRR	< 0.1	0.18±0.01	< 0.2	1.95±0.01	< 0.1	13.1±0.3	< 0.1	< 0.1
SI-058-07	LRR	< 0.1	< 0.1	< 0.2	0.30±0.01	< 0.1	0.80±0.05	< 0.1	< 0.1
SI-004-08	LRR	< 0.1	< 0.1	< 0.2	0.12±0.01	< 0.1	0.52±0.05	< 0.1	< 0.1
SI-039-06	MB-01	2.83±0.01	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-057-07	MB-01	0.42±0.01	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-160-04	REN	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0.15±0.05	< 0.1	< 0.1
SI-203-04	REN	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SI-068-05	REN	0.35±0.01	0.32±0.01	< 0.2	< 0.1	< 0.1	0.26±0.05	< 0.1	< 0.1
SI-006-06	REN	0.47±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.21±0.05	< 0.1	< 0.1
SI-126-06	REN	0.18±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.17±0.05	< 0.1	< 0.1
SI-176-06	REN	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0.12±0.05	< 0.1	< 0.1
SI-050-07	REN	0.60±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.42±0.05	< 0.1	< 0.1
SI-121-07	REN	0.15±0.01	< 0.1	< 0.2	< 0.1	< 0.1	0.13±0.05	< 0.1	< 0.1

The stable element concentrations in the Table 1 and Table 2 were compared to the maximum permitted level demanded for liquid effluent release into São Paulo State environmental rules [9]. The effluents samples that presented values higher that allowed limit were SI -026/06, that crossed the maximum value of the Cadmium element in approximately 140 times, and the sample SI-127/06 that crossed the value of the Zinc element in approximately 2,5 times, and showed the nickel element concentration very close to the maximum permitted limit value of the regulation [9].

The sample SI-026/06 correspond to 50 liters total volume and the sample SI-127/06 was stored in a retention tank, representing 3.000 liters. These two effluents represented 0,75% and 0,01% of the total release volume, respectively, of the liquid radioactive effluent in the 2006 year.

3. CONCLUSIONS

The presented atomic absorption spectrometry methodology was adequate to analyse radioactive liquid effluent for the investigated nonradioactive chemical elements: Ag, Cd, Cr, Fe, Mn, Ni, Pb, and Zn.

The standard solutions and reference materials were adequate for calibration curves and method verification, respectively.

The determination of stable elements concentration in radioactive liquid effluent was very important in this study, due to practical checking that a discarded effluent sample is subject to differentiated legal demand, which should be accomplished in the institutional environmental managing.

The two effluents samples that crossed the legal limits for the stable elements were below detectable minimum detectable concentration (dmc) of the detection system for radioactive isotopes. It is showed that for a liquid radioactive effluent release, there might be restrictions due to the presence of stable elements.

Besides of determination of stable elements concentrations by atomic absorption spectrometry this methodology showed to be able to visualize the periodic occurrence from several studied IPEN's facilities. The variability of low concentrations, although being below the permissible limit release, it makes possible implantation of environmental managing procedures and improvements integrated administration.

REFERENCES

1. G. F. KNOLL, *Radiation Detection and Measurement.* John Wiley e Sons Inc, New York:, U.S.A (2000).
2. M. B. NISTI, "Sistema Ambiental Aplicado à Liberação de Efluente Radioativo Líquido". *Master Degree Dissertation.* Universidade de São Paulo, São Paulo (2009).
3. CNEN. Comissão Nacional de Energia Nuclear. "Diretrizes Básicas de Proteção Radiológica", *Norma CNEN-NN-3.01*, Brasília (2005).

4. CNEN, Comissão Nacional de Energia, Nuclear. “Posição Regulatória 3.01 / 008”,. *Norma CNEN-NN-3.01*, Brasília (2005).
5. CNEN, Comissão Nacional de Energia Nuclear. “Posição Regulatória 3.01 / 009”. *Norma CNEN-NN-3.01*, Brasília (2005).
6. M. B. NISTI, A. J. G SANTOS, “Assessment of Radioactive Liquid Effluents Release at IPEN-CNEN/SP”. The Natural Radiation Environment. Ed American Institute of Physics, p. 505-508, 2008.
7. M. A. HORTELANI, J. E. S. SARKIS, D. M. S. ABESSA, E.C.P.M. SOUSA, “Avaliação da contaminação por elementos metálicos dos sedimentos do estuário de Santos-São Vicente”, *Quim. Nova*. **V.31(1),** p. 10-19, 2008.
8. INMETRO INSTITUTO NACIONAL DE METROLOGIA, NORMALIZAÇÃO E QUALIDADE INDUSTRIAL. “*Orientação sobre validação de métodos de ensaios químicos***”**. **DOQ-CGCRE-008, Revisão 02,** Brasília, 2007
9. DOE-SP. Diário Oficial do Estado de São Paulo, “Aprova o regulamento da lei n° 997, que dispõe sobre a Prevenção e Controle do Meio Ambiente”, **Decreto Lei n° 8468**, São Paulo (1976).