Performance of the Radiotoxicology Laboratory of IPEN-Brasil in intercomparison exercises for bioassay purposes

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Abstract. The Radiotoxicology Laboratory Laboratorio de Radiotoxicologia (LRT) of Instituto de Pesquisa Energéticas e Nucleares, IPEN/CNEN has participated in intercomparation exercises of the National Brazilian Intercomparation Program Assays in Environmental Samples (Programa Nacional de Intercomparação, PNI) since 2001, twice a year. In the last two rounds, the PNI matrix, has adopted spiked water, following the same routine procedures used in the analysis of urine samples from workers exposed to intakes of ^{238}U, ^{3}H and some gamma emitters. The changes made in the procedures introduced a loss in the accuracy of the results, however contributed to a better check over the reliability of the LRT in the future results. In the first time, the changes also showed that the LRT gamma spectrometry detection limits do not attend the PNI levels. However, a brief study showed that concentrated aliquots from de original PNI matrix could be used to check the LRT gamma spectrometry quality control for the main radionuclides present in unsealed radioactive sources used in IPEN. ^{238}U and ^{3}H had better accuracy and precision in the last round. The laboratory global performance started a process of validation for others radionuclides determination procedures as bioassay purposes and to attend the radioprotection program. In the present time, the PNI matrix of ^{232}Th from the last three years are analyzed to optimize an instrumental neutron activation analysis (INAA) before present results in the next PNI exercise.

KEYWORDS: Intercomparison exercises; Quality control; Bioassay; Radionuclides.

1. Introduction

The proposal of the Laboratorio de Radiotoxicologia (LRT) of Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN is to develop and to improve analytical methods to determinate radionuclides in biological samples for estimation of the intake of workers exposed to internal contamination.

Accuracy and reproducibility of results in radionuclides bioassays has an important impact on the internal dosimetry. In addition to laboratory performance measures, analytical success can be judged on the ability to estimate doses at below levels than the occupational limits, sometimes near levels commonly observed in unexposed persons.

To attend a laboratory quality assurance program, the LRT has participated in 13 exercises of the National Brazilian Intercomparation Program Assays in Environmental Samples (Programa Nacional de Intercomparação, PNI) since 2001, twice a year, beginning on April 2001.

The PNI artificial low level environmental matrices (spiked samples of water) are free of charge and a good approximation to urine. In this case, the LRT uses the PNI water matrices only for comparison aims, because urine samples is the biological matrix most widely used in bioassay methods for assessing radionuclides intakes.

The laboratory performance evaluation takes into account the deviation between the experimental laboratory mean value and the activity concentration reference value and their repeatability of the measures.

2. Methodologies

2.1. Methods used by LRT to determination of Uranium, Tritium and Gamma emitters measurement

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Before 2006 the participation in the PNI exercises used to process the allow matrices as water, however without pre-concentration or mineralization sample steps. Currently, the PNI samples are analyzed as urine matrices, how described above.

Routine measurements of natural uranium in urine are frequently made with fluorimetric technique, which determines the mass of Uranium present. The fluorimetric method is the fastest and the oldest method employed by the LRT with excellent results since 1973. It possibilities the total procedure of analyze in only a day with a minimum detection activity (MDA) of 1.0μg U per liter [1].

Aliquots from the total volume collected by the worker in 24 hours are firstly freed from organic matter by a series of wet ashings with concentrated nitric acid and oxygen peroxide. The mineralized sample is solubilised in 1N nitric acid and the Uranium is extracted from the aqueous phase with trioctylphosphine oxide (TOPO)-hexane solution. Five aliquots from the TOPO solution are pipetted in platinum dishes with a fluorescent mixture of carbonate and fluoride, three of them spiked with internal standard of natural Uranium, and melted in a muffled furnace. Cooled samples are measured in a fluorimeter.

The urinalysis of Tritium determination by Liquid Scintillation Counting (LSC), also is fast and can be performed in a few hours with a MDA of 15Bq H^3 per liter.

An exception to need 24h collection for an aliquot from the 24h collection is stirred with activated carbon and filtered by a quantitative filter paper in order to extract the pyridines and other colored compounds to prevent the quenching during the measurement by liquid scintillation counting. From the cleared urine, three aliquots are taken and added 15ml of liquid scintillation cocktail bland are dispensedinto each vial. Aliquots of H^3 standard as well as a reagent blank each set are used as internal standard and measured also with each set of samples.

Actually, the determination of gamma emitters in urine is not a current bioassay method of the LRT for individual monitoring purposes. These measurements have been carried out by Laboratory 'in vivo' in order to attend the Radioprotection Service of IPEN. However, the LRT uses a NaI detector to measure specific Gamma emitter radionuclides.

The participation of LRT in PNI gamma emitters exercise is only to check the LRT gamma spectrometry as a quality control. The gamma spectrometer system is used in the determination of Thorium by nuclear activation analysis (NAA) [2].

The bioassay methods to determinate Thorium use urine and feces matrices. The Thorium NAA method based in the reaction $^{232}Th\ (n,\gamma)\ ^{233}Pa$ is very sensitive with a MDA of 1ng Th/L of urine. All the urine 24h pull is freed of organic interference by nitric acid treatment and pre concentrated by precipitation with hydroxide, reduced to mineral ashes in a muffled furnace and transformed in a white residue with a minimum of elements that could be activated in the reactor. After the neutron activation, the ^{233} Pa needs to be separated of the co-activated matrix by a new sequence of radiochemical steps. Because of the large number of separation steps without an internal standard as tracer, this analytical procedure results had not good repeatability. The Instrumental Nuclear Activation Analysis, without the post irradiation radiochemical separation of the ^{233} Pa also had not good repeatability in the analysis of PNI matrix of the last three runs, if compared with the results of measurements of the same samples by alpha spectrometry using ^{229}Th as tracer.

2.2. Statistical analysis criteria of PNI

The PNI results are analyzed using two statistical criteria; the normalized standard deviation, defined as the difference between the laboratory mean value of three independent determination results (X) and the reference value (U) normalized to the standard deviation of the reference value (*su)* divided by $n^{1/2}$,where *n* is the number of independent determinations[3,4]:

$$D = \frac{(X - U)}{\frac{su}{\sqrt{n}}} \quad (1)$$

When the results are comprised between $-2 \leq D \leq +2$ the laboratory has good performance. Results in the intervals $-3 \leq D \leq -2$ or $+2 \leq D \leq +3$ are considered acceptable and results with $D \leq -3$ or $D \geq +3$ indicates that the measurement system is out of control and the performance is non-acceptable.

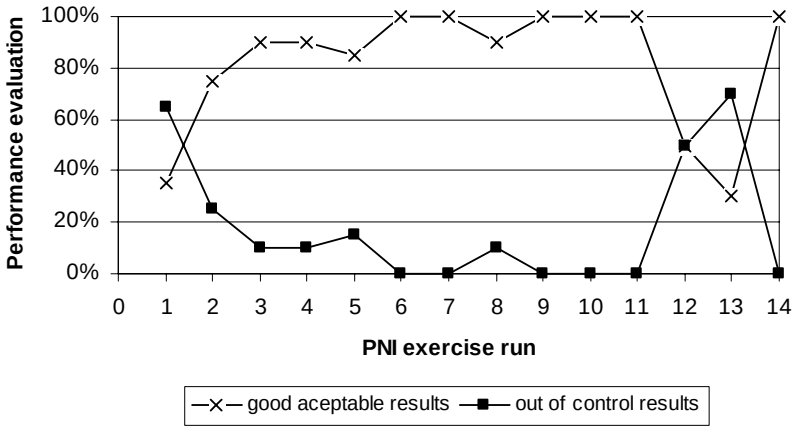
The second criterion evaluates the laboratory measurement repeatability by the coefficient of variation gives by the standard deviation of the laboratory determination results (s) divided by the mean value of three laboratory independent determinations (X):

$$Cv = \frac{s}{X} \quad (2)$$

3. Results and discussion

A general view of the LRT performance in the PNI exercises in the period from 2001 to 2007 is shown in the Fig. 1. The control losses over the measurement system can be observed in the runs 11 (August/2006) and 12 (April/2007) measurements, were did not attempt good marks due the lack of sensibility of the gamma spectrometer to measure the low levels radionuclides in the PNI matrices. The change in the pre-concentration procedures of analytical methods and the consequent influence over the results of Uranium and Tritium improved the results in the April/2004 run.

Figure 1: LRT performance in 13 runs of the PNI during 2001 to 2007 take into account all matrices and radionuclides measured.



The study of the repeatability of the Thorium determination by INAA was carried with PNI water matrices from the exercises April/2006, April/2007 and December/2007 and its results are presented in the **Table 1.**

The high values of standard deviation show that method needs a better measurement control before its improvement.

Table 1: Results of the study of repeatability of Thorium determination by INAA carried with PNI water matrices from the exercise April/2006, April/2007 and December/2007.

Radionuclide	Sample	Reference Values (Bq/L)	LRT Results(Bq/L)
Th-232	April/2006	0.110±0.017	0.084±0.032
	April/2007	0.080±0.012	0.061±0.033
	December/2007	0.066±0.010	0.076±0.028

4. Conclusions

The participation in intercomparison in PNI is an importante tool of improving LRT analytical methodologies in bioassays to determine radionuclides.

After an adjustment period, the LRT performance in the determination of 238U and 3H had better accuracy and precision in the last run. The treatment of the PNI samples as urine matrix is necessary to adopt the PNI exercises as a quality control resource over the LRT analysis methods.

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