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EVALUATION OF PROFICIENCY TEST RESULTS OF GAMMA RAY SPECTROMETRY IN DETERMINATION OF ANTHROPOGENIC AND NATURAL RADIONUCLIDES

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Abstract. *This paper aims to evaluate the performance of gamma-ray spectrometry in the Institute of Applied Nuclear Physics (IANP), Albania using Proficiency Tests (PTs). Participation in different proficiency tests is an essential tool for the improvement and testing of High Purity Germanium detector (HPGe) performance. The gamma - ray spectrometry laboratory in the last years has participated in different worldwide open proficiency tests organized by International Atomic Energy Agency (IAEA) with satisfactory results. For this paper, we selected the proficiency test organized by the IAEA in 2020 due to the analytical challenge of recognizing radioactive disequilibrium and applying appropriate decay corrections, especially for ingrowing radionuclides of broken natural decay series. The PTs of gamma-ray spectrometry measurements are carried out to improve the laboratory's ability to measure the radioactivity in the environment and foodstuffs at typical routine levels. The activity concentration of the test samples and the evaluation of the associated uncertainties are the main requirements of the test results. This PT was focused on the determination of anthropogenic and natural radionuclides in water, fish, and simulated aerosol filter samples. For this proficiency test, the Laboratory Sourceless Calibration Software (LabSOCS) is used for simulating the absolute efficiency curve. This paper presents the results and discusses the quality of the gamma spectrometry measurements performed in the IANP. The overall performance evaluation showed that 100 % of all reported results have been acceptable. Thus, the gamma-ray spectrometry using an HPGe detector showed high performance in the determination of anthropogenic and natural radionuclides in water, fish and simulated aerosol filter samples.*

Keywords: *Proficiency test, Gamma-Ray Spectrometry Laboratory, HPGe detector*

1. Introduction

The gamma spectrometry laboratory at the Institute of Applied Nuclear Physics plays an important role in the Environmental Radiation Monitoring of different samples, also including foodstuffs in Albania.

It is now widely recognized that for a laboratory to produce consistently reliable data, it must implement an appropriate program of quality assurance measures. In such measures is the need for the laboratory to demonstrate that its analytical systems are under statistical control, to use methods of analysis that are validated, that its results are 'fit-for-purpose', and that it participates in proficiency testing exercises [1].

The measurement of radionuclide activity concentrations in different environmental matrices by gamma spectrometry is a widely used method [2].

As our gamma spectrometry laboratory aims to be part of accredited laboratories in the future, we have participated in the last years in different intercomparisons and proficiency tests for the determination of natural and artificial radionuclides in different samples like soil, water, fish, building material, simulated air filters, etc.

One of the main objectives of this proficiency test organized by the IAEA in 2020 selected for this paper was to recognize radioactive disequilibrium and apply appropriate decay corrections, especially for ingrowing radionuclides of broken natural decay series.

The decay and ingrowth Bateman equations have been used to estimate the activity of a radioactive decay family of two or more members. The solution given by Bateman is valid only at a single point in time and does not necessarily apply to the situation where there is a finite measurement time, especially when this time is comparable to the half-lives of any members of the decay chain [3].

2. Materials and methods

2.1. Samples

Six different samples with Labcode 178 (two water samples, one fish sample and three simulated aerosol filters) were prepared and measured in the adopted fixed counting geometry. Sample 1 (water) was spiked with anthropogenic gamma emitters, whereas sample 2 (water) and sample 4 (fish) contained radionuclides from the broken decay chain of the (^{232}Th) – ^{228}Ra in disequilibrium. Three simulated aerosol filters coded samples 5, 6 and 7 were distributed on one paper.

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2.2. Measurements

For the measurement of six samples a gamma spectrometer with high-purity P-type coaxial germanium detectors (HPGe) of relative efficiency of 40% was used. To reduce background radiation, the detectors were housed in a 10 cm lead shield surrounded by a 0.5 cm copper layer to attenuate X-rays emitted by the lead. The detector was connected to standard electronics and the spectra were accumulated in 8192 Multichannel analyzer. The counting time of samples was set to be 48 hours with good statistical significance for the gamma-ray energy peaks of the radionuclides of interest in the samples. Energy calibration is carried out routinely, using a multi-gamma-ray emitter source. Efficiency calibration for various compositions and densities was performed by using the Laboratory Sourceless Calibration Software (LabSOCS) [4]. The spectra were analyzed using Genie 2000 software from Canberra Version 3.3.1 which includes peak search, nuclide identification, activity and uncertainty calculation modules.

3. Evaluation Criteria

To evaluate the bias of the reported results, the relative bias between the laboratory ($Value_{Lab}$) and the IAEA value ($Value_{IAEA}$) for a best estimation of the true value is expressed by the following equation:

$$Bias_{relative} = \frac{Value_{Lab} - Value_{IAEA}}{Value_{IAEA}} * 100\% \quad (1)$$

If the $|Bias_{relative}| \leq$ MARB (Maximum Acceptable Relative Bias) given in equation 1, the result will be "Accepted" for accuracy.

For evaluation of precision, an estimator P is calculated for each participant according to the following equation:

$$P = \sqrt{\left(\frac{u_{IAEA}}{A_{IAEA}}\right)^2 + \left(\frac{u_{Lab}}{A_{Lab}}\right)^2} * 100 \quad (2)$$

If both the P ≤ MARB and $Bias_{relative} \leq k*P$ are fulfilled according to equation 2, the reported results will be "Accepted" for the precision, where k is the coverage factor for the 99% confidential level. If one of them is insufficient, the result will be assigned the "Not accepted" status for precision.

In addition, the z-score is calculated in accordance with following formula:

$$z = \left|\frac{Value_{Lab} - Value_{IAEA}}{robustsd}\right| \quad (3)$$

where robust standard deviation without refinement, is given by formula:

$$robustsd = 1.483 * median\ of\ |Value_{Lab} - Value_{IAEA}|$$

The laboratory performance is evaluated from equation 3. If |z-score| ≤ 2 is satisfactory; questionable for 2 < |z-score| < 3, and unsatisfactory for |z-score| ≥ 3 [5].

4. Results

For sample 1, it was important to recognize the coincidence between gamma emission and positron annihilation to do the appropriate correction.

Whereas for samples 2 and 4, it was important to recognize the disequilibrium in the broken part of the ^{232}Th series, specifically from the unsupported ^{228}Ra via its progenies down to ^{208}Tl.

For the decay correction of daughter radionuclides, which are not in equilibrium with their mother, the general Bateman equation was used [6]:

This equation may be solved for the activity of the daughter nuclide expressed at the reference date:

$$A_2(0) = \frac{A_2 - A_1(0) * \frac{\lambda_2}{\lambda_2 - \lambda_1} * (e^{-\lambda_1 t} - e^{-\lambda_2 t})}{e^{-\lambda_2 t}} \quad (4)$$

The activity of the parent radionuclide at the reference date may be calculated by the usual decay correction. The limitation of this calculation is that only one layer of parent-daughter combination can be considered. Three simulated aerosol filters were contaminated by various ratios of ^{75}Se and ^{110m}Ag allowing checking the true coincidence summing correction [5].

The results and evaluation for the proficiency test conducted within the IAEA-TEL-2020-03 worldwide open proficiency test exercise are shown in tables 1, 2, 3a/b and 4a/b. The natural and anthropogenic radionuclides determined in this PT have been as follows: ^{134}Cs, ^{137}Cs, ^{228}Ac, ^{212}Bi, ^{212}Pb, ^{208}Tl, ^{214}Bi, ^{214}Pb, ^{210}Pb, ^{110m}Ag and ^{75}Se. For each of the analytes in scope the IAEA value, the IAEA uncertainty and the MARB are listed. On the other hand, in scope, the Laboratory value (Lab. Value), Lab uncertainty, relative bias and z-score are listed too.

The performance of the laboratory was assessed based on z-score values obtained for various radionuclides, analyzed in different matrices for each proficiency test. These covered low, medium and high energy ranges.

The laboratory showed high performance as all values of the z score lay between 0.00 and 1.50.

Table 1. Evaluation result of anthropogenic radionuclides for sample 1 (water). Values and uncertainties are expressed in Bq/kg

S 1	**^{134}Cs**	**^{137}Cs**
IAEA Value	**33.5**	**64.4**
Lab. Value	**32.2**	**62.8**
IAEA Uncertainty	0.5	0.9
Lab. Uncertainty	1.3	3.8
MARB	20 %	20 %
Relative Bias	3.88 %	-2.48 %
Robust SD	1.4	1.7
Z-Score	**0.93**	**0.94**
Accuracy	A	A
P	4.30	6.21
Precision	A	A
Final Score	**A**	**A**

Table 2. Evaluation result of natural radionuclides for sample 2 (water). Values and uncertainties are expressed in Bq/kg

S 2	^{228}**Ac**	^{212}**Bi**	^{212}**Pb**	^{208}**Tl**
IAEA Value	**24.7**	**6**	**6**	**2.2**
Lab. Value	**25.8**	**7.9**	**6.4**	**2.5**
IAEA Uncertainty	1	0.5	0.5	0.2
Lab. Uncertainty	1	1.3	1.2	0.4
MARB	25 %	60 %	35 %	40 %
Relative Bias	4.45 %	31.67 %	6.67 %	13.64 %
Robust SD	1.9	3.4	2.9	2.2
Z-Score	**0.58**	**0.56**	**0.14**	**0.14**
Accuracy	A	A	A	A
P	5.60	18.45	20.52	18.40
Precision	A	A	A	A
Final Score	**A**	**A**	**A**	**A**

Table 3a. Evaluation result of anthropogenic radionuclides for sample 4 (fish). Values and uncertainties are expressed in Bq/kg

S 4	^{134}**Cs**	^{137}**Cs**
IAEA Value	**119.4**	**18.9**
Lab. Value	**120**	**19.3**
IAEA Uncertainty	5	1
Lab. Uncertainty	5.1	1.2
MARB	20 %	25 %
Relative Bias	0.5 %	2.12 %
Robust SD	8.8	1.3
Z-Score	**0.07**	**0.31**
Accuracy	A	A
P	5.97	8.16
Precision	A	A
Final Score	**A**	**A**

Table 3b. Evaluation result of natural radionuclides for sample 4 (fish). Values and uncertainties are expressed in Bq/kg

S 4	^{212}**Bi**	^{214}**Bi**	^{210}**Pb**	^{212}**Pb**	^{214}**Pb**
IAEA Value	**11.5**	**13.5**	**95.8**	**11.5**	**13.5**
Lab. Value	**12.3**	**13.7**	**112**	**12.5**	**13.5**
IAEA Uncertainty	0.8	0.8	5	0.8	0.8
Lab. Uncertainty	2.7	0.9	16.7	1.9	0.8
MARB	60 %	30 %	30 %	30 %	30 %
Relative Bias	6.96 %	1.48 %	16.91%	8.7 %	0.0 %
Robust SD	5.2	3.2	16.2	4.1	3.3
Z-Score	**0.15**	**0.06**	**1.00**	**0.24**	**0.00**
Accuracy	A	A	A	A	A
P	23.03	8.85	15.8	16.72	8.38
Precision	A	A	A	A	A
Final Score	**A**	**A**	**A**	**A**	**A**

Table 4a. Evaluation result of anthropogenic radionuclides for 5, and 6 samples (simulated air filters). Values and uncertainties are expressed in Bq/filter

S 5	^{110}**Ag**	^{75}**Se**	**S 6**	^{110}**Ag**	^{75}**Se**
IAEA Value	**55.1**	**18.1**		**35.1**	**31.3**
Lab. Value	**52.5**	**16.0**		**33.5**	**27.9**
IAEA Uncertainty	4	1		3	1.5
Lab. Uncertainty	1.6	0.9		1	1.6
MARB	30 %	25 %		30 %	25 %
Relative Bias	-4.72 %	-11.6 %		-4.56 %	-10.86 %
Robust SD	8.9	1.4		5.9	3.4
Z-Score	**0.29**	**1.5**		**0.27**	**1**
Accuracy	A	A		A	A
P	7.87	7.88		9.05	7.47
Precision	A	A		A	A
Final Score	**A**	**A**		**A**	**A**

Table 4b. Evaluation result of anthropogenic radionuclides for sample 7 (simulated air filters). Values and uncertainties are expressed in Bq/filter

S 7	^{110}**Ag**	^{75}**Se**
IAEA Value	**19.2**	**113.4**
Lab. Value	**18.6**	**102.0**
IAEA Uncertainty	1.4	2
Lab. Uncertainty	0.6	5.8
MARB	30 %	25 %
Relative Bias	-3.12 %	-10.05 %
Robust SD	3.2	12.8
Z-Score	**0.19**	**0.89**
Accuracy	A	A
P	7.97	5.95
Precision	A	A
Final Score	**A**	**A**

5. Conclusion

A total of 214 laboratories from 58 different countries including our gamma spectrometry laboratory with Labcode 178, have reported data in the frame of the IAEA-TEL-2020-03 proficiency test exercise.

The overall performance evaluation showed that 100 % of all reported results have been "Acceptable". Thus, the gamma-ray spectrometry using an HPGe detector showed high performance in the determination of anthropogenic and natural radionuclides in water, fish and simulated aerosol filter samples.

However, in a few cases, the value of relative bias is high due to the small number of counts in the corresponding peak.

To assess the precision of gamma analysis, specific equipment of high performance, calibrated detectors, use of adequate standard and reference materials and necessary corrections are required.

In this PT, the most powerful tools during the radionuclide analyses have been human logic and the very good skills of the staff.

Our gamma spectrometry laboratory will continue to participate annually in proficiency tests organized by the IAEA or EU to achieve traceable, accurate and reliable data in the determination of radionuclides activity concentrations of different samples.

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