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Proficiency test: a quality assurance method for high-purity gamma spectrometry system

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Abstract. As part of the implementation of the quality system on ISO 17025 and accreditation, SALROM laboratory participated in the last year in intercomparison exercises, national and international, for determination of natural and man-made radionuclides. This paper describes results obtained in intercomparison exercise organized by IAEA in 2011. The reported values were mostly in good agreement with the resulting reference values.

1 Introduction

The activity of SALMROM laboratory, part of Life and Environmental Physics Department from IFIN-HH, consists in regular monitoring of the environmental radioactivity, on daily/monthly bases, in the area of the institute and nearby. Routinely measured isotopes in environmental samples are ^{40}K, ^{60}Co, ^{137}Cs, ^{241}Am and progenies of ^{238}U and ^{232}Th series. Some other activities, devoted to research programs, are related to the evaluation of radon concentration in salt mines, caves, construction sites or former industrial areas, to radionuclide inventory in water, soil or vegetation in the environment.

The laboratory has a quality system implemented and accredited to ISO 17025. In the frame of accreditation systems, the use of reference materials, both for quality control and proficiency testing, has therefore increased in recent years [1]. In addition, proficiency testing that includes distribution of homogenous portions of the test material for analysis as an unknown is a method for assessing and documenting the reliability and accuracy of the analytical data produced [2]. This paper presents the results obtained by the laboratory in an intercomparison exercise organized by IAEA in 2011, the first year when the laboratory has participated in such proficiency test.

2 Materials and methods

The equipment used for certified activities such as radiological monitoring of the environment is a germanium detector, with a diameter of 59.1 mm and a length of 54.3 mm, corresponding to a volume and mass of active germanium of 149 cm^3 and 0.8 kg, respectively. It is a coaxial p-type HPGe detector (ORTEC, model GEM 30P4) having a relative efficiency of 35% and energy resolution of 1.85 keV at 1332.5 keV, ^{60}Co. The detector is surrounded by a specially designed shield consisting of 10 cm lead and 2 mm copper. The detector is linked to an appropriate data acquisition system

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DigiDART Ortec and to a spectrum analysing software tool MAESTRO-32 6.06. The metrological traceability of the equipment is assured by using radioactive standards provided by Radionuclide Metrology Laboratory (RML) IFIN-HH.

In this paper, the quality assurance of the laboratory for gamma spectrometry measurements has been assessed by the annually organized proficiency test (PT) by IAEA. These PTs evaluate the validity and reliability of the analytical results. Through the provision of reference materials, control and performance assessment by the organization of proficiency tests and inter-comparison exercises, IAEA has been assisting laboratories in testing, improving and maintaining the reliability and quality of analyses of radioactive material [2]. The data presented are the results submitted for the IAEA-TEL-2011-03 world-wide open proficiency test on spiked water and soil samples.

The spiked samples were distributed to the participating laboratories and, using a rating system, the obtained analytical results are compared to the reference values assigned. For this PT four different samples were received and measured: three spiked water samples of 500 ml each and one soil sample of 200g. It is of major importance to obtain accurate analytical results of radionuclides, our laboratory producing acceptable results for most of the radionuclides reported: ^{60}Co, ^{133}Ba, ^{137}Cs, ^{152}Eu and natural radionuclides. For few radionuclides, ^{134}Cs, ^{241}Am and ^{226}Ra, the need for corrective actions in the analysis process is indicated.

To reach the final score "Acceptable", "Warning" or "Not acceptable" for the laboratory results various statistics such Z-scores and U-scores are used. The final evaluation includes both the total combined uncertainty associated with the target value of proficiency testing samples (unc_{IAEA}) and the total uncertainty reported by the participating laboratories ($unc_{Laboratory}$). According to this approach, the reported results are evaluated against the acceptance criteria for trueness and for precision. A result must pass both criteria to be assigned the final status of ''acceptable''. Based on the uncertainties assigned to the reported values the laboratory can establish its individual acceptance range and from the methodological point of view the credibility of uncertainty statement is checked.

In the final evaluation report for each laboratory one of the first parameter calculated is the bias of the reported result "$Value_{Laboratory}$". This is calculated relative to the assigned value "$Value_{IAEA}$" according to Eq. 1:

$$Relative\ bias = \frac{Value_{Laboratory} - Value_{IAEA}}{Value_{IAEA}} \times 100\% \quad (1)$$

A high relative bias is the first indication that a result obtained by the laboratory is not in agreement with the target value. Further, the Z-score is calculated from the laboratory results, the assigned value and a standard deviation in accordance to Eq. 2 as follows:

$$Z_{score} = \frac{Value_{Laboratory} - Value_{IAEA}}{\sigma} \quad (2)$$

where the standard deviation (σ) is $0.10 \times Value_{IAEA}$ (for the "fitness for purpose") and the laboratory performance is evaluated as satisfactory if $|Z_{Score}|<2$, questionable for $2<|Z_{Score}|<3$ and unsatisfactory for $|Z_{Score}|>3$.

As can be observed from Eqs.1-2 the uncertainty of the laboratory is yet not taken into account. This is considered in U-score, Eq. 3:

$$U_{test} = \frac{|Value_{IAEA} - Value_{Laboratory}|}{\sqrt{Unc_{IAEA}^2 + Unc_{Laboratory}^2}} \quad (3)$$

The ''acceptable'' criteria for trueness of the laboratory result is based on A1≤A2 where:

$$A1 = |Value_{IAEA} - Value_{Laboratory}| \quad (4)$$

$$A2 = 2.58 \times \sqrt{Unc_{IAEA}^2 + Unc_{Laboratory}^2} \quad (5)$$

The limiting value for the U-test parameter is 2.58 for a level of probability at 99% to determine whether a result passes the test ($U<2.58$).

For the evaluation of precision, an estimator "P" is calculated.

$$P = \sqrt{\left(\frac{Unc_{IAEA}}{Value_{IAEA}}\right)^2 + \left(\frac{Unc_{Laboratory}}{Value_{Laboratory}}\right)^2} \times 100\% \quad (6)$$

Then P directly depends on the laboratory uncertainty measurement. The IAEA defines an acceptance limit for precision (LAP) for each analyte which is set to about 15-20% to include any adjustment due to the concentration or activity level of the analytes concerned and the complexity of the analytical problem. The laboratory results are scored as 'Acceptable' for precision when P ≤LAP.
In the final evaluation, both scores for trueness and precision are combined. A result should have 'Acceptable' score in both criteria to be assigned final score 'Acceptable'. Obviously, if a score 'Not Acceptable' was obtained for both, trueness and precision, the final score will also be 'Not Acceptable'. In cases where either precision or trueness is 'Not Acceptable', further check is applied. The value of the relative bias (RB) is compared with the maximum acceptable bias (MAB), which is defined by the IAEA in advance, similarly as for LAP about 15-20%. If RB ≤ MAB, the final score will be 'Warning'. If RB > MAB, the result will be 'Not Acceptable'. 'Warning will reflect mainly two situations. The first situation will be a biased result with small measurement uncertainty, however still within MAB. The second situation will appear when result close to the assigned property value will be reported, but the associated uncertainty is large [3].

3 Results

The results obtained by the laboratory for the spiked water samples and soil sample are presented in Tables 1-2. In general, as can be observed from Table 1 for spiked water samples the target value of the specific activity in the samples is low, in the order of few Becquerels. This makes the analysis process for these samples very complex, because any variable in the activity formula [4] should be correctly evaluated. Any overestimation/underestimation of any variable, such as net peak area or background subtraction, easily can lead to an overestimation/underestimation of the activity.

Table 1. Evaluation of the proficiency test for water samples (S1-S3).

	Am-241	Ba-133	Co-60	Cs-134	Cs-137	Eu-152
IAEA S1	4.7 ± 0.01	5.0 ± 0.1	15.3 ± 0.2	7.7 ± 0.1	6.2 ±0.1	15.4 ± 0.2
Lab S1	3.85 ± 0.36 (A)	5.60 ± 0.37 (A)	14.57 ± 0.60 (A)	5.9 ± 0.6 (A)	6.55 ± 0.31 (A)	14.19 ± 0.86 (A)
IAEA S2	2.4 ± 0.1	2.5 ± 0.1	7.6 ± 0.1	3.8 ± 0.1	3.1 ± 0.1	7.7 ± 0.1
Lab S2	4.61 ± 0.44 (N)	3.04 ± 0.30 (A)	7.74 ± 0.36 (A)	5.4 ± 0.5 (N)	3.33 ± 0.20 (A)	9.4 ± 0.90 (A)
IAEA S3	3.3 ± 0.1	3.5 ± 0.1	10.7 ±0.2	5.4 ± 0.1	4.4 ± 0.1	10.8 ± 0.2
Lab S3	8.71 ± 0.63 (N)	3.88 ± 0.38 (A)	10.63 ± 0.46 (A)	6.72 ± 0.61 (A)	4.67 ± 0.25 (A)	11.23 ± 0.80 (A)

A – acceptable result
N – not acceptable result

Although most of the laboratory results were acceptable, there were a few which were not acceptable as can be notice in Table 1, such as ^{241}Am (for the second and the third sample of water) and ^{134}Cs (for second sample of water).

Table 2. Evaluation of the proficiency test for soil sample S4.

	Ac-228	Bi-214	Cs-137	K-40	Pb-212	Pb-214	Ra-226	Tl-208
IAEA S4	41.0 ± 2.0	50.0 ± 2.8	14.4 ± 0.6	485 ± 11	36.5 ± 1.6	50.0 ± 3.8	50.2 ± 2.0	13.0 ± 0.7
Lab S4	38.3 ± 2.9 (A)	42.5 ± 2.9 (A)	14.6 ± 0.6 (A)	465.9 ± 17.0 (A)	37.6 ± 1.6 (A)	43.6 ± 2.0 (A)	39.6 ± 1.7 (N)	13.5 ± 1.0 (A)

In case of soil sample only for ^{226}Ra the result was not acceptable. In this case the value was underestimated, and this could be due to radionuclide interferences with ^{235}U isotope. All the other results passed the trueness and precision criteria.

In all our failure results the relative bias was high, and the acceptability criteria A1≤A2 for trueness was not passed, whereas the acceptability criteria for precision P ≤LAP was passed. In all the above not acceptable results the activity was overestimated. We assume that the overestimation could be due to a mismatch of the net peak area estimation with background subtraction and the need for corrective actions in the analysis process is indicated.

4 Conclusions

The overall performance evaluation results of our laboratory showed a high number of acceptable scores, presented in Tables 1 - 2. For few radionuclides, ^{134}Cs, ^{226}Ra and ^{241}Am, it was indicated the need for corrective actions in the analysis process. In case of ^{241}Am failure could be also due to inaccurate efficiency calibration in gamma-ray spectrometry in the energy range lower than 100keV, difficult to obtained due to the lack of suitable radionuclide standards, as well as to a high background in this low energy region. Also, the correct estimation of the correction coefficient for self-attenuation could be a source of error, especially in our case for ^{241}Am.

Gamma spectrometry analysis is a complex task that requires specific equipment to be used but also a high skill level to achieve accurate analyses with good precision. Multiple factors can affect the precision and accuracy of gamma measurement in samples, such as:

- performance of the detector,
- detector calibration for used geometries,
- matrix sources,
- internal background interference,
- sample characteristics.

As we have mentioned, the accuracy of the measurements could also be affected by the laboratory internal/external background interference and stability of the background.

Based on the lessons learned, to optimize accuracy measurement the laboratory should use an appropriate matrix reference material for quality control and an appropriate self- attenuation correction factor should be applied. In order to assess the precision of gamma analysis, the quality assurance protocol includes regular measurement and records of backgrounds, and should be used to obtain accurate and valid measurements in the mid-and long term.

Moreover, the laboratory will continue to participate to the annually proficiency tests organized by the IAEA or to national intercomparison to achieve traceable, accurate, reliable and comparable measurement result for large set of radionuclides in soil, water, hay or other types of samples.

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