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METHODOLOGY DEVELOPMENT FOR THE DETERMINATION OF GAMMA EMITTING RADIONUCLIDES IN MOSS-SOIL (IAEA-447) AND STATISTICAL EVALUATION OF THE PROFICIENCY TEST RESULTS SUBMITTED TO THE IAEA

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The gamma spectrometry laboratory, Chemistry Division, PINSTECH, participated in the world-wide proficiency test organized by the International Atomic Energy Agency (IAEA) for the determination of radionuclides in moss-soil (IAEA-447). The analysis methodology involved five standards IAEA-RGU-1, IAEA-RGTh-1, 9803SO, 9903SO and 0003SO for the quantification of ^{228}Ac, ^{214}Bi, ^{137}Cs, ^{40}K, ^{212}Pb, ^{214}Pb and ^{234}Th. Although, all of our results were declared acceptable by the IAEA performance evaluation criteria even then we suggest the use of *z*-score, sum of rescaled *z*-score and sum of square of *z*-score as useful indicators.

Keywords: IAEA-447, Moss-soil, Gamma-emitting radionuclides, z-score, Sum of rescaled *z*-score, Sum of square of *z*-score

1. Introduction

Implementation of quality assurance (QA) [1] in a laboratory under ISO 17025 is getting more and more importance with time. QA deals with the organization and functionality of the whole organization including the details about personnel, documents, facilities involved and standard operating procedures. The part of QA, which deals with the measurement process itself, is called quality control (QC). The major aspects of QC are related with the calibration and statistical process control. It also includes the analyses of reference materials and participation in proficiency test exercises [2-4]. Under the proficiency testing scheme the test organizer distributes portions of a material for analysis in the participating laboratories by an unspecified method. The concentration of the analyte is unknown to the participant at the time of analysis. The participant reports the result to the test organizer by a deadline. A report is then issued containing the true or consensus value of the analyte concentration and a summary of the results of all the participants. A score is calculated against each reported measurement that provides an indicator of the accuracy. The primary purpose of proficiency testing is to check accuracy of the method applied and thereby allow participant to detect and subsequently rectify faulty procedures or systematic errors. Accreditation agencies require laboratories to participate in proficiency tests if a relevant one is available, and may take interest in the scores obtained and the documented efforts of the laboratory to reduce notable inaccuracies. Participation in the proficiency tests should not be considered as an alternative to the internal quality control, which should be carried out in every run of analysis.

Gamma-ray spectrometry laboratory of Chemistry Division at PINSTECH is involved in the determination of radioactivity in different media. In the terrestrial environment, soil is the main reservoir of radionuclides and it acts as a medium of migration for the transfer of radioactivity to the biosphere. A reliable determination of natural and artificial radionuclides in soil samples is essential to fulfill with the radiation protection and environmental regulations. International Atomic Energy Agency (IAEA) has a long history of assisting Member States laboratories by producing reference materials and conducting proficiency

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tests. Usually, the participating laboratories are requested to quantify gamma-emitting radionuclides including ^{40}K, ^{134}Cs, ^{137}Cs, ^{208}Tl, ^{210}Pb, ^{212}Pb, ^{214}Pb, ^{212}Bi, ^{214}Bi, ^{228}Ac, ^{234}Th and ^{226}Ra. The participants are informed that they have to report on those radionuclides, which can be measured reliably. The main purpose of this study is to present the methodology for the determination of gamma emitting radionuclides in moss-soil sample provided by the IAEA under the proficiency test IAEA-CU-2009-03 and to statistically compare our results with the results submitted by other participating laboratories.

2. Experimental

2.1. *Proficiency Test Sample*

In this proficiency test, a terrestrial moss-soil material was prepared and distributed by the IAEA. Mosses are considered excellent bio-monitors for fallout radioactivity measurement. The material was collected in 2007 from a deserted red marble mine in “Gerecse Mountain” located on north-west part of Hungary, by the Reference Radiological Laboratory, Ministry of Agriculture and Rural Development Hungarian in collaboration with the Reference Materials Group of the IAEA Terrestrial Environment Laboratory [5]. Both natural and artificial radionuclides from the fall-out were accumulated on this moss-soil for the last 40 years. Hence, the collected mosses with the eroded soil adhered to it, were representing an accumulated history of the radionuclides fall out of the last four decades. Three hundred kg of the collected bulk material was first air dried in an oven and then the bulk sample was milled and homogenized by using a rolling-drum of 300 liters capacity. Bottling of the material was done under normal laboratory conditions and sterilized using gamma ray irradiation with a total dose of 25 kGy using a ^{60}Co source. Finally, 150 g of moss-soil material was sent to each participating laboratory [5].

2.2. *Counting*

After receiving the moss-soil sample from the IAEA, it was transferred to a clean plastic bottle and kept stored for 1 month to attain equilibrium among different daughter products of ^{226}Ra and ^{232}Th series radionuclides. Later, each sample was counted for 16 hrs at 2 cm from the detector top. The background was measured under similar conditions with empty bottle for the same time. All gamma-ray spectra were acquired with a p-type HPGe coaxial detector (Eurisys Mesures, France) of volume 245cm^3, coupled through a 570 spectroscopy amplifier (ORTEC, USA) to Trump PCI 8k ADC/MCA card with GammaVision-32 ver. 6 software (ORTEC). The detector has 60% relative efficiency and 1.95 keV FWHM at 1332 keV γ-ray of ^{60}Co and a peak/Compton ratio of 70:1. The detector was surrounded by a 10 cm thick lead shielding to minimize the room background [6]. All calculations were done in Microsoft Excel 2007 (Microsoft Corp., USA) and Origin Pro 7.5 (OriginLab. Corp., USA).

Detector background plays an important role in setting up the analytical sensitivity or limit of detection of a spectrometer. In the assessment of environmental radioactivity the background must be kept as low as possible. Our laboratory background shows peaks of ^{228}Ac, ^{212}Bi, ^{214}Bi, ^{234m}Pa, ^{212}Pb, ^{214}Pb, ^{226}Ra, ^{208}Tl, ^{40}K, ^{75m}Ge, ^{152}Eu, ^{154}Eu, ^{134}Cs, ^{60}Co and ^{137}Cs [7].

2.3. *Method Validation*

The method was validated by analyzing soil sample 0003SO [QAP-52, Environmental Monitoring Laboratory (EML), US DoE] [8]. The analysis results of 0003SO are shown in Figure 1, which reveals that the EML reference activities are within the 95% confidence interval (coverage factor=2) of the measured activities of all radionuclides, showing good accuracy of the method.

3. Performance Evaluation Methods

To check the performance of a laboratory, a number of rating systems have been developed. The meanings of the evaluation of different scoring systems are not necessarily always comparable. Among various statistics, *z*-score is most often used.

3.1. *z-score*

The *z*-score conveys the same information about accuracy irrespective of the data scale. It is given by

$$z = \frac{x_{reported} - x_{target}}{\sigma_{target}}$$

where x_{target} is the target activity, $x_{reported}$ is the reported activity and σ_{target} is the uncertainty of

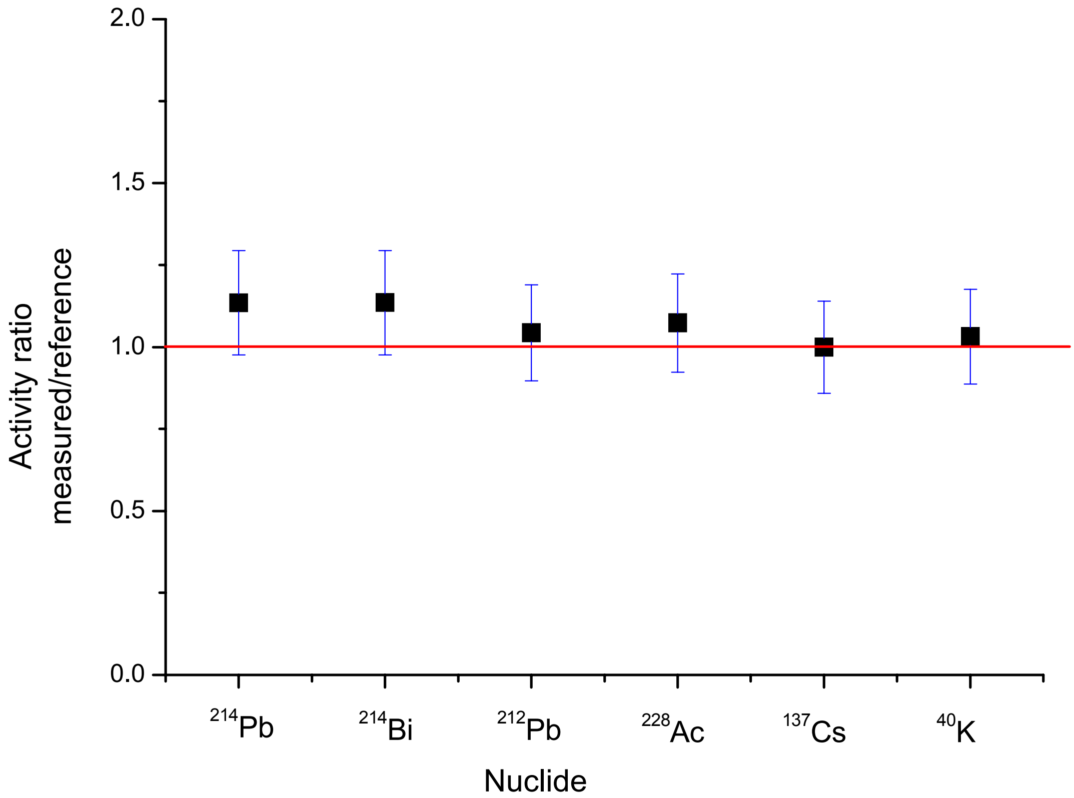

Figure 1. Ratio of activity (measured/reference) with error bars showing coverage factor = 2 for reference soil sample 0003SO (EML, US DoE).

the target value. All *z*-scores within the range ±2 are regarded as fit, whereas scores outside the range ±3 are rejected. The assigned value x_{target}, released only after the deadline for submission of results, is the best available estimate of the true concentration of the analyte. Assigned value is sometimes calculated as the consensus of the participants' results. This value may be inadequate if there is a general bias in the results because of the widespread use of a biased analytical method. The drawback of *z*-scores is that the uncertainty of the participant's measurement result is not taken into account for the evaluation of performance.

3.2. IAEA Performance Evaluation Criteria

The IAEA performance criteria evaluate individual results against combined criteria of trueness and uncertainty measure of the reported activity. A result is acceptable only when both criteria are fulfilled. Trueness and assessment of uncertainty is further explained below.

3.2.1. Trueness

The participant result is assigned acceptable for trueness if:

$$A1 \leq A2$$

$$A1 = \left| x_{target} - x_{reported} \right|$$

$$A2 = 2.58 \times \sqrt{u_{target}^2 + u_{reported}^2}$$

where u_{target} is the uncertainty in target activity and $u_{reported}$ is the uncertainty in reported activity.

3.2.2. Uncertainty Assessment

An estimate of measurement uncertainty, P, is calculated as:

$$P(\%) = \sqrt{\left(\frac{u_{target}}{x_{target}}\right)^2 + \left(\frac{u_{reported}}{x_{reported}}\right)^2} \times 100$$

The Limit of Acceptable Precision (LAP) for each analyte is defined for the proficiency test in advance. A result is scored "acceptable" when P≤LAP.

Although these indicators for individual result furnish useful information, however, a single figure of merit that summarises the overall performance of a laboratory will also be helpful for the assessment of a laboratory's long-term performance. To assign a number to the overall performance of a laboratory, we suggest the combined use of "rescaled sum of *z*-score" [9,10] and "sum of square of *z*-score" [9,10].

3.3. Rescaled Sum of Z-score (RSZ)

The rescaled sum of *z*-score is defined as:

$$RSZ = \sum_{i=1}^{I} z_i \Big/ \sqrt{I}$$

where I is the total number of scores being combined. RSZ is zero-centred with variance I, it is interpreted as standard normal deviates. The RSZ value of 3 or more indicates a significant event, which means a consistent positive or negative bias.

3.4. Sum of Square of Z-score (SSZ)

The sum of square of *z*-score is defined as:

$$SSZ = \sum_{i=1}^{I} z_i^2$$

This score has a chi-squared distribution with I degrees of freedom. If SSZ is higher than the critical value of chi-squared, it indicates the presence of values with big discrepancy.

4. Results and Discussion

4.1. Quantification

In the gamma-ray emitting radionuclides category, the participants were requested to analyze ^{228}Ac, ^{241}Am, ^{214}Bi, ^{137}Cs, ^{40}K, ^{210}Pb, ^{212}Pb, ^{214}Pb, ^{226}Ra, ^{234}Th and ^{208}Tl. Among these radionuclides the ^{241}Am, ^{210}Pb, ^{226}Ra and ^{208}Tl were not quantified by us either because of their small peak areas or the unavailability of reference concentrations. Figure 2 shows gamma-spectrum of the IAEA-447 with the location of different peaks for their corresponding radionuclides. The results alongwith peak energies used for quantification are reported in Table 1. The activities were calculated by relative method using two IAEA standards IAEA-RGU-1 and IAEA-RGTh-1 and three soil standards of Environmental Monitoring Laboratories (EML), US Department of Energy (US DoE), 9803SO, 9903SO and 0003SO. During data compilation step, it was assured that the results from those samples and standards were included which had similar densities. All data with small peak areas or relatively higher uncertainties were also discarded. The final results include uncertainties in weight, peak areas and standards' concentrations. All errors reported in this study are at 1 sigma level and were calculated by using error propagation rules. The reference date for all activities given in this paper is 15th November 2009.

4.2. Performance Evaluation

A total of 266 laboratories from 69 countries participated in this proficiency test. The participants were asked to submit their result in one month period. Among all measurements, 66% were in the acceptable limits, 26% were not acceptable and 8% were acceptable with warning. Our laboratory reported seven gamma emitting radionuclides, which passed the IAEA evaluation criteria as shown in Table 1. We have calculated percentile positions for different radionuclides reported by our laboratory using the relative deviation measure. The analysis places ^{214}Bi and ^{212}Pb at 75th percentile, ^{214}Pb at 71st percentile, ^{40}K at 70th percentile, ^{137}Cs at 65th percentile, ^{234}Th at 62nd percentile and ^{228}Ac at 41st percentile. On the average most of our measurements are at good percentiles in comparison to the world data. The IAEA does not make use of *z*-scores but it suggests a value of $\sigma_{target} = 0.1 \times x_{target}$. We have calculated *z*-scores and included them in Table 1. All our measurements produce *z*-scores within ±2.

Two more statistics *RSZ* and *SSZ* were calculated, as single figure of merit, using the radionuclides data given in Table 1. The *RSZ* for our results was 0.6, which is quite less than the critical value of 3. On the basis of *RSZ* our laboratory stands on 80th percentile among all other laboratories. The *SSZ* for our laboratory was 6.2, which is also less than the critical limit of 14. In comparison to the other participating laboratories our position in *SSZ* score is 74th percentile. On the basis of RSZ and SSZ for all other submitted results show that 127 out of 251 laboratories passed both test.

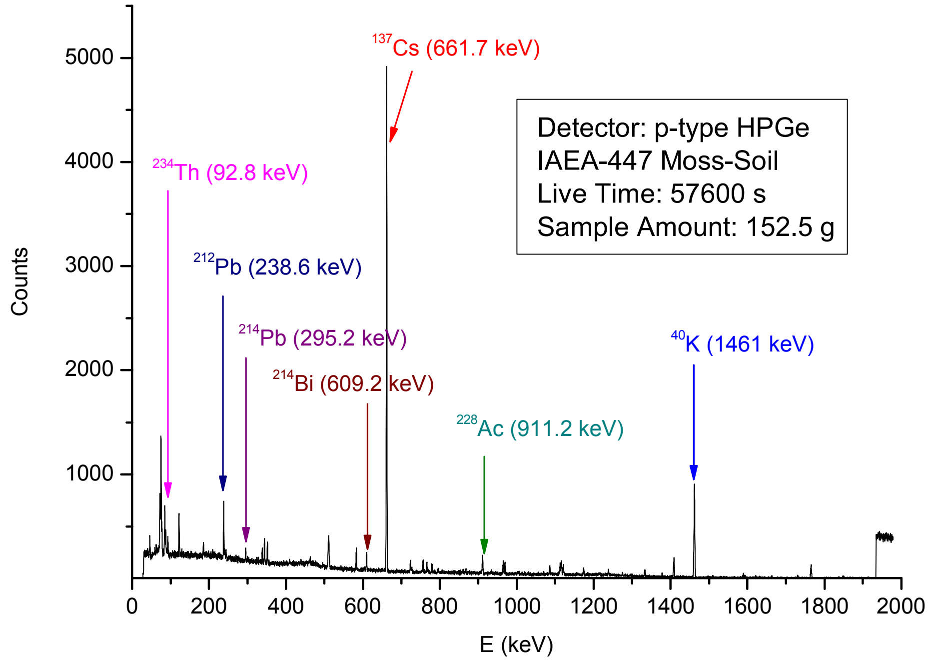

Figure 2. Spectrum of IAEA-447 Moss-Soil showing the main peaks of different radionuclides.

Table 1. Results of our laboratory alongwith peak energies, limit of detection (LoD) and performance evaluation by z-score and by the IAEA criteria.

Nuclides	Energy (keV)	IAEA Value (Bq kg^{-1})	Lab. Value (Bq kg^{-1})	LoD (Bq kg^{-1})	*Z*-score	IAEA score	Percentile position
^{228}Ac	911.2	37.0±2.0	41.1±3.7	4.0±0.2	1.10	Acceptable	41
^{214}Bi	609.2	24.8±2.0	22.5±1.7	14.4±0.9	-0.94	Acceptable	75
^{137}Cs	661.7	425.0±10.0	409.4±13.3	1.0±0.0	-0.37	Acceptable	65
^{40}K	1461.0	550.0±20.0	580.6±20.8	48.2±1.9	0.56	Acceptable	70
^{212}Pb	238.6 300.1	37.0±1.5	39.2±2.3	0.8±0.0	0.60	Acceptable	75
^{214}Pb	295.2 351.9	26.0±2.0	23.7±2.4	7.4±0.9	-0.87	Acceptable	71
^{234}Th	92.8	25.5±3.0	29.6±3.6	6.5±0.6	1.61	Acceptable	62

5. Conclusions

It has been shown that the gamma emitting radionuclides ^{228}Ac, ^{214}Bi, ^{137}Cs, ^{40}K, ^{212}Pb, ^{214}Pb and ^{234}Th can be measured accurately in moss-soil (IAEA-447) if densities of sample and standards are similar. Moreover, uncertainties in peak areas after background subtraction play an important role in establishing accuracy therefore, it should be as low as practically achievable. All our results submitted under this proficiency test were declared acceptable by the IAEA. We have applied z-score criteria and found all our results within ±2, indicating good accuracy. Further analysis using sum of rescaled *z*-score and sum of square of *z*-score indicated very good position of our laboratory in terms of percentile. The overall statistical analysis shows that on average our laboratory performed better than most of the other participating laboratories.

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