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Implementation of Quality Assurance System in Gamma Spectroscopy Laboratory: Best Practice for Accreditation

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Abstract: Based on ISO/IEC-17025 standards for testing and calibration laboratories, a quality assurance system was implemented at the gamma spectroscopy laboratory-at the Lebanese Atomic Energy Commission. Nowadays, routine analyses of natural and artificial gamma emitters in various matrices are performed. The laboratory has been accredited since 2012 by Hellentic Accreditation System (ESYD). All applied analytical procedures are documented. Traceability of the results has been assured through the frequent use of standards and reference materials. Method validation procedure was applied for three sets of gamma spectrometers with High Purity Germanium (HPGe) detectors. Internal validation in terms of accuracy has been achieved using various reference materials and left over proficiency test samples. The accuracy was evaluated by relative bias, repeatability and reproducibility limits, as well as precision estimator. The calculated biases for selected radionuclides were below the Maximum Acceptable Bias (MAB = 15 %). The precision estimator values were conform to the acceptance criteria, as being below acceptable limit of precision (ALP = 20 %.). The detection limit (L_D) and the minimum detectable activity (MDA) were calculated according to Curie formula. Combined and expanded standard uncertainties were calculated. Quality control procedure is applied routinely; data obtained were acceptable based on Shewhart control chart rules. For external validation, the laboratory participates at least twice a year in proficiency tests. Based on the counter measure, the laboratory showed high performance, through the acceptable values of z- score that found to lie between -2 and +2.

Keywords: Method validation, proficiency test, ISO 17025.

1 Introduction

The implementation of quality assurance (QA) in testing laboratories is a total process to guarantee the quality of the laboratory reports, and assure confidence and comparability of their results. It involves all laboratory activities and includes good laboratory practice and proper management skills. The establishment of quality management system (QMS) and quality control procedures (QCP) are the backbone of the QA processes. The implementation of a quality management system according to ISO 17025 is an essential requirement to improve the analytical performance and competence of the laboratory, as well as to increase the credibility, reliability and accuracy of the results through the proper calibration of equipment and application of validated analytical procedures. It includes management and technical requirements. A testing or calibration laboratory should comply with both requirements to prove its competence in the field. The management requirements comprise mainly, but not limited to, full documentation concerning the organization, subcontracting, purchase, internal audits, complaints, and control of records and control of data. The technical requirements are mainly related to the analytical methods applied, such as personnel applying working procedures, equipments used, traceability and track-ability, calibration, handling of standards and reference materials, reporting of results, and corrective and preventive actions [1]. Noting that written procedures should be available covering all practices carried out in the laboratory.

The method validation is a basic technical requirement of ISO 17025 standard [2,3]. It is an essential part of quality assurance system [4]. It makes use of a set of tests that demonstrate whether the method is fit for its intended use [5] as well as to prove the qualification, performance and competency.

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The Gamma Spectroscopy Laboratory at the Lebanese Atomic Energy Commission undergoes routine analyses of natural and artificial gamma emitters in various matrices for various purposes such as service, research and radiation monitoring. The main sample's types that are covered are environmental samples such as soil, air filters, water and sediment; organic dry samples such as cereals, milk powder, rice, wheat, pulses; and organic wet such as fruits and vegetables, dairy products, and meat and poultry. Data obtained are the basic milestone for public dose assessment, economic, legal and environmental radiation management decisions as well as for national laws [6].

Therefore, it has been highly significant to implement a quality management system according to ISO 17025 standards [1,7] in order to improve the overall analytical performance. The goal was achieved and the laboratory was accredited by Hellentic Accreditation System ESYD, Certificate No. 788 dated 20 January 2012. The scope of accreditation included three gamma spectrometers with HPGe detectors. All management and technical requirements are fulfilled. We present hereby the method validation for the standard method using IEC 1452:1995. Internal validation was expressed in terms of trueness, repeatability (within run precision), reproducibility (between run precision), limit of detection, minimum detectable activity and combined uncertainty calculation. Also, a quality control procedure is applied periodically, and shewhart control charts are used to evaluate the results [8]. In this article, data for the gamma spectrometer with HPGe of relative efficiency 50% (set C) will be presented.

For external validation, the gamma spectroscopy laboratory participates on annual base in proficiency tests organized by Analytical Laboratories for the Measurements of Environmental Radioactivity - International Atomic Energy Commission (ALMERA Network- IAEA) and by Mixed Analyte Performance Evaluation Program (MAPEP-DOE-USA). These tests aim to evaluate the laboratory performance for the determination of natural and artificial gamma emitters in environmental samples (mainly soil, vegetation, air filter and water).

2 Materials and Methods

2.1 Samples

Three reference material samples represent different environmental matrices (soil, milk powder and water), were prepared and measured in the adopted fixed counting geometry. A reference milk powder sample (IAEA-152) from the International Atomic Energy Agency was measured as representing organic dry samples and based on $C_6H_{12}O_6$ composition (wheat, milk powder, rice, ...). For soil, sand and sediment samples based on SiO_2 and $CaCO_3$ as composition, a standard multi-gamma -ray emitters sand sample from Eckert and Zeigler (EG-ML-1195-11-1) was measured. While for organic wet samples (vegetations, fruits, etc) based on water H_2O as composition, a left over proficiency test water sample (IAEA-CU-2006-03) was measured. While for routine quality control, the multi-gamma-ray emitters sand and two left over proficiency test samples vegetation and water of code (MAPEP-13-RdV-28) and (IAEA-TEL-2012-04) respectively, were counted and analyzed routinely.

2.2 Measurements

A standard method [9] was applied for the measurements and the analysis using three sets of gamma spectrometers with high purity P-type coaxial germanium detectors (HPGe) of relative efficiency 30%, 40% and 50%. The detectors were connected to standard electronics and the spectra were accumulated in 8K Multichannel analyzer. In order to reduce background radiation the detectors were housed in 10 cm lead shield surrounded by 0.5 cm copper layer to attenuate X-rays emitted by the lead. Energy calibration is carried out routinely, using multi-gamma-ray emitter source, with a tolerance of 0.3 keV. Efficiency calibration and efficiency curves curves for various compositions and densities were performed and corrected for attenuation and absorption. Europium-152 (^{152}Eu) point source was counted routinely to check the performance of the detectors. Two parameters were tested, resolution and full energy peak efficiency (at low and high energies, 122 keV and 1408 keV respectively). Control charts were used to evaluate statistically the data obtained. An empty container was counted periodically to obtain background spectra that were used to correct samples activity concentrations. For quality control and method validation purposes, the counting time was set to be 7 hours with good statistical significance for the gamma-ray energy peaks of the radionuclides of interest in the samples. The spectra were analyzed using Genie 2000 software from Canberra Version V3.1b 2007 that includes peak search, nuclide identification, activity and uncertainty calculation modules.

2.3 Internal Method Validation

The main purpose of the validation is to evaluate and ensure the acceptance of the analytical performance at low, medium and high energy ranges. These were represented respectively by ^{241}Am (59.5 keV), ^{137}Cs (661.7 keV), ^{60} Co (1171.2 and 1332.5 keV) and ^{40}K (1460.8 keV).

Internal method validation was expressed in different parameters. The trueness was used to test the closeness of test result to the accepted value and it was quantified in terms of bias [2,3,6]. Each sample matrix was counted and analyzed at 10 duplicates, in the same counting conditions. The precision parameter was applied to test the closeness of independent test results under stipulated conditions. It was expressed in terms of repeatability and reproducibility limits (r and R), and the precision estimator calculated according as follow [10,11].

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$$\mathrm{P(\%)} = \sqrt{\left(\frac{Unc\ Reference\ Value}{Reference\ Value}\right)^2 + \left(\frac{Unc\ Mean\ Value}{Mean\ Value}\right)^2} \times 100 \qquad (1)$$

For repeatability, the reference sample was counted and analyzed at 10 duplicates under identical conditions. While for reproducibility, it was counted and analyzed at 10 duplicates, but with one parameter changed [5] e.g. operator, counting time, equipment, background spectrum and analysis parameters (fixed tail, resolution, fit singlet and different efficiency file).

The smallest net signal that can be reliably detected was expressed in terms of minimum detection limit (L_D) while the smallest quantified activity concentration was defined as minimum detectable activity (MDA) that is dependent on the counting time, full energy peak efficiency, emission probability, sample mass and decay constant. Curie Formula [12,13] was used to calculate both L_D and MDA as follow:

$$\mathrm{L_D} = K^2 + 2K \times L_c \qquad (2)$$

$$\mathrm{L_D} = 2.71 + 3.29\left(\sqrt{B + \left(\frac{N}{2n}\right)^2 (B_1 + B_2)}\right) \qquad (3)$$

Where,
L_C is the decision Limit
N is the number of channels in the Peak ROI
n is the number of continuum channels on each side
B_1 and B_2 are the sum of counts in the continuum region to the left and right of the peak ROI respectively
B is the sum of B_1 and B_2,
K = 1.645 at 95% confidence level.

$$\mathrm{MDA} = \frac{L_D}{\mathrm{t(sec)} \times \varepsilon \times \mathrm{P}\gamma \times \mathrm{m} \times \mathrm{Kc}} \qquad (4)$$

An essential parameter in method validation is the combined uncertainty. The main sources of uncertainty that were taken in consideration were the net peak area (N), background correction, full energy peak efficiency (ε), emission probability (Pγ) of the corresponding gamma line, the radionuclide half-life ($T_{1/2}$) and sample mass [14]. The combined standard uncertainty of the activity concentration was calculated by "propagation law". It is the square root of the sum of the square of the individual relative standard uncertainty [15,16]. The combined uncertainty is then multiplied by a constant factor K=2 at 95% Confidence Level to calculate the expanded uncertainty.

2.4 Quality Control and Control Chart

Another tool for internal validation and for checking the reliability of results was the statistical analysis of measurements using acceptance control charts [8,17-19]. A quality control procedure was applied since 2007, through the periodic measurement and analysis of reference samples in the same counting conditions as the samples to be analyzed. Shewhart control charts were used to evaluate the results obtained. The chart was established through the determination of the mean value of repeated measurements, minimum 20, which represent the central line. In case of certified reference materials, the upper and lower action levels were settled to be the certified confidence levels. For left over proficiency test samples, the upper and lower warning levels are settled to be the mean value ± 2 standard deviation, while the upper and lower action levels were the mean value ± 3 standard deviation. This was applied for many years to the three sets of gamma spectrometers with high purity germanium detectors. Data the set with HPGe detector of relative efficiency 50% are presented here.

2.5 External method Validation

Regular participation in proficiency tests, minimum twice a year, was achieved based on the determination of various gamma emitters in different sample matrices. The laboratory performance and data are considered satisfactory for z-score between -2 and +2, and unsatisfactory for outside the range from -3 to +3 [6,11,20]. Z score values from 2006 till 2016 for different radionuclide in soil, vegetation and water samples are presented.

3 Results and Discussion

While applying performance test procedure, two parameters were tested; the resolution expressed in terms of full width at half maximum (FWHM) and the full energy peak efficiency. Results at low and high energy ranges were evaluated statically using control charts. Results for the year 2016 were presented in figure 1 and figure 2 respectively, where the central line is the average value of the data collected in previous year, and the upper and lower warning levels are the average ± 2standard deviation while the upper and lower action levels are the average ± 3standard deviation. Based on shewhart control chart all data of the performance test, were acceptable except one point that lied out of 3δ in resolution control chart. In this case, according to written procedures available at the laboratory, a non-conforming case was reported to the quality manager and a study for root-cause analysis was done according to the corrective actions instruction and the control of non-conforming work instruction. The reason of the non-

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conformity was attributed to preamplifier troubleshooting caused by moisture accumulation. The corrective actions taken were the decrease of high voltage, turning off the system, and drying the preamplifier chamber. After that the system was run again, energy calibration was carried out, performance test was repeated and acceptable data were obtained.

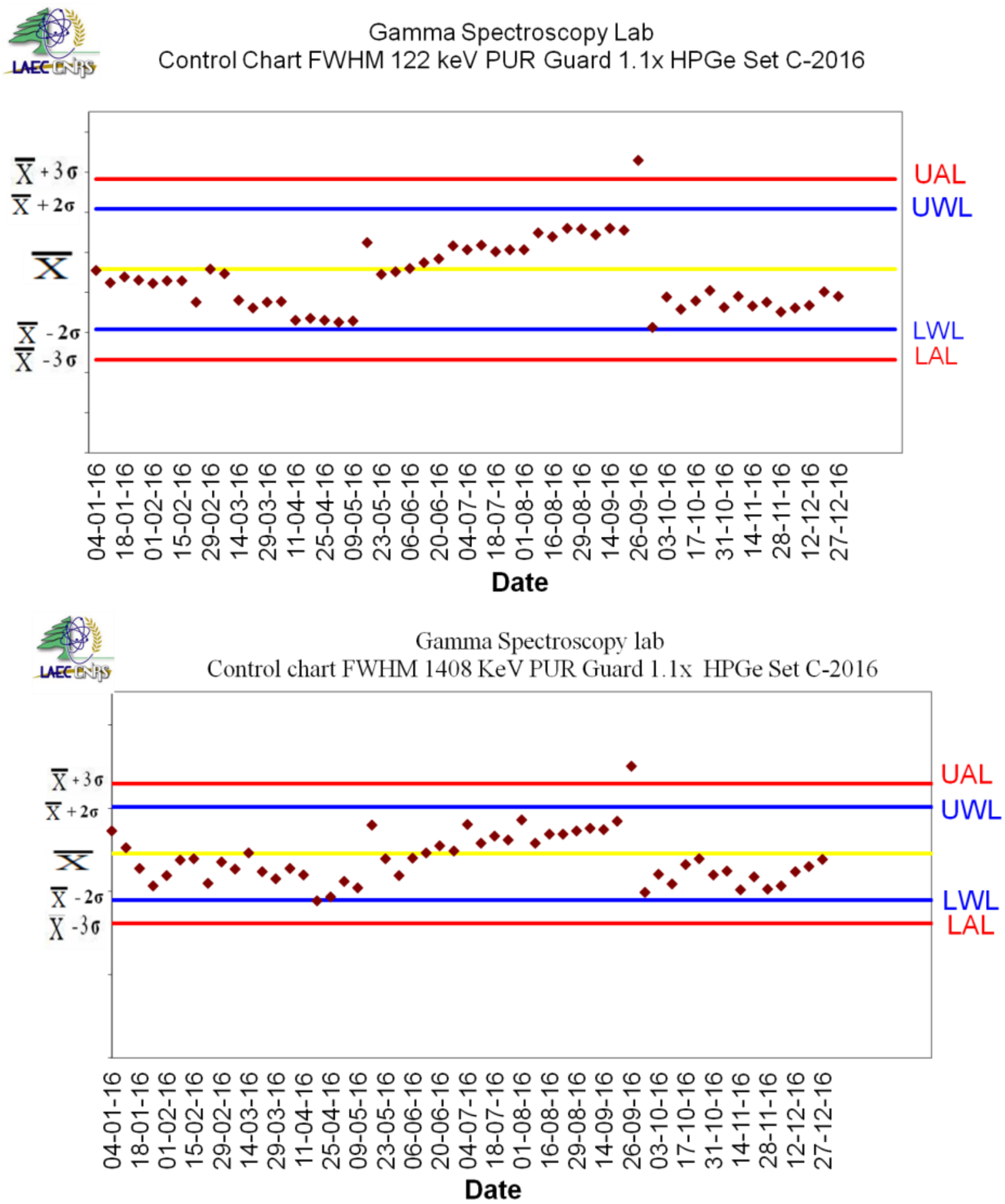

Figure 1. Resolution (FWHM) at low (122 keV) and high (1408 keV) energy using Eu-152 point source

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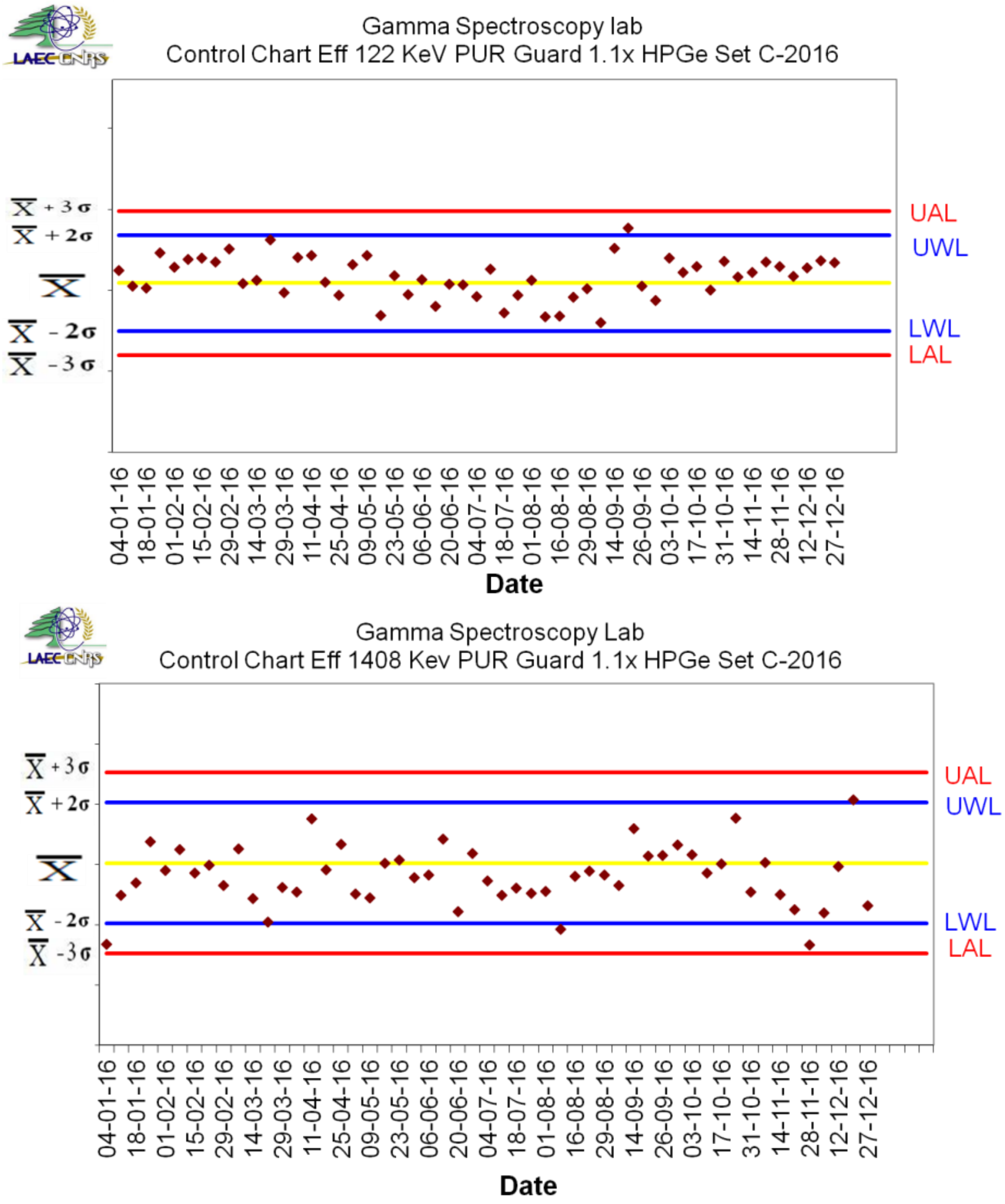

Figure 2. Full energy peak efficiency at low (122keV) and high (1408 keV) energy using Eu-152 point source

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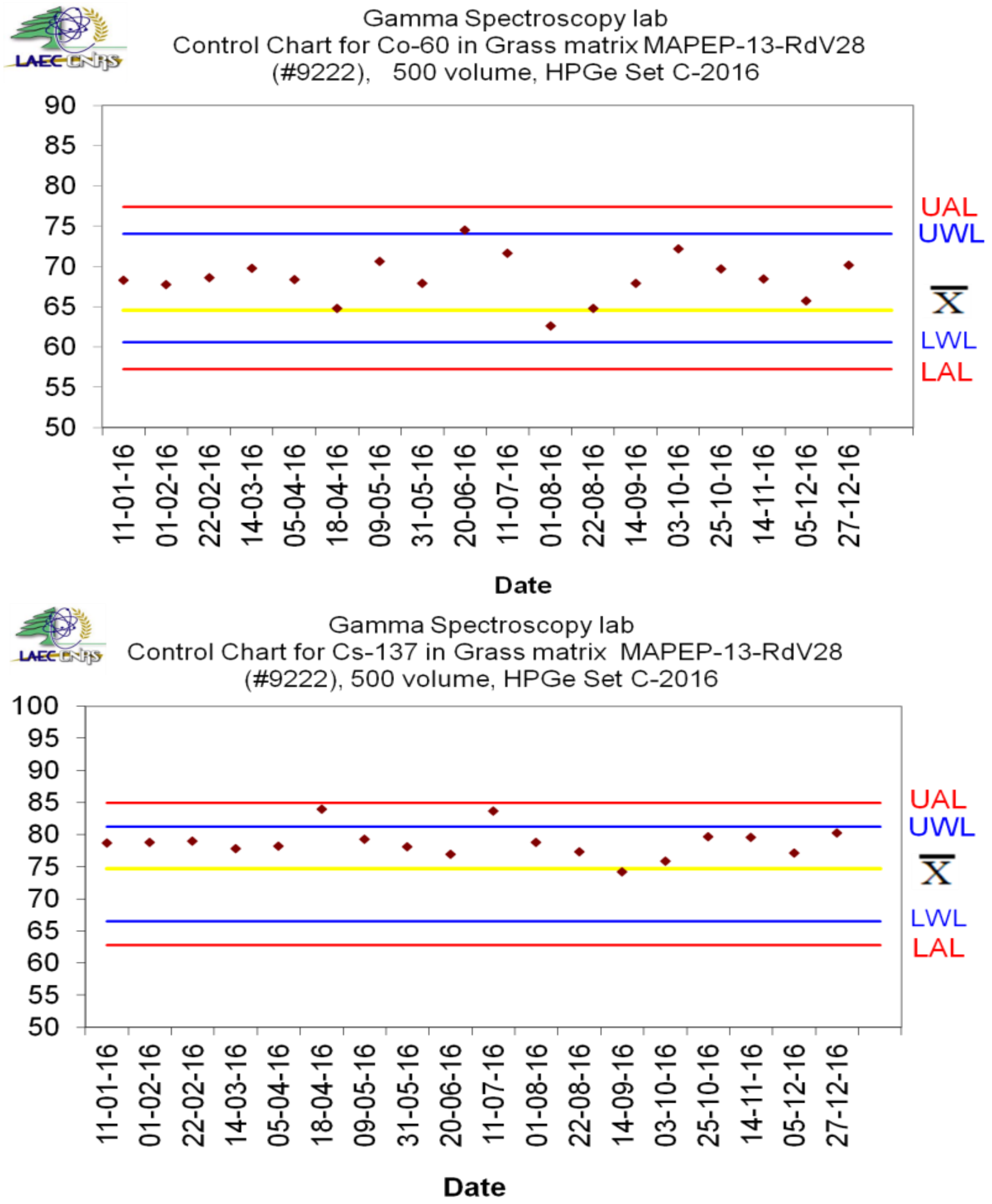

Figure 3. Control chart for ^{137}Cs and ^{60}Co in grass sample

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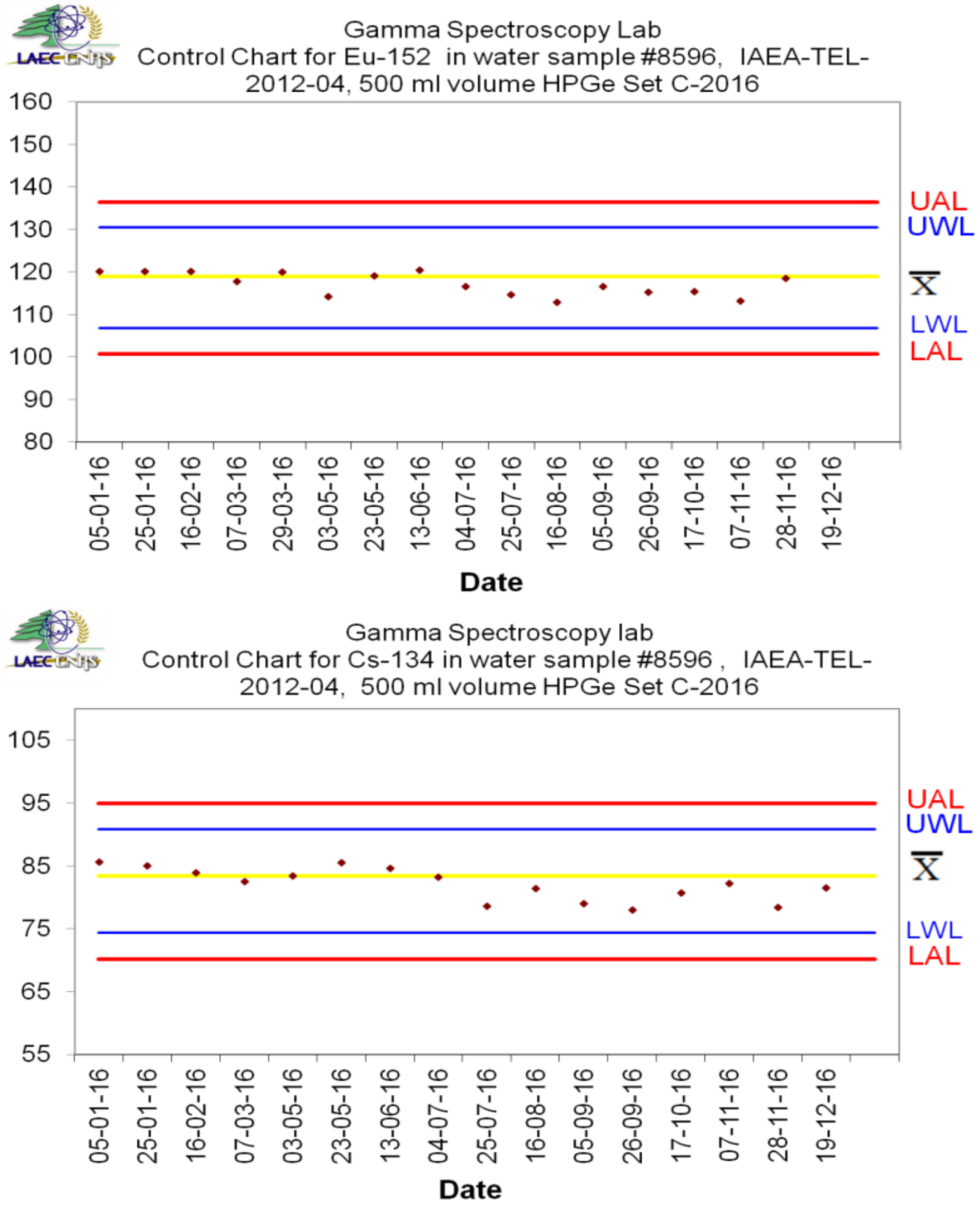

Figure 4. Control chart for ^{134}Cs and ^{152}Eu in water sample

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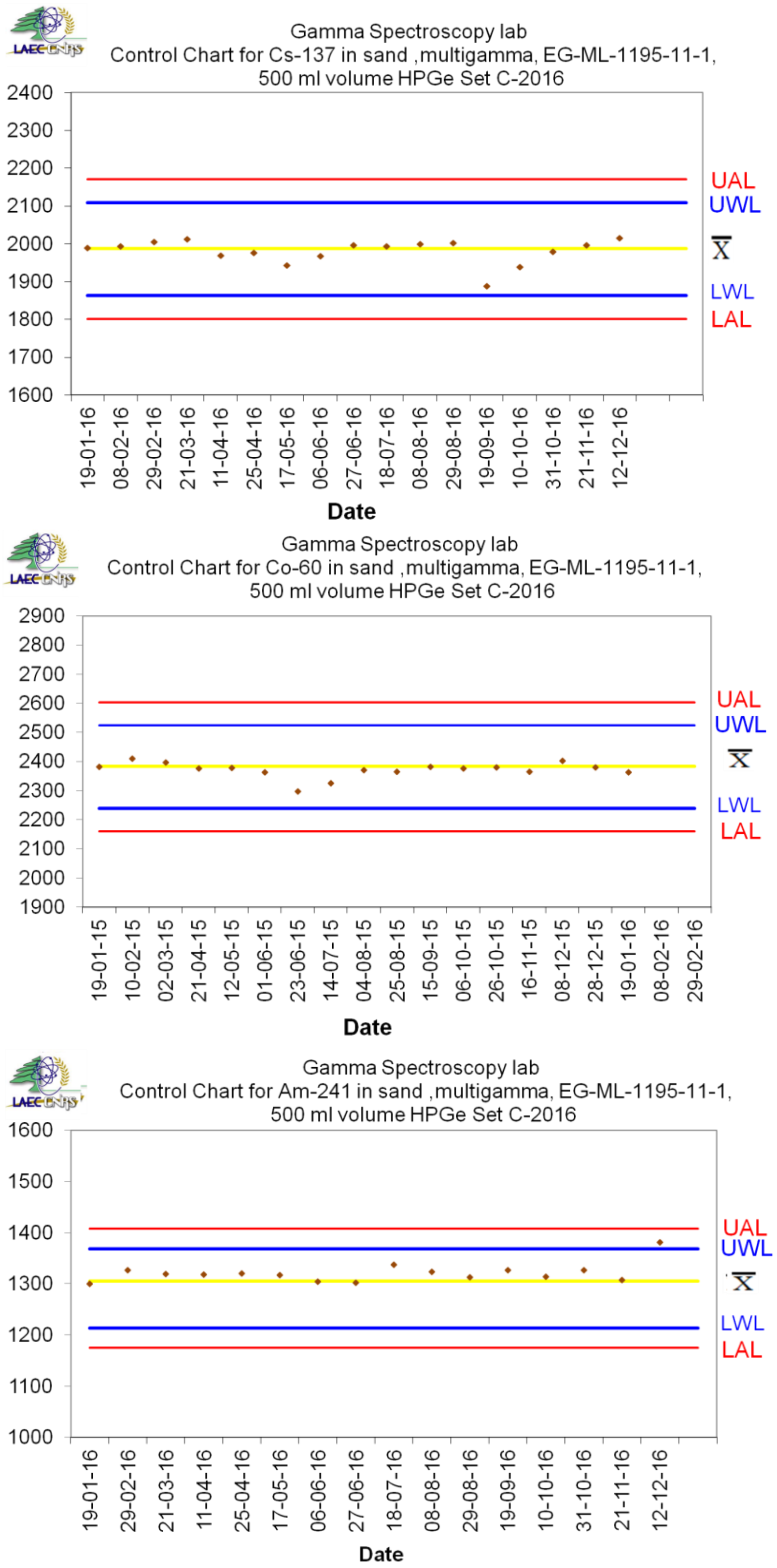

Figure 5. Control chart for ^{137}Cs and ^{60}Co and ^{241}Am in sand sample

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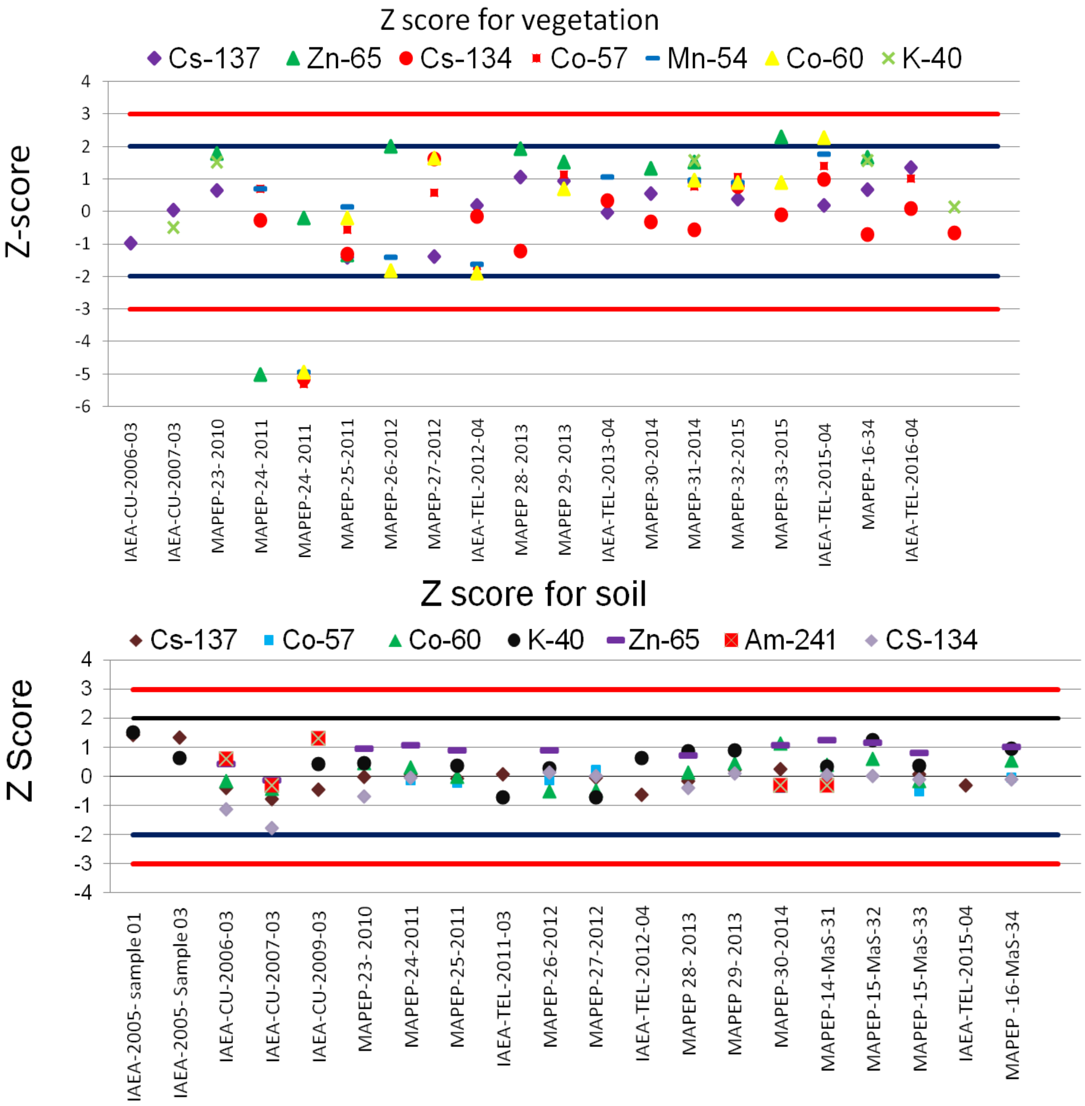


Figure 6. Z score values for vegetation and soil samples

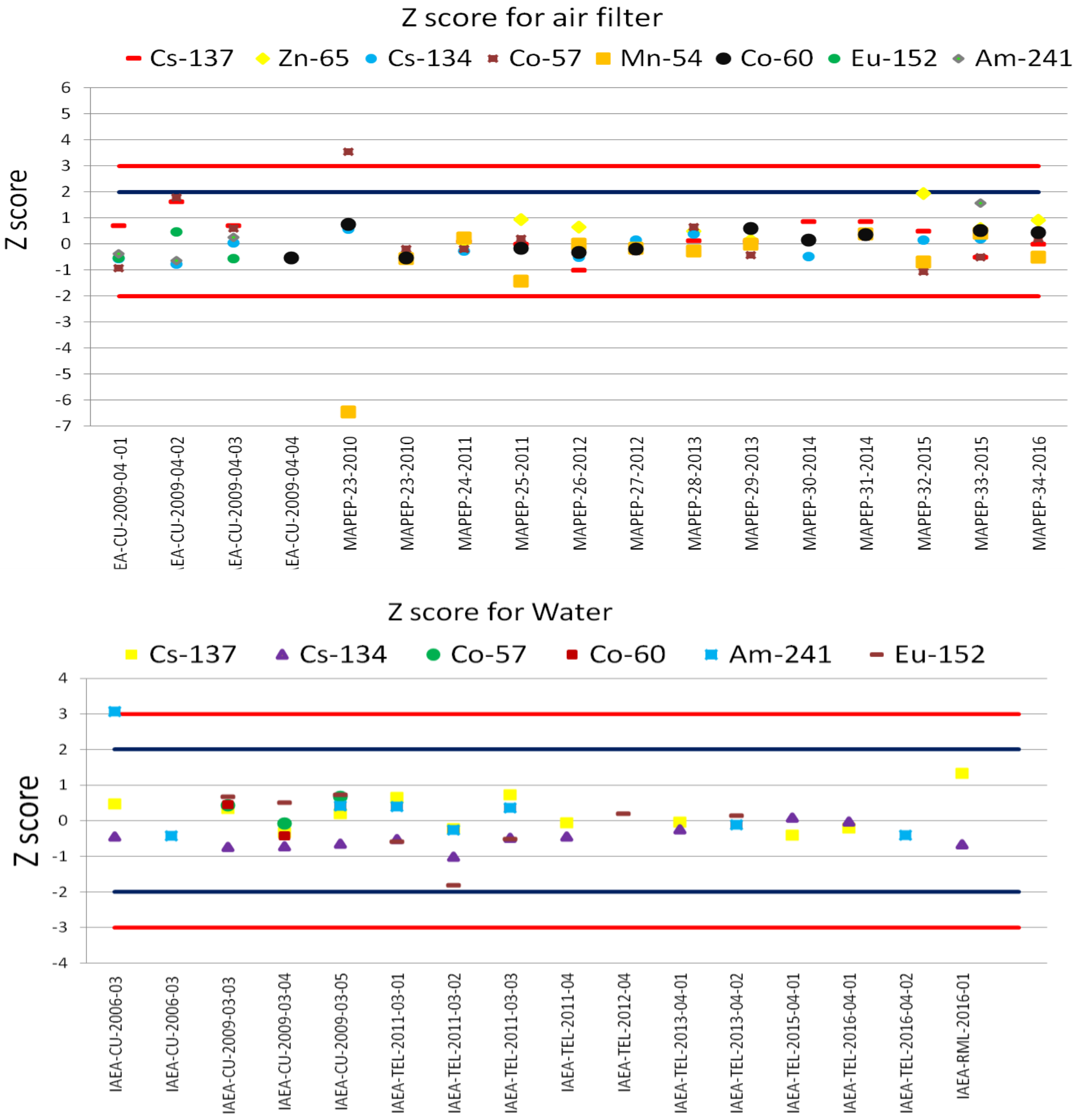
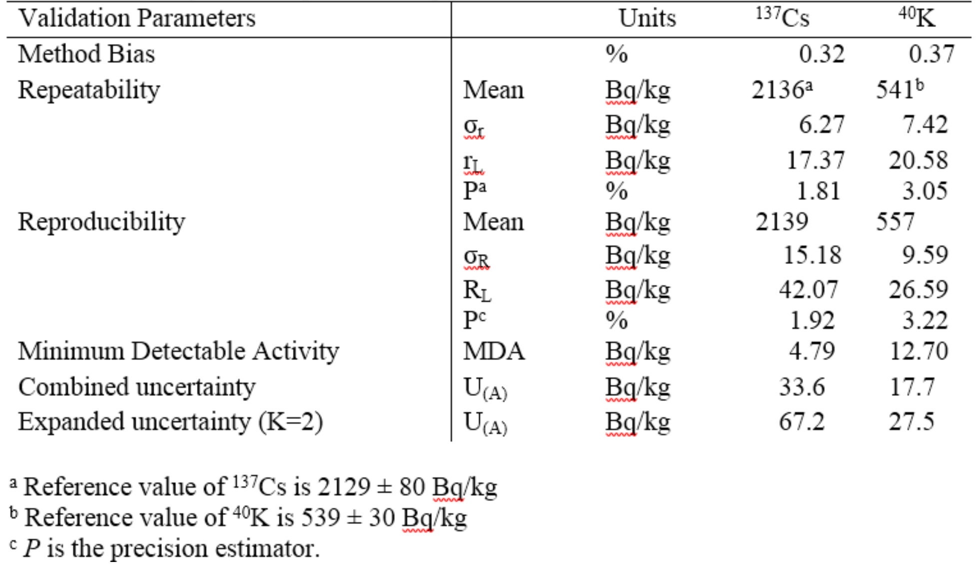


Figure 7. Z score values for air filters and water samples

Table 1. Validation parameters for gamma spectrometer with HPGe set C of 50 % relative efficiency for milk powder sample IAEA-152



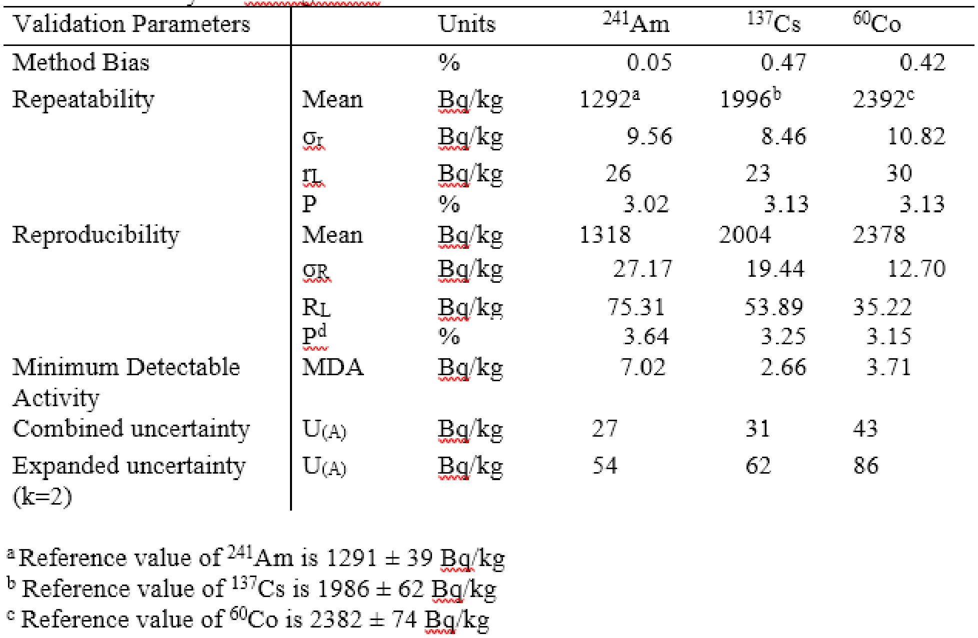
Validation Parameters		Units	^{137}Cs	^{40}K
Method Bias		%	0.32	0.37
Repeatability	Mean	Bq/kg	2136[a]	541[b]
	σ_r	Bq/kg	6.27	7.42
	r_L	Bq/kg	17.37	20.58
	P[a]	%	1.81	3.05
Reproducibility	Mean	Bq/kg	2139	557
	σ_R	Bq/kg	15.18	9.59
	R_L	Bq/kg	42.07	26.59
	P[c]	%	1.92	3.22
Minimum Detectable Activity	MDA	Bq/kg	4.79	12.70
Combined uncertainty	$U_{(A)}$	Bq/kg	33.6	17.7
Expanded uncertainty (K=2)	$U_{(A)}$	Bq/kg	67.2	27.5

[a] Reference value of ^{137}Cs is 2129 ± 80 Bq/kg

[b] Reference value of ^{40}K is 539 ± 30 Bq/kg

[c] *P* is the precision estimator.

Table 2. Validation parameters for gamma spectrometer with HPGe set C of 50 % relative efficiency for multigamma sand EG-ML-1195-11-1



Validation Parameters		Units	^{241}Am	^{137}Cs	^{60}Co
Method Bias		%	0.05	0.47	0.42
Repeatability	Mean	Bq/kg	1292[a]	1996[b]	2392[c]
	σ_r	Bq/kg	9.56	8.46	10.82
	r_L	Bq/kg	26	23	30
	P	%	3.02	3.13	3.13
Reproducibility	Mean	Bq/kg	1318	2004	2378
	σ_R	Bq/kg	27.17	19.44	12.70
	R_L	Bq/kg	75.31	53.89	35.22
	P[d]	%	3.64	3.25	3.15
Minimum Detectable Activity	MDA	Bq/kg	7.02	2.66	3.71
Combined uncertainty	$U_{(A)}$	Bq/kg	27	31	43
Expanded uncertainty (k=2)	$U_{(A)}$	Bq/kg	54	62	86

[a] Reference value of ^{241}Am is 1291 ± 39 Bq/kg

[b] Reference value of ^{137}Cs is 1986 ± 62 Bq/kg

[c] Reference value of ^{60}Co is 2382 ± 74 Bq/kg

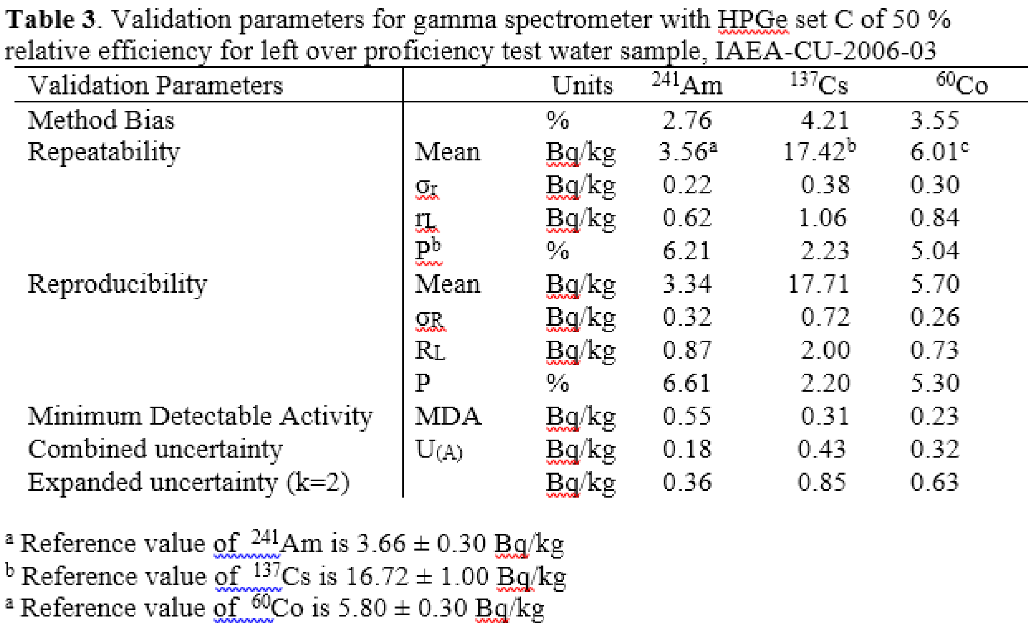


Table 3. Validation parameters for gamma spectrometer with HPGe set C of 50 % relative efficiency for left over proficiency test water sample, IAEA-CU-2006-03

Validation Parameters		Units	^{241}Am	^{137}Cs	^{60}Co
Method Bias		%	2.76	4.21	3.55
Repeatability	Mean	Bq/kg	3.56[a]	17.42[b]	6.01[c]
	σ_r	Bq/kg	0.22	0.38	0.30
	r_L	Bq/kg	0.62	1.06	0.84
	P^b	%	6.21	2.23	5.04
Reproducibility	Mean	Bq/kg	3.34	17.71	5.70
	σ_R	Bq/kg	0.32	0.72	0.26
	R_L	Bq/kg	0.87	2.00	0.73
	P	%	6.61	2.20	5.30
Minimum Detectable Activity	MDA	Bq/kg	0.55	0.31	0.23
Combined uncertainty	$U_{(A)}$	Bq/kg	0.18	0.43	0.32
Expanded uncertainty (k=2)		Bq/kg	0.36	0.85	0.63

[a] Reference value of ^{241}Am is 3.66 ± 0.30 Bq/kg

[b] Reference value of ^{137}Cs is 16.72 ± 1.00 Bq/kg

[a] Reference value of ^{60}Co is 5.80 ± 0.30 Bq/kg

The internal validation data for three matrices milk powder, sand and water are shown in table 1, table 2 and table 3 respectively. Validation parameters for different radionuclides designating the low, medium and high energy ranges were calculated and presented. All bias values for different matrices were acceptable as being lower than the Maximum Acceptable Bias (MAB=15%). The percentage precision estimators under repeatability and reproducibility conditions were lower than the Acceptable Limit of Precision (ALP = 20%). The values of minimum detectable activity obtained for the radionuclides of interest were found to be lower than the pre-established background levels in the Lebanese environment.

For the quality control procedure, obtained activity concentrations of radionuclides of interest were evaluated statistically based on Shewhart control charts rules stated in the corresponding working procedure and in the ISO standards 8258 and 7966. Data for grass, water and sand were presented in figures 3, 4 and 5 respectively. All values were acceptable as no one lies outside the upper and lower action levels, and hence the requirement of shewhart control chart is fulfilled.

The performance of the laboratory was assessed based on z score values obtained for various radionuclides, analysed in different matrices for each proficiency tests. These covered low, medium and high energy ranges. The z score since 2005 till 2016 for vegetation and soil were represented in figure 6, while those for air filter and water were shown in figure 7. The laboratory showed high performance as all values lied between -2 and +2. In 2010, the results of ^{57}Co and ^{54}Mn were not acceptable in air filter. After investigation, the efficiency curve should be corrected at low and high energy. This was carried out and the analysis is repeated and conformed data were obtained as shown in figure 7. As well, in 2011, the results of all radionuclides in vegetation were not acceptable, Z score below -3. According to the non-conforming procedure and corrective actions procedures, non conforming form was filled and root-cause analysis was carried out. The reason was personnel mistake, the mass of the sample was entered wrong and hence the activity concentration in Bq kg^{-1} was not acceptable. The analysis was repeated with the correct mass and acceptable result was obtained.

4 Conclusion

Quality assurance is essential tool to assure confidence and increase reliability and accuracy of results. Management and technical requirements of ISO 17025 should be fulfilled. The principles of validation as described in EURACHEM Guide could be applied to gamma spectroscopy and other nuclear analytical techniques. The main goal of method validation is to verify that the method used fits to its intended use. Both internal and external validations are necessary to increase the reliability and accuracy of results as well as to prove the performance and credibility of the laboratory.

References

[1] ISO/IEC-17025. *General Requirements for the Competence of Testing and Calibration Laboratories. International Organization for Standardization*, Geneva, Switzerland: 28 pp, 2005

[2] I. Taverniers, M. De Loose, and E.V. Bockstaele, Trends in quality in the analytical laboratory. II. Analytical method validation and quality assurance. *Trends Anal. Chem.*, 23(8): 535-552, 2004

[3] M. Thompson, S.L.R. Ellison, and R.Wood, Harmonized guidelines for single- laboratory validation of methods of analysis IUPAC Technical Report, *Pure Appl.*

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Chem., 74 (5), 835-855, 2002

[4] Z. Ahmad, M.W. Yii and A.K. Ishak, *Method of software validation for ^{137}Cs and ^{226}Ra activity measurements in environmental samples using gamma spectrometry system*, in Validation procedures of software applied in nuclear instruments, IAEA-TECDOC-1565, International Atomic Energy Agency, Vienna, Austria: 55-63, 2007

[5] B. Magnusson, and U.Ornemark, *Eurachem Guide: The Fitness for Purpose of Analytical Methods − A Laboratory Guide to Method Validation and Related Topics*, second edition, 70 pp, 2014

[6] A. Shakhashiro, U.Sansone, P.Martin, Z.Makarewic, and A. Mohaghehi, *Report on the IAEA-CU-2006-08 proficiency test on the determination of gamma emitting radionuclides in seawater*, International Atomic Energy Agency, Vienna, Austria, 71 pp, 2007.

[7] S.J. Parry, Quality assurance in the nuclear sector. *Radiochim. Acta*, 100 (8-9): 495-501, 2012

[8] M.S. Al- Masri, A. Shakhashiro, and Y.A Aba, Method validation procedures for environmental radiochemical measurements at AECS, *Accredit Qual Assur*, 9 (6): 361-368, 2004

[9] IEC 1452:1995 – *Nuclear instrumentation-Measurement of gamma-ray emission rates of radionuclides – calibration and use of germanium spectrometers*, International Electrochemical Commission, Geneva, Switzerland, 192 pp, 1995

[10] ISO 5725-4, *Accuracy (trueness and precision) of measurement methods and results- Part 4: Basic methods for the determination of the trueness of a standard measurement method*, International Standards Organization, first edition, Geneva, Switzerland, 23 pp. 1994

[11] IAEA, *Analytical quality in nuclear applications No 22. IAEA/AQ/22 Worldwide open proficiency test: Determination of natural and artificial radionuclides in Moss- soil and water IAEA-CU-2009-03*. International Atomic Energy Agency, Vienna, Austria, 261pp, 2012

[12] L.E. De Geer, Currie detection limits in gamma –ray spectroscopy. *Appl. Radiat. Isotopes*, 61: 51-61, 2004

[13] M. Herranz, R. Idoeta, and F. Legarda, Evaluation of uncertainty and detection limits in radioactivity measurements. *Nucl Instr Meth Phys Res A*, 595: 526-534, 2008

[14] C. Dovlete, and P.P. Povinec, *Quantification of uncertainty in gamma-spectrometric analysis of environmental samples*, in Quantifying Uncertainty in Nuclear Analytical Measurements, IAEA-TECDOC-1401, International Atomic Energy Agency, Vienna, Austria: 103-126, 2004

[15] Joint Committee for Guides in Metrology (JCGM/WG 1), *Evaluation of measurement data — Guide to the expression of uncertainty in measurementGUM*, 134 pp. 2008.

[16] K.Heydorn, Evaluation of the uncertainty of environmental measurements of radioactivity, *Radioanal. Nucl. Chem.*, 262 (1): 249-253, 2005.

[17] H. Hovind, B. Magnusson, M. Krysell, U. Lund, and I. Makinen, *Nordtest Report TR 569 : Internal quality control – Handbook for chemical laboratories*, fourth edition, Nordic Innovation Centre, Stensberggata, Norway, 52 pp, 2011

[18] ISO 7966, *Acceptance control charts*, first edition, International Organization for Standardization, Geneva, Switzerland, 22 pp, 1993.

[19] ISO 7870-2, *Control charts- General guide and introduction*, first edition, International Organization for Standardization, Geneva, Switzerland, 44 pp, 2013.

[20] M. Thompson, S.L.R. Ellison, and R. Wood, The international harmonized protocol for the proficiency testing of analytical chemistry laboratories. IUPAC Technical Report. *Pure Appl. Chem.*, 78 (1): 145-196, 2006