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Gamma Spectrometric Method Validation for the Measurements of ^{40}K and ^{137}Cs in the Milk Powder

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Abstract: In this study, gamma spectrometric method validation of the ^{40}K and ^{137}Cs in the milk powder was investigated. Each component of the method validation is evaluated and quantified. For this purpose, HpGe detectors with 20% efficiency n-type and 150% efficiency p-type were used.

Süt Tozundaki ^{40}K ve ^{137}Cs Ölçümleri için Gama Spektrometrik Metot Validasyonu

Anahtar Kelimeler
Gama spektrometri,
Metot validasyonu,
Süt tozu,
^{40}K,
^{137}Cs

Özet: Bu çalışmada, süt tozundaki ^{40}K ve ^{137}Cs'nin gama spektrometrik metot validasyonu araştırılmıştır. Metot validasyonun her bir parametresi değerlendirilmiş ve belirlenmiştir. Bu amaçla, %20 verimli n-tipi ve %150 verimli p-tipi HPGe dedektörler kullanılmıştır.

1. Introduction

Performance and suitability of the equipment, method or system is important for nuclear analytical laboratories. Method performance in the nuclear analytical laboratories depends on the laboratory conditions, equipment, chemical standards, operator experience, and sample matrixes. Method used in an nuclear analytical laboratory must be evaluated and tested to ensure that obtained results valid and suitable for their intended purposes. For the reliable, precise, accurate, traceable and inter-comperable measurements, method validation process can be applied to the nuclear analytical method.

Method validation, with the well documentation, is a measurement procedure for the determination of the performance and suitability of the equipment, method or system for the accordance with aims, scopes and standards [1]. Method validation is a necessity for laboratories which aiming for accreditation. Before routine analysis application, method which will be used in laboratory must be validated and documented by the laboratory person in accordance with the laboratory conditions. Method validation must carried on when new method developed, a parameter changed in method, method used in laboratory for the first time, validated method used in different laboratory. Validation parameters must be determined depending on the aim and the scope of the applied method. The general validation parameters are specificity, detection limit, ruggedness (reproducibility), bias (accuracy), precision (repeatability), and robustness [2].

Gamma spectrometric method is well-established radioanalytical method. Wide variety of the radionuclide, energy range, radioactivity concentration level, sample shape and sample composition of the naturally occurring and artificial radionuclides can be measured with the gamma spectrometric technique. Main purpose of the gamma spectrometric technique is to determine the radioactivity concentration and measurement uncertainty of the gamma-emitting radionuclide [3, 4, 5, 6].

In this study, gamma spectrometric method validation of the ^{40}K and ^{137}Cs measurements in the milk powder is investigated. Each method validation parameter is evaluated and quantified. For this purpose, n-type 20% efficiency and p-type 150% efficiency HPGe detectors were used.

2. Material and Method

The IAEA-154 and IAEA-152 certified milk powder standards were put into analysis containers and

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weighed. Each container had 6x5 cm (diameter x height) dimension. The spectrometers which n-type 20% efficiency and p-type 150% efficiency HPGe detectors were used for the radioactivity measurements. Energy calibration was done by using ^{241}Am, ^{137}Cs and ^{60}Co standard point radioactive sources. For the determination of the background effects, an empty analysis container counted in the same counting geometry as the samples.

Standard comparison method used to determine radioactivity concentrations. For this purpose, IAEA-152 standard reference material was used as a standard. The activity concentration of ^{40}K was calculated by using 1460.8 keV photopeak. The activity concentration of ^{137}Cs was determined from 661.7 keV photopeak. Minimum detectable activity (MDA) calculations were performed by using the Curie-MDA standard expression [7]:

$$MDA = \frac{L_D}{\varepsilon \cdot \gamma \cdot t_s \cdot m \cdot C_1 \cdot C_2 \cdot C_3 \cdot C_4 \cdot C_5}$$

$$L_D = 2.71 + 3.29 \cdot \sqrt{\left[B \cdot \left(1 + {}^{n}/_{2m}\right)\right]} \qquad (1)$$

where
L_D is the detection limit of the system,
ε is efficiency,
γ is the gamma emission probability,
t_s is measurement time,
m is dried sample weight,
B, n, and m are background area, gross count peak region channel number and background channel number respectively,
C_1 is the correction factor for nuclear decay from sample collection to the start of the measurement,
C_2 is the correction factor for nuclear decay during counting period,
C_3 is the self-attenuation correction factor,
C_4 is the correction factor for pulse losses due to random summing,
C_5 is the coincidence correction factor.

Precision/Repeatability

Precision or repeatability is closeness of the results of successive measurements carried out under the same conditions of measurement. In the precision measurements person, measuring instrument, measurement procedure, location, laboratory conditions are the same and successive measurements carrying out short period of time [8]. Repeatability is the reliability of the measurement results and is the essential parameter of the quality system, validation of the method and uncertainty budget. Additionally, precision is the random error and expressed as the standard deviation(s) or the percent relative standard deviation.

Specificity

Specificity is the distinguishability of radionuclide to be measured from other radionuclides available in the matrix. Specificity is important for the quality of the gamma spectrometric analysis results. For accurate, precise and reliable radioactivity measurement, specificity must be taken into account. The specificity of the detection system is determined by using the IAEA-154 milk powder standard, which contains both ^{137}Cs and ^{40}K radionuclides. Gamma spectrometer has been calibrated in 30-2000 keV energy regions. ^{137}Cs and ^{40}K radionuclides gamma-ray energies are within this energy region. There is no interference with the ^{137}Cs and ^{40}K radionuclide gamma-rays.

Bias/Accuracy

Accuracy is the closeness of the true radioactivity concentration with the result from average of the repeated measurements. Accuracy is the systematic error (bias). The relative bias between the measured value and the target value is expressed by the following equation

$$Bias(relative) = \frac{A_s - A_{ref}}{A_{ref}} \times 100\% \qquad (2)$$

The accuracy of the measurement can also be evaluated with Z-score.

$$z = \frac{A_s - A_{ref}}{s^*} \qquad (3)$$

$$s^* = 1{,}483 \cdot median\ of\ \left|A_s - A_{ref}\right|$$

where A_s is the measured radioactivity value, A_{ref} is reference radioactivity value. When $z < 2$, the quality of measurement is satisfactory.

Robustness

Experimental conditions in the laboratory may change while applying the method. Minor changes in the experimental conditions affect measurement results. These minor changes determine robustness of the method. Robustness is a degree of the sensitivity of gamma spectrometric method in the presence of minor differences in the experimental conditions.

Ruggedness/Reproducibility

Ruggedness or reproducibility is closeness of results of measurements carried out under changed conditions of measurement - reference standard, method of measurement, measuring instrument, operator, location, conditions of use, time-. Ruggedness is a measure of the method performance under changed conditions. The ruggedness or reproducibility of the method was determined by using different equipment. [8].

Limit of Detection

The detection limit is the minimum number of the counts that can be measured confidently. The detection limit is also the minimum activity that can be measured with in a confidence level. Curie-MDA standard expression was used to calculate detection limit. MDA was calculated by using the Curie-MDA standard expression in Equation 1.

3. Results and Discussion

Precision/Repeatability

Ten consecutive measurements were carried out for the precision/repeatability measurements. Statistical two-tail student t-test applied to the obtained results. Measured average ^{137}Cs radioactivity concentration was 3735.0 Bq/kg. t-value was found to be -1.01 which less than t_{crit} value.

Average ^{40}K radioactivity concentration measured as 1580.4 Bq/kg. t-value was 1.06 which less than t_{crit} value. Repeatability condition is fulfilled and measurement repeatable. Statistical two-tail student t-test results of the ^{137}Cs and ^{40}K activity measurements are shown at Table 1.

Table 1. Statistical student two-tail t-test results of the ^{137}Cs and ^{40}K activity measurements (Bq/kg)

	^{137}Cs		^{40}K
1	3763.9		1588.6
2	3778.4		1568.6
3	3766.8		1575.1
4	3742.3		1577.2
5	3735.1		1550.9
6	3764.6		1590.2
7	3691.9		1568.1
8	3641.4		1602.1
9	3727.9		1595.8
10	3738.1		1587.7
Mean	3735.0	Mean	1580.4
Std. Dev.	41.3	Std. Dev.	15.4
Ref. Value	3749	Ref. Value	1575
t	-1.01	t	1.06
t_{crit}	1.83	t_{crit}	1.83
RSD	0.011	RSD	0.0097
%RSD	1.10	%RSD	0.97

Specificity

IAEA-154 standard contains ^{137}Cs and ^{40}K radionuclides. ^{137}Cs has 661.65 keV and ^{40}K has 1460.82 keV gamma energies. Ten consecutive measurements were carried out for the specificity measurements. Energy line, FWHM (Full Width at Half Maximum) values of the ^{137}Cs and ^{40}K are shown at Table 2.

The small energy line shift for ^{40}K and ^{137}Cs may be due to the environmental effect, system stability, interaction of the high energy gamma-ray with the active volume of the detector, etc. Generally, up to 1 keV energy line shift is acceptable and this shift is negligible. As can be seen, ^{137}Cs and ^{40}K radionuclide in the sample could easily be identified with the help of related energy line. Although there was the small energy line shift, method was able to identify and specify intended radionuclides with their related gamma ray energies.

Table 2. Energy line and FWHM of the ^{137}Cs and ^{40}K

	^{137}Cs		^{40}K	
	Energy	FWHM	Energy	FWHM
1	661.65	1.85	1460.94	2.27
2	661.66	1.63	1460.88	2.00
3	661.66	1.72	1460.94	2.21
4	661.66	1.86	1460.92	2.29
5	661.65	1.88	1460.91	2.31
6	661.66	1.83	1460.93	2.25
7	661.68	1.89	1460.85	2.38
8	661.67	1.60	1460.85	2.26
9	661.67	1.62	1460.99	2.00
10	661.70	1.90	1461.00	2.39

Bias/Accuracy

The certified value of the ^{137}Cs and ^{40}K are 3749 and 1575 Bq/kg respectively. According to the certificate, radioactivity concentration of the ^{137}Cs and ^{40}K ranged between 3613-3887 and 1511-1644 Bq/kg interval in the 95% confidence level. Bias and Z-score values were obtained to determine whether the bias conditions fulfilled or not. Ten consecutive measurements were carried out for the bias/accuracy measurements. Z-score was found to be smaller than 2. ^{137}Cs and ^{40}K radioactivity concentration measurements were satisfactory. Bias and Z-score values of the ^{137}Cs and ^{40}K were shown at Table 3.

Robustness

In gamma spectrometric analyses, measurement conditions may change. This can be done by changing one of the measurement conditions such as analyst, detector, or laboratory. Changing of the condition affects the measurement results at some degree. In this study, different operators measured same reference material for the robustness. Three analysts were measured IAEA-154 standard twenty times. Mean, standard deviation, RSD, RSD% and Z-score values are shown in Table 4. As can be seen from the table, Z-score values of the measurements are smaller than 2. As a result, robustness condition is fulfilled.

Ruggedness/Reproducibility

The ruggedness / reproducibility of the method were determined by using different detectors. Two different HPGe detectors which had different efficiencies were used. These detectors were 20% n-type and 150% p-type reverse electrode coaxial HPGe detector. Ten consecutive measurements were carried out for each detectors and radionuclides.

Ruggedness/reproducibility results are shown at Table 5 and Table 6. Statistical f-test was applied to the obtained results. F values were found to be 0.21 and 0.23 for ^{137}Cs and ^{40}K respectively. F values were smaller than F-critic values. As a result, ruggedness/reproducibility condition was fulfilled.

Table 3. Bias and Z-score values of the ^{137}Cs(Bq/kg) and ^{40}K(Bq/kg) radioactivity concentrations

	^{137}Cs	Bias	Z-score	^{40}K	Bias	Z-score
1	3763.9	0.4	0.6	1588.6	0.9	0.7
2	3778.4	0.8	1.2	1568.6	-0.4	-0.3
3	3766.8	0.5	0.7	1575.1	0.0	0.0
4	3742.3	-0.2	-0.3	1577.2	0.1	0.1
5	3735.1	-0.4	-0.6	1550.9	-1.5	-1.2
6	3764.6	0.4	0.6	1590.2	1.0	0.8
7	3725.2	-0.6	-1.0	1568.1	-0.4	-0.4
8	3722.1	-0.7	-1.1	1602.1	1.7	1.4
9	3727.9	-0.6	-0.9	1595.8	1.3	1.1
10	3738.1	-0.3	-0.4	1587.7	0.8	0.7

Table 4. Robustness measurement of the ^{137}Cs (Bq/kg)

	Analyst#1	Analyst#2	Analyst#3
1	3763.9	3753.5	3773.6
2	3778.4	3768.2	3758.7
3	3766.8	3796.7	3746.8
4	3742.3	3762.3	3762.6
5	3735.1	3738.1	3755.3
6	3764.6	3754.3	3784.5
7	3691.9	3702.9	3705.5
8	3641.4	3741.2	3690.3
9	3727.9	3717.9	3757.5
10	3738.1	3758.2	3728.4
11	3723.9	3753.7	3765.1
12	3788.4	3778.4	3758.2
13	3756.8	3746.2	3776.5
14	3752.3	3726.1	3780.5
15	3725.1	3771.7	3825.5
16	3774.6	3754.3	3734.7
17	3701.9	3721.1	3751.9
18	3661.4	3631.9	3761.4
19	3732.9	3730.5	3762.5
20	3742.1	3743.6	3762.7
Mean	3735.4	3742.5	3757.1
Std. Dev.	37.9	34.1	28.5
RSD	0.010	0.0091	0.0075
RSD%	1.01	0.91	0.75
Z-score	-0.11	1.17	0.09

Limit of Detection

There were important statistical concepts in the gamma spectrometric analysis. These concepts were critical limit (L_C), upper limit (L_U), detection limit (L_D), and minimum detectable activity (MDA) [3]. Critical limit is a decision limit. Critical limit means whether the net count significant or not. Upper limit determines statistical significance of the count. Therefore the critical limit is the threshold value of the upper limit. Detection limit is the reliability of the counts and means what is the minimum number of the counts which can be detected confidently.

$$L_c = 1.645 \cdot \sqrt{2 \cdot B} \quad (4)$$

$$L_U = A + 1.645 \cdot \sqrt{\left[A + B \cdot \left(1 + {}^{n}/_{2m}\right)\right]} \quad (5)$$

$$L_D = 2.71 + 3.29 \cdot \sqrt{\left[B \cdot \left(1 + {}^{n}/_{2m}\right)\right]} \quad (6)$$

where, B, A, n, and m are background area, net peak area, gross count peak region channel number and background channel number respectively [3].

Table 5. ^{137}Cs reproducibility results for different detector (Bq/kg)

	Detector#1	Detector#2
1	3763.9	3847.2
2	3778.4	3765.1
3	3766.8	3768.2
4	3742.3	3860.9
5	3735.1	3650.8
6	3764.6	3737.7
7	3691.9	3573.4
8	3641.4	3724.0
9	3727.9	3710.1
10	3738.1	3641.9
F-Test Variances for two samples		
	Variable 1	Variable 2
Mean	3735.0	3730.4
Variance	1704.2	8064.7
Observations	10	10
df	9	9
F	0.21	
P(F<=f) one-tail	0.02	
F Critic two-tail	0.32	
RSD	0.011	0.024
RSD%	1.11	2.40

Table 6. ^{40}K reproducibility results for different detector (Bq/kg)

	Detector#1	Detector#2
1	1588.6	1518.3
2	1568.6	1556.2
3	1575.1	1585.4
4	1577.2	1577.5
5	1550.9	1524.5
6	1590.2	1550.9
7	1568.1	1624.6
8	1602.1	1540.2
9	1595.8	1560.5
10	1587.7	1583.1
F-Test Variances for two samples		
	Variable 1	Variable 2
Mean	1580.4	1562.1
Variance	235.96	1011.32
Observations	10	10
df	9	9
F	0.23	
P(F<=f) one-tail	0.02	
F Critic two-tail	0.31	
RSD	0.010	0.020
RSD%	0.97	2.04

IAEA-154 standard milk powder sample was counted at the 20% efficiency n-type detector. Counting times were 3600 s and 58600 s. The results of the critical limit, upper limit, detection limit, and minimum detectable activity calculations are given in Table 7 and Table 8.

Table 7. L_C, L_U, L_D, and MDA values for n-type 20% efficiency HPGe detector (3600 sn)

	L_C	L_U	L_D	MDA(Bq/Kg)
^{137}Cs	9.8	5370.3	80.4	8.4
^{40}K	12.8	344.4	103.0	17.2

Table 8. L_C, L_U, L_D, and MDA values for n-type 20% efficiency HPGe detector (58600s)

	L_C	L_U	L_D	MDA(Bq/Kg)
^{137}Cs	16.2	44059.2	123.3	1.4
^{40}K	18.1	2437.5	144.1	2.2

IAEA-152 standard milk powder sample was counted at the 150% efficiency p-type detector. Counting times were 5000 s and 75000 s. The results of the critical limit, upper limit, detection limit, and minimum detectable activity calculations are given in Table 9 and Table 10.

Table 9. L_C, L_U, L_D, and MDA values for p-type 150% efficiency HPGe detector (5000 s)

	L_C	L_U	L_D	MDA(Bq/Kg)
^{137}Cs	16.5	15537.1	141.3	2.8
^{40}K	9.0	740.9	80.2	16.7

Table 10. L_C, L_U, L_D, and MDA values for p-type 150% efficiency HPGe detector (75000s)

	L_C	L_U	L_D	MDA(Bq/Kg)
^{137}Cs	7.4	232000.6	67.3	0.3
^{40}K	10.4	10182.8	94.0	1.5

System stability is an requirement for the method validation. For the system stability measurements, Quality Control/Quality Assurance study carried out using IAEA-154 certified reference standard. Ten measurements carried out. Count rate and the full width at half maximum (FWHM) values for ^{137}Cs and ^{40}K obtained. Control charts of the count rate and FWHM are shown at Figure 1, Figure 2, Figure 3 and Figure 4. Count rate and FWHM values are within the 2σ statistical limit.

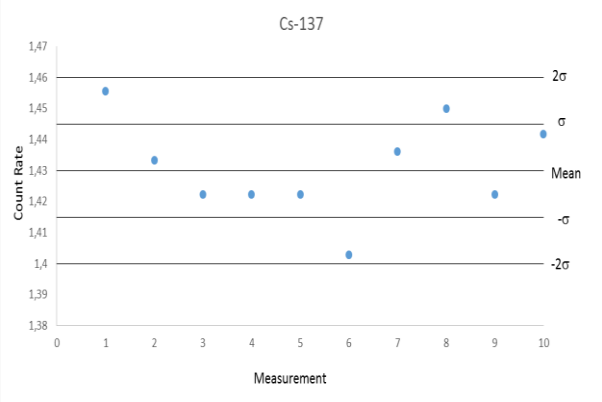

Figure 1. Control chart of the ^{137}Cs count rate

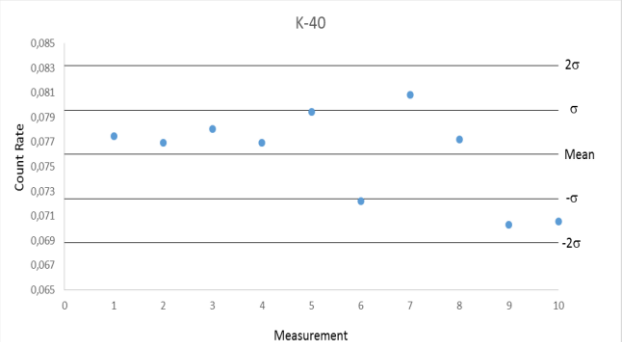

Figure 2. Control chart of the ^{40}K count rate

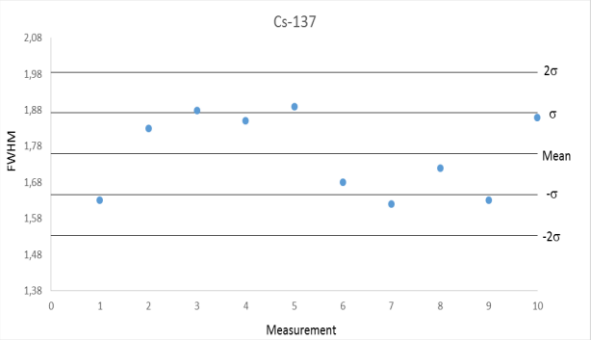

Figure 3. Control chart of the ^{137}Cs full width at half maximum

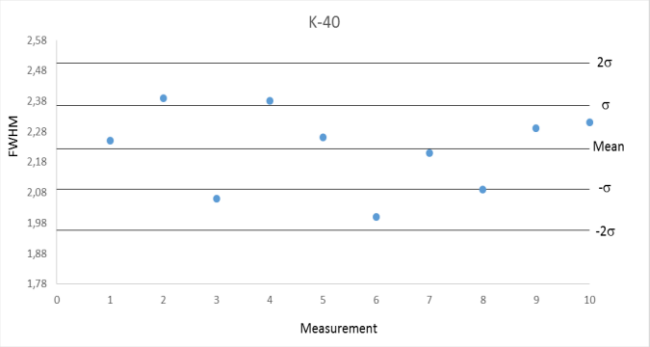

Figure 4. Control chart of the ^{40}K full width at half maximum

4. Conclusions

Gamma spectrometric method validation of the ^{40}K and ^{137}Cs measurements in the milk powder is investigated. Specificity, detection limit, ruggedness (reproducibility), bias (accuracy), precision (repeatability), and robustness parameters were evaluated and quantified. For this purpose, n-type 20% efficiency and p-type 150% efficiency HPGe detectors were used. Homogeneity conditions ensured using IAEA-154 and IAEA-152 certified milk powder standards. In the specificity measurements, energy line shifts were measured as 0.05 and 0.15 keV for ^{137}Cs and ^{40}K respectively. Since up to 1keV shift is acceptable for the measurements, these results are reasonable.

For the precision /repeatability measurements, statistical two-tail student t-test were applied. -1.01 and 1.06 values obtained for ^{137}Cs and ^{40}K. t_{crit} value

was 1.83, obtained values were smaller than t_{crit} value. Bias and Z-score values of the ^{137}Cs and ^{40}K measurements were found to be smaller than 2. ^{137}Cs and ^{40}K radioactivity concentration measurements were satisfactory. Robustness measurements were performed, Z-score values of the measurements were smaller than 2.

Ruggedness/reproducibility measurements were performed. Statistical f-test was applied obtained results. F values were 0.21 and 0.23 for ^{137}Cs and ^{40}K respectively. F values were smaller than F-critic values. Critical limit (L_C), upper limit (L_U), detection limit (L_D), and minimum detectable activity (MDA) values for the detectors were obtained. Quality Control/Quality Assurance measurements were carried out. Count rate and the full width at half maximum (FWHM) values for ^{137}Cs and ^{40}K obtained. Count rate and FWHM values were within the 2σ statistical limit. Obtained results showed that method validation parameters requirements fulfilled.

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