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Interlaboratory comparison material homogeneity testing

Abstract: The homogeneity of fertilizer samples for interlaboratory γ-ray spectrometry comparison was tested by determination of the total γ count rate and the count rates for two ^{238}U γ lines, one ^{40}K line and one common ^{235}U and ^{226}Ra line. Homogeneity testing was accomplished by determination of the minimum, maximum, mean and standard deviation for each parameter and comparison of their standard deviations with predefined tolerances, by Cochran's test, and by a one-way ANOVA. The standard deviations were all less than these tolerances. All samples passed Cochran's test and the one-way ANOVA test for homogeneity.

Keywords: proficiency test, gamma spectrometry, Cochran's test

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1 Introduction

Interlaboratory comparisons are widely used for laboratory performance evaluation and are obligatory for accredited laboratories. The results can confirm that the laboratory consistently produces reliable data. The usual format is based on blind test sample distribution to the participant laboratories, which analyze the material and return their results. The provider converts these into scores reflecting the laboratories' performance.

Materials prepared for these tests are usually heterogeneous, despite the best efforts to ensure homogeneity. When the material is split the units produced vary slightly in composition. "Sufficient homogeneity" in such materials means that this variation (the sampling standard deviation) is negligible compared to the measurement variation. Appropriate statistical techniques should be used to evaluate homogeneity testing data. One suitable approach is the International Harmonized Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories, cooperatively produced by ISO and IUPAC [1].

The Serbian accreditation body organized an interlaboratory comparison of fertilizer γ spectrometry. The test samples were prepared and checked for homogeneity in the Department of Radiation Protection and Environmental Monitoring, Vinča Institute of Nuclear Sciences.

2 Experimental Procedure

Bulk fertilizer (10 kg) was obtained from the producer. Samples (m=7; 1160.4–1161.4 g) were randomly taken from the bulk. Each was homogenized and divided into two subsamples (each 580.2–580.7 g), giving 14 subsamples for homogeneity measurements. The samples were placed in 0.5 L polypropylene Marinelli beakers.

The γ spectrum of each sample was measured once. A high-purity germanium detector system was used by a standard method (t=3600 s) [2]. After background subtraction the spectra were analyzed using the VMS Standard Peak Search of the GENIE2000 software package. This algorithm locates the peaks and calculates the net count by fitting the best Gaussian [3].

Between-sample homogeneity was tested by determining the total γ counting rate and the count rate for two ^{238}U γ lines (63 keV and 1001 keV), one ^{40}K line (1461 keV) and one ^{235}U and ^{226}Ra common line (186 keV).

The system reproducibility was tested by repeated measurements of one sample without moving it. To test the measurement stability, one of the first group of 7 samples was randomly chosen and measured twice consecutively. One from the second group was measured 3 times consecutively.

These results are shown in Table 1. Homogeneity and stability were examined from the means and relative

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standard deviations by (1) comparisons with predefined tolerances, (2) Cochran's test [1,4], and (3) a one-way ANOVA test [5,6].

After testing all the samples were mixed together and 3 final test samples (1216–1216.9 g) were removed. These were placed in 1 liter polypropylene Marinelli beakers and measured as above (Table 9). Due to the small number of samples Cochran's test was not applied.

2.1 Comparing standard deviation with maximum tolerance

The minimum, maximum, mean and relative standard deviation for each parameter were determined. The relative standard deviations were compared to the predefined 10 % tolerance for the total count rate and all radionuclides exept ^{238}U, which was 15 %. The tolerances were half the acceptable precision limits in the IAEA Proficiency test [7].

2.2 Cochran test procedure for duplicate results

The difference, D_i, of each pair of duplicates, for i = 1, ..., m and the sum of squares S_{DD} of the m differences is:

$$D_i = X_{i1} - X_{i2} \quad (1)$$

$$S_{DD} = \sum_{i=1}^{7} D_i^2 \quad (2)$$

Cochran's test statistic is the ratio of D^2_{max}, the largest squared difference, to this sum of squared differences:

$$C = \frac{D^2_{\max}}{S_{DD}} \quad (3)$$

The critical C value at the 95% confidence level for m=7 duplicates is 0.727.

2.3 One-way ANOVA test

ANOVA (Analysis Of VAriance) is used to analyze the differences between group means [5,6]. The one-way analysis of variance tests the claim that two or more population means are equal, *i.e.* the null hypothesis is that two group means are equal.

Between Sums of Squares (BSS) is (for 2 groups of n samples):

$$BSS = \frac{(\sum X_{i1})^2}{n} + \frac{(\sum X_{i2})^2}{n} - \frac{(\sum X_{i1} + \sum X_{i2})^2}{2n} \quad (4)$$

Within Sum of Squares (WSS) is:

$$WSS = \sum (X_{i1})^2 + \sum (X_{i2})^2 - \frac{(\sum X_{i1} + \sum X_{i2})^2}{2n} \text{ -BSS} \quad (5)$$

The F ratio is:

$$F = \frac{BSS}{WSS} \cdot (2n\text{-}2) \quad (6)$$

The critical F value for two groups is 4.74 at the 95% confidence level.

3 Results and Discussion

Measurements for all samples (two groups, 14 samples in total) were made once, except one chosen randomly from the first group of samples which was measured twice consecutively and one from the second group, which was measured 3 times. These subsequent measurements were perfomed in order to prove the stability of the measurement system. The mass of each sample varied between 580.2 g and 580.7 g. The count rates for the certain γ lines the total spectrum count rate, the minimum, maximum, mean and standard deviation for each parameter and each group of samples are presented in Table 1.

The observed relative standard deviations (Table 1) for all count rates are much lower than the predefined tolerances, exept for ^{238}U (1001 KeV), which was 13% – slightly less than the predefined tolerance – 15%.

The results obtained by applying Cochran's test are presented in Tables 2-6. The count rates for the certain γ lines measured for the first (X_{i1}) and the second group of samples (X_{i2}), as well as the difference (D_i) between each pair of duplicates; the sum of squares (S_{DD}) of the m differences, and critical values for the Cochran test statistic for duplicates are presented in Tables 2-5. In Table 6 similar results for total spectrum of counting rates are presented.

Samples measured without moving generally gave much smaller relative standard deviations in count rates, demonstrating good system reproducibility.

The results obtained by applying ANOVA test are presented in Tables 7 and 8. The count rates for the certain γ lines, for the first (X_{i1}) and the second group of samples (X_{i2}); squared and summarized values, variation between groups and within groups, F values and critical value are listed.

Table 1: Homogeneity testing results

Radionuclide		All samples measured once (14 samples)	One sample measured twice consecutively	One sample measured 3 times consecutively
^{238}U (63 keV)	Minimum (cps)	1.1514	1.1514	1.2072
	Average (cps)	1.225 ± 0.036	1.175 ± 0.033	1.253 ± 0.042
	Rel.st.dev. (%)	2.9	2.9	3.3
	Maximum (cps)	1.2583	1.1994	1.2889
^{238}U (1001 keV)	Minimum (cps)	0.0306	0.0558	0.0453
	Average (cps)	0.0503 ± 0.0075	0.0567 ± 0.0011	0.0475 ± 0.0022
	Rel.st.dev. (%)	15.0	2.1	4.5
	Maximum (cps)	0.0606	0.0575	0.0494
^{226}Ra+^{235}U (186 keV)	Minimum (cps)	0.9892	1.0206	1.0217
	Average (cps)	1.041 ± 0.021	1.023 ± 0.004	1.037 ± 0.015
	Rel.st.dev. (%)	2.1	0.4	1.4
	Maximum (cps)	1.0656	1.0261	1.0511
^{40}K (1461 keV)	Minimum (cps)	0.1358	0.1608	0.1442
	Average (cps)	0.1475 ± 0.0075	0.1625 ± 0.0022	0.1481± 0.0056
	Rel.st.dev. (%)	5.1	1.3	3.8
	Maximum (cps)	0.1611	0.1639	0.1544
Total count rate	Minimum (cps)	40.2	40.9	39.5
	Average (cps)	41.6 ± 1.6	41.1 ± 0.2	39.7 ± 0.3
	Rel.st.dev. (%)	3.7	0.6	0.8
	Maximum (cps)	46.2	41.3	40.1

Table 2: Cochran's test for homogeneity using the 63 keV γ line.

X_{i1} [cps]	X_{i2} [cps]	$D_i = X_{i1} - X_{i2}$	D_i^2	D^2_{max}	S_{DD}	C	$C < 0.727$
1.1400	1.1117	0.0283	0.000803				
1.0908	1.1639	-0.0731	0.005337				
1.1333	1.1031	0.0303	0.000917				
1.0514	1.1058	-0.0544	0.002964	0.011556	0.03348	0.345	**Yes**
1.0686	1.1761	-0.1075	0.011556				
1.0800	1.1700	-0.0900	0.008100				
1.0533	1.1150	-0.0617	0.003803				

Table 3: Cochran's test for homogeneity using the 1001 keV γ line.

X_{i1} [cps]	X_{i2} [cps]	$D_i = X_{i1} - X_{i2}$	D_i^2	D^2_{max}	S_{DD}	C	$C < 0.727$
0.0306	0.0492	-0.0186	0.000346				
0.0500	0.0539	-0.0039	0.000015				
0.0547	0.0597	-0.0050	0.000025				
0.0547	0.0461	0.0086	0.000074	0.000357	0.000827	0.431	**Yes**
0.0528	0.0497	0.0031	0.000009				
0.0506	0.0497	0.0008	0.000001				
0.0417	0.0606	-0.0189	0.000357				

Table 4: Cochran's test for homogeneity using the 186 keV γ line.

X_{i1} [cps]	X_{i2} [cps]	$D_i = X_{i1} - X_{i2}$	D_i^2	D^2_{max}	S_{DD}	C	$C < 0.727$
1.0203	1.0525	-0.0322	0.001038				
1.0383	1.0594	-0.0211	0.000446				
1.0244	1.0558	-0.0314	0.000985				
0.9892	1.0331	-0.0439	0.001926	0.001926	0.006397	0.301	**Yes**
1.0567	1.0272	0.0294	0.000867				
1.0608	1.0586	0.0022	0.000005				
1.0319	1.0656	-0.0336	0.00113				

Table 5: Cochran's test for homogeneity using the 1461 keV γ line.

X_{i1} [cps]	X_{i2} [cps]	$D_i = X_{i1} - X_{i2}$	D_i^2	D^2_{max}	S_{DD}	C	$C < 0.727$
0.1561	0.1481	0.0081	0.000065				
0.1431	0.1483	-0.0053	0.000028				
0.1497	0.1422	0.0075	0.000056				
0.1411	0.1611	-0.0200	0.000400	0.0004	0.001	0.398	**Yes**
0.1431	0.1497	-0.0067	0.000044				
0.1358	0.1444	-0.0086	0.000074				
0.1425	0.1608	-0.0183	0.000336				

Table 6: Cochran's test for homogeneity using the total count rate.

X_{i1} [cps]	X_{i2} [cps]	$D_i = X_{i1} - X_{i2}$	D_i^2	D^2_{max}	S_{DD}	C	$C < 0.727$
42.7	40.5	2.145	4.600				
41.8	40.3	1.588	2.520				
41.1	41.5	-0.429	0.184				
40.7	46.2	-5.566	30.979	30.979	45.564	0.680	**Yes**
41.4	43.4	-1.992	3.968				
41.3	42.7	-1.406	1.977				
41.7	40.5	1.156	1.337				

The 186 keV and 1461 keV lines passed the one-way ANOVA tests. The other lines and total count rate also passed (not shown).

After testing all samples were combined, 3 samples were prepared from the resulted bulk sample. The mass of each sample varied between 1216.0 g and 1216.9 g. The count rates for the certain γ lines and the total spectrum, the minimum, maximum, mean and standard deviation for each parameter are presented in Table 9. Due to the small number of samples Cochran's test was not applied to this group. The samples were homogenous.

4 Conclusions

Between-sample homogeneity was tested by the determination of total count rate and the count rates for two ^{238}U γ lines, one ^{40}K line and one ^{235}U and ^{226}Ra common line.

The measurement reproducibility was very good and the samples' relative standard deviations were less than the predefined tolerances. The samples' relative standard deviations were similar to the method repeatability relative standard deviation, demonstrating satisfactory

Table 7: One-way ANOVA test for homogeneity using the 186 keV line (X_i in cps).

	X_{i1}	X_{i2}	$(X_{i1})^2$	$(X_{i2})^2$	$X_{i1} + X_{i2}$
	1.020278	1.0525	1.040967	1.107756	2.072778
	1.038333	1.059444	1.078136	1.122423	2.097778
	1.024444	1.055833	1.049486	1.114784	2.080278
	0.989167	1.033056	0.978451	1.067204	2.022222
	1.056667	1.027222	1.116544	1.055185	2.083889
	1.060833	1.058611	1.125367	1.120657	2.119444
	1.031944	1.065556	1.064909	1.135409	2.097500
Σ	7.221667	7.352222	7.453861	7.723418	14.57389

Variation	*SS*	*F*	*F crit*	*F< Fcrit*
Between Groups	0,001217	3,069818	4,74	**YES**
Within Groups	0,004759			

Table 8: One-way ANOVA test for homogeneity using the 1461 keV line.

	X_{i1} [cps]	X_{i2} [cps]	$(X_{i1})^2$	$(X_{i2})^2$	$X_{i1} + X_{i2}$
	0.156111	0.148056	0.024371	0.021920	0.304167
	0.143056	0.148333	0.020465	0.022003	0.291389
	0.149722	0.142222	0.022417	0.020227	0.291944
	0.141111	0.161111	0.019912	0.025957	0.302222
	0.143056	0.149722	0.020465	0.022417	0.292778
	0.135833	0.144444	0.018451	0.020864	0.280278
	0.142500	0.160833	0.020306	0.025867	0.303333
Σ	1.011389	1.054722	0.146386	0.159255	2.066111

Variation	*SS*	*F*	*F crit*	*F < Fcrit*
Between Groups	0.000134	2.716577	4.74	**YES**
Within Groups	0.000592			

sample homogeneity. All samples passed both Cochran's and the one-way ANOVA tests for homogeneity.

After the homogeneity testing, the final 3 test samples were sent to the accreditation body of Serbia for distribution to participants in the fertilizer γ-ray spectrometry interlaboratory comparison.

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Table 9: Homogeneity testing of the final test samples.

Radionuclide		All samples measured once (3 samples)	One sample measured 3 times without moving
^{238}U (63 keV)	Minimum (cps)	1.5308	1.5894
	Average (cps)	1.567 ± 0.033	1.604 ± 0.021
	Rel.st.dev. (%)	2.1	1.3
	Maximum (cps)	1.5956	1.6281
^{238}U (1001 keV)	Minimum (cps)	0.0650	0.0650
	Average (cps)	0.0714 ± 0.0092	0.0692 ± 0.0042
	Rel.st.dev. (%)	13	6.0
	Maximum (cps)	0.0819	0.0733
^{226}Ra+^{235}U (186 keV)	Minimum (cps)	1.4139	1.4156
	Average (cps)	1.425 ± 0.018	1.423 ± 0.013
	Rel.st.dev. (%)	1.2	0.9
	Maximum (cps)	1.4450	1.4378
^{40}K (1461 keV)	Minimum (cps)	0.2061	0.2061
	Average (cps)	0.2106 ± 0.0050	0.2069 ± 0.0011
	Rel.st.dev. (%)	2.3	0.6
	Maximum (cps)	0.2158	0.2083
Total count rate	Minimum (cps)	61.6	60.7
	Average (cps)	62.6 ± 1.3	62.1 ± 1.7
	Rel.st.dev. (%)	2.0	2.8
	Maximum (cps)	64.0	64.0

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