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# Summary Report of the Proficiency Test for the Determination of Anthropogenic γ-emitting Radionuclides in a Mineral Matrix

***(Name of Analyst: Christos Ath. Maramathas)***

## 1. Comparison of your results against the IAEA values

(Reporting date: 15 March 2002)

**Spiked matrix (Sample Code 017A)**

*Reference date: 1 January 2002*

| Analyte | IAEA Data Value [Bq/kg d.w.] | IAEA Data Uncertainty* [Bq/kg d.w.] | Reported Results Value [Bq/kg d.w.] | Reported Results Uncertainty* [Bq/kg d.w.] | Relative bias [%] | z-Score | u-test score | Analyst/IAEA ratio | 1σ |
|---|---|---|---|---|---|---|---|---|---|
| $^{54}Mn$ | 36.5 | 0.92 | 40.415 | 0.997 | 10.8 | 0.87 | 2.91 | 1.11 | 0.04 |
| $^{57}Co$ | 33.9 | 0.87 | 32.84 | 2.11 | -3.2 | -0.25 | 0.48 | 0.97 | 0.07 |
| $^{60}Co$ | 145 | 3.6 | 121.49 | 1.21 | -16.0 | -1.87 | 6.06 | 0.84 | 0.02 |
| $^{65}Zn$ | 23.0 | 0.71 | 21.494 | 0.620 | -6.4 | -0.46 | 1.57 | 0.94 | 0.04 |
| $^{88}Y$ | 34.9 | 0.93 | 36.792 | 0.933 | 5.5 | 0.44 | 1.45 | 1.05 | 0.04 |
| $^{134}Cs$ | 76 | 1.9 | 70.00 | 1.25 | -7.4 | -0.73 | 2.47 | 0.93 | 0.03 |
| $^{137}Cs$ | 160 | 4.6 | 152.08 | 3.70 | -4.9 | -0.59 | 1.33 | 0.95 | 0.04 |
| $^{241}Am$ | 64 | 1.6 | 40.00 | 4.66 | -37.5 | -1.99 | 4.87 | 0.62 | 0.07 |

* *Combined standard uncertainty expressed as the square root of the sum of variances of all known sources of uncertainty.*

Reported dry/wet ratio: 99.7526%

*Note: in addition, the Analyst reported results for the following radionuclides:*

| Analyte | Value | Uncertainty | Limit of Detection |
|---|---|---|---|
| | [Bq/kg d.w.] | | |
| *$^{109}Cd$* | *558.8* | *25.5* | *19.5* |
| *$^{125}Sb$* | *41.04* | *3.69* | *5.19* |
| *$^{152}Eu$* | *43.80* | *1.79* | *2.38* |
| *$^{155}Eu$* | *57.29* | *2.62* | *2.14* |

*These radionuclides were not present in the spiked sample.*

**Standard solution (Sample Code 017B)**

*Reference date: 1 January 2002*

| Analyte | IAEA Data Value | Uncertainty* | Reported Results Value | Uncertainty* | Relative bias [%] | z-Score | u-test score | Analyst/IAEA ratio | 1σ |
|---|---|---|---|---|---|---|---|---|---|
| | [Bq/kg] | | [Bq/kg] | | | | | | |
| $^{54}Mn$ | 18.2 | 0.10 | 18.481 | 0.176 | 1.6 | 0.20 | 1.48 | 1.02 | 0.01 |
| $^{57}Co$ | 5.84 | 0.038 | 6.1590 | 0.0820 | 5.5 | 0.46 | 3.57 | 1.06 | 0.02 |
| $^{60}Co$ | 24.9 | 0.10 | 23.925 | 0.257 | -3.8 | -0.53 | 3.45 | 0.96 | 0.01 |
| $^{65}Zn$ | 3.95 | 0.073 | 4.2453 | 0.0622 | 7.4 | 0.55 | 3.06 | 1.07 | 0.03 |
| $^{88}Y$ | 10.4 | 0.10 | 10.1882 | 0.0892 | -2.2 | -0.23 | 1.70 | 0.98 | 0.01 |
| $^{134}Cs$ | 13.01 | 0.066 | 11.408 | 0.104 | -12.3 | -1.37 | 12.97 | 0.88 | 0.01 |
| $^{137}Cs$ | 27.0 | 0.40 | 26.817 | 0.387 | -0.7 | -0.10 | 0.32 | 0.99 | 0.02 |
| $^{152}Eu$ | 14.6 | 0.15 | 14.0081 | 0.0741 | -4.2 | -0.48 | 3.73 | 0.96 | 0.01 |
| $^{241}Am$ | 17.0 | 0.10 | 4.600 | 0.322 | -72.9 | -8.88 | 36.65 | 0.27 | 0.02 |

* *Combined standard uncertainty expressed as the square root of the sum of variances of all known sources of uncertainty.*

*Note: in addition, the Analyst reported results for the following radionuclides:*

| Analyte | Value | Uncertainty | Limit of Detection |
|---|---|---|---|
| | [Bq/g] | | |
| *$^{109}Cd$* | *1.567* | *0.150* | *0.366* |
| *$^{155}Eu$* | *0.1926* | *0.0214* | *0.00952* |

*These radionuclides were not present in the spiked sample.*

Explanation of the tables presented above:

The difference between the IAEA value and the reported value is expressed using three parameters:

A) The relative bias between the Analyst's value and the IAEA value expressed as a percentage:

$$Relative\ \ bias = \frac{Value_{Analyst} - Value_{IAEA}}{Value_{IAEA}} \times 100\%$$

B) The z-Score value calculated according to the following equation:

$$z_{Score} = \frac{Value_{Analyst} - Value_{IAEA}}{\sigma}$$

The target values for the standard deviation (σ) have been assigned on the basis of the reproducibility standard deviation (the standard deviation of the consensus mean after outlier rejection which expresses inter-laboratory precision) calculated for this exercise as follows:

| Analyte | Sample 017A | Sample 017B |
|---|---|---|
| $^{54}Mn$ | 12.4% | 8.0% |
| $^{57}Co$ | 12.7% | 11.9% |
| $^{60}Co$ | 8.6% | 7.2% |
| $^{65}Zn$ | 14.1% | 13.6% |
| $^{88}Y$ | 12.6% | 9.7% |
| $^{134}Cs$ | 10.2% | 9.0% |
| $^{137}Cs$ | 8.3% | 7.0% |
| $^{152}Eu$ | - | 8.6% |
| $^{241}Am$ | 18.9% | 8.2% |

C) The value of the u-test score calculated according to the following equation[1]:

$$u_{test} = \frac{\left|Value_{IAEA} - Value_{Analyst}\right|}{\sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2}}$$

The calculated u-test value is compared with the critical values listed in the t-statistic tables to determine if the reported result differs significantly from the expected value at a given level of probability:

| Condition | Probability | Status |
|---|---|---|
| $u < 1.64$ | Greater than 0.1 | The reported result does not differ significantly from the expected value |
| $1.95 > u > 1.64$ | Between 0.1 and 0.05 | The reported result probably does not differ significantly from the expected value |
| $2.58 > u > 1.95$ | Between 0.05 and 0.01 | It is not clear whether the reported result differs significantly from the expected value |
| $3.29 > u > 2.58$ | Between 0.01 and 0.001 | The reported result is probably significantly different from the expected value |
| $u > 3.29$ | Less than 0.001 | The reported result is significantly different from the expected value |

It should be noted that the choice of the significance level is subjective. For this proficiency test we have set the limiting value for the u-test parameter to 2.58 to determine if a result passes the test ($u \leq 2.58$).

## 2. Acceptance criteria

Your results were evaluated against the following acceptance criteria for accuracy and precision and assigned the status "passed" or "rejected" accordingly. A result must pass both criteria to be assigned the final status of "passed".

1. Accuracy: result passes if

$$\left|Value_{IAEA} - Value_{Analyst}\right| \leq 2.58 \times \sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2}$$

2. Precision (dependent on the activity level): the result passes if:

$$\sqrt{\left(\frac{Unc_{IAEA}}{Value_{IAEA}}\right)^2 + \left(\frac{Unc_{Analyst}}{Value_{Analyst}}\right)^2} \times 100\%$$

is less than, or equal to the reproducibility standard deviation as given in the table for z-Scores.

[1] Brookes, C.J., Betteley, I.G. and Loxton, S.M.; Fundamentals of Mathematics and Statistics, Wiley 1979

**Spiked matrix (Sample Code 017A)**

| Sample Code | Accuracy criteria | | | Precision criteria | | Final status |
|---|---|---|---|---|---|---|
| | $\lvert Value_{IAEA} - Value_{Analyst} \rvert$ | $2.58 \times \sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2}$ | Status | [%] | Status | |
| $^{54}$Mn | **3.95** | 3.50 | *failed* | 3.5 | passed | *rejected* |
| $^{57}$Co | 1.09 | **5.89** | passed | 6.9 | passed | **passed** |
| $^{60}$Co | **23.13** | 9.84 | *failed* | 2.7 | passed | *rejected* |
| $^{65}$Zn | 1.48 | **2.43** | passed | 4.2 | passed | **passed** |
| $^{88}$Y | 1.91 | **3.40** | passed | 3.7 | passed | **passed** |
| $^{134}$Cs | 5.63 | **5.88** | passed | 3.1 | passed | **passed** |
| $^{137}$Cs | 7.87 | **15.27** | passed | 3.8 | passed | **passed** |
| $^{241}$Am | **24.02** | 12.73 | *failed* | 11.9 | passed | *rejected* |

**Standard solution (Sample Code 017B)**

| Sample Code | Accuracy criteria | | | Precision criteria | | Final status |
|---|---|---|---|---|---|---|
| | $\lvert Value_{IAEA} - Value_{Analyst} \rvert$ | $2.58 \times \sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2}$ | Status | [%] | Status | |
| $^{54}$Mn | 0.30 | **0.52** | passed | 1.1 | passed | **passed** |
| $^{57}$Co | **0.32** | 0.23 | *failed* | 1.5 | passed | *rejected* |
| $^{60}$Co | **0.95** | 0.71 | *failed* | 1.1 | passed | *rejected* |
| $^{65}$Zn | **0.29** | 0.25 | *failed* | 2.4 | passed | *rejected* |
| $^{88}$Y | 0.23 | **0.35** | passed | 1.3 | passed | **passed** |
| $^{134}$Cs | **1.60** | 0.32 | *failed* | 1.0 | passed | *rejected* |
| $^{137}$Cs | 0.18 | **1.45** | passed | 2.1 | passed | **passed** |
| $^{152}$Eu | **0.61** | 0.42 | *failed* | 1.1 | passed | *rejected* |
| $^{241}$Am | **12.38** | 0.87 | *failed* | 7.0 | passed | *rejected* |

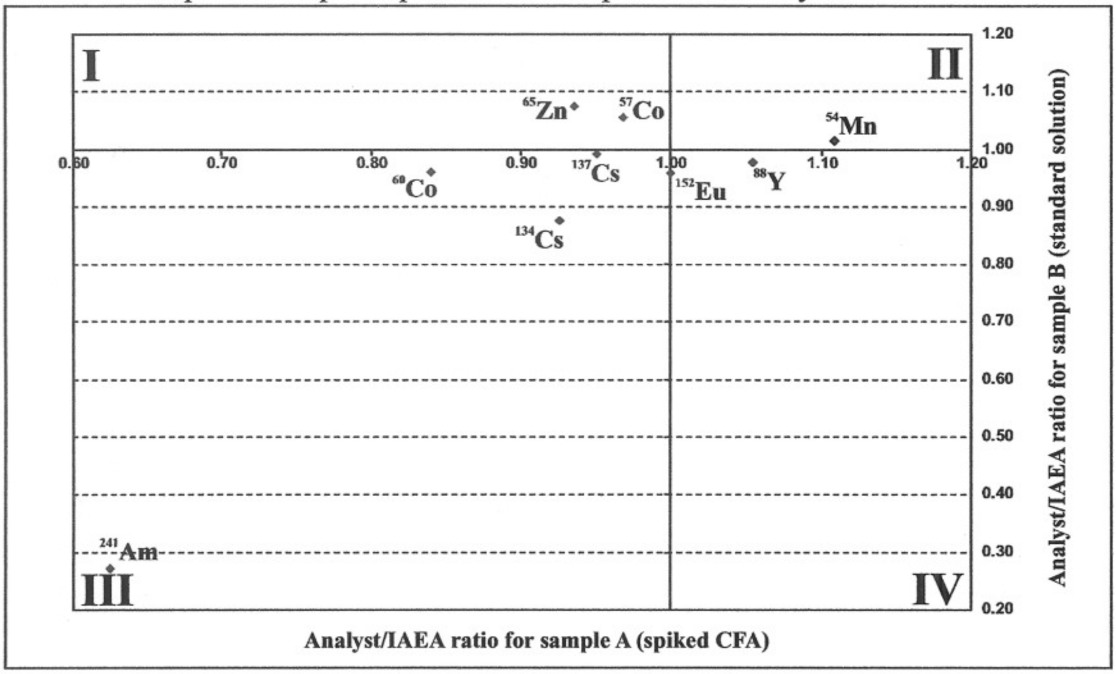
Comments:

Each analyst was requested to report his/her result together with the corresponding combined standard uncertainty expressed as the square root of the sum of variances of all known sources of uncertainty. It is the responsibility of the analyst to report an accurate and precise value and to provide a reliable estimate of the uncertainty. Therefore, for calculation of critical values for accuracy and precision, the evaluation procedure used by the IAEA involves the reported value and its corresponding combined standard uncertainty as well as the IAEA target value and its estimated combined standard uncertainty. However, this latter term is relatively small since certified radioactive standards were used for sample preparation. Therefore, in cases where an analyst reports an unrealistically small uncertainty, a "*Rejected*" final status could be assigned to the result. This is because the difference between the target and the reported values falls outside the range determined by the uncertainties assigned to the values (failed accuracy criterion). To determine the acceptance range for a result to pass the accuracy criterion for this proficiency test, we have set the two-tailed value for Students t distribution to the 0.01 significance level. There could be a number of cases where the result that passes the z-Score criterion is rejected due to the accuracy criterion. This is due to the fact that the z-Score does not include any uncertainty associated with the analyst's value but rather the target standard deviation derived from the inter-laboratory precision (expressed as a reproducibility standard deviation) which in this case is relatively large (see Table on Page 3). The second criterion (precision) defines the maximum acceptable uncertainty which could be assigned to the reported value and was set as the reproducibility standard deviation (which expresses the inter-laboratory precision) for this exercise.

## 3. Summary

The results reported for the same analyte in both samples are presented as a Youden plot in Figure 1. This type of graph displays the scatter of results obtained by a laboratory and enables an analyst to determine if the major source of scatter of the data is due to random measurement errors or due to systematic errors (calibration, self-attenuation, summing etc.). Since Eu-152 was present only in the standard solution, its point is shown only on the Y axis. Other radionuclides will also lie on the X or Y axes in cases where an analyst has only detected (or reported) a single value for the radionuclide in question. Please note that all radionuclides except Eu-152 were present in both samples. If the scatter of the results is due entirely to random error, the points would be distributed equally in all four quadrants of the chart. If however, systematic errors are the dominant cause of the scatter, this would lead to a predominance of the points in the top right (II) and the lower left (III) quadrants of the chart. In the hypothetical absence of random errors, all the points would lie on a 45° diagonal on the chart for two samples of the same matrix. However, since in this case, the two samples represent two different matrices, the contribution from various systematic errors could be of different magnitude (e.g. self-attenuation in solution and mineral matrix or "true coincidence summing" for different counting geometries) which could yield points lying along a line of slope differing from 45° or points appearing in the top left (I) and lower right (IV) quadrants of the chart.

Figure 1 Youden plot of the participants' results expressed as Analyst/IAEA ratio




Figures 2 and 3 present the distribution of results expressed as the Analyst/IAEA ratio for the spiked coal fly ash sample (017A) and standard solution (017B) respectively. The error bars used in both figures represent the combined standard uncertainties for the Analyst/IAEA ratio values. Analytes are organized in ascending order according to the major energy lines that are commonly used for data interpretation and evaluation (from $^{241}$Am – 59.54 keV to $^{88}$Y – 1836.06 keV). The $^{152}$Eu was present in the standard solution only. If the dominant source of scatter was random error, the points would be distributed equally above and below the line of Analyst/IAEA ratio (equal to 1.0). If however, systematic errors were the main cause of the scatter, this would lead to a shift of the points above or below the 1.0 target line (calibration error). If the analyst did not correct his/her results for coincidence summing for $^{60}$Co, $^{88}$Y, $^{134}$Cs and $^{152}$Eu or neglected to count for self-attenuation in the case of $^{241}$Am, results would fall below the 1.0 target line.

Figure 2 Results for sample 017A expressed as Analyst/IAEA ratio

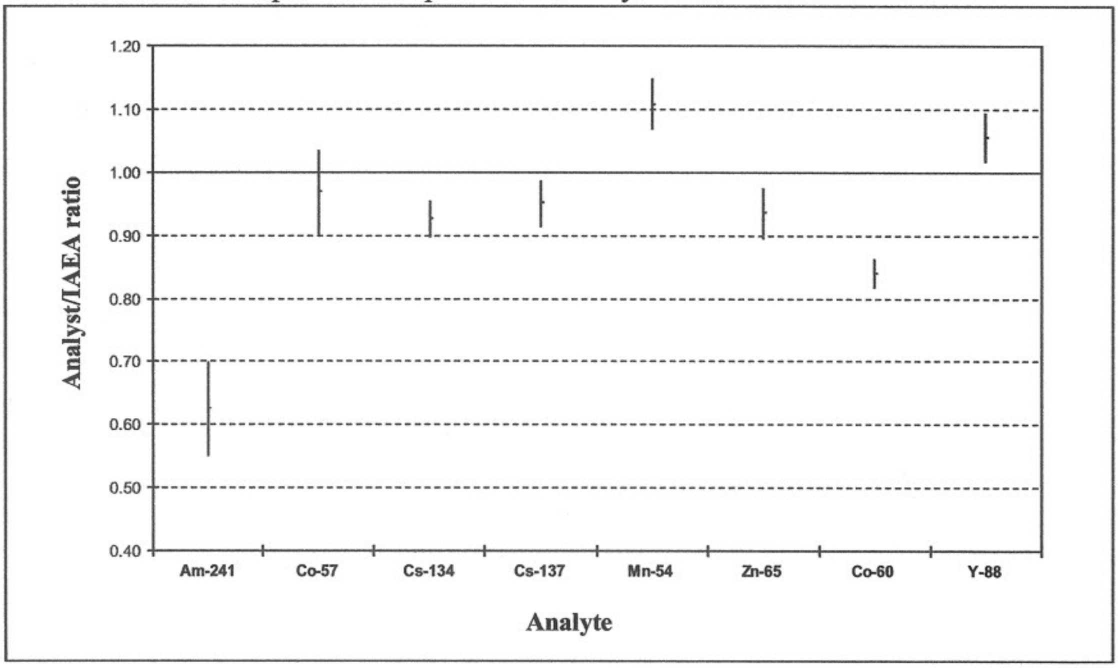
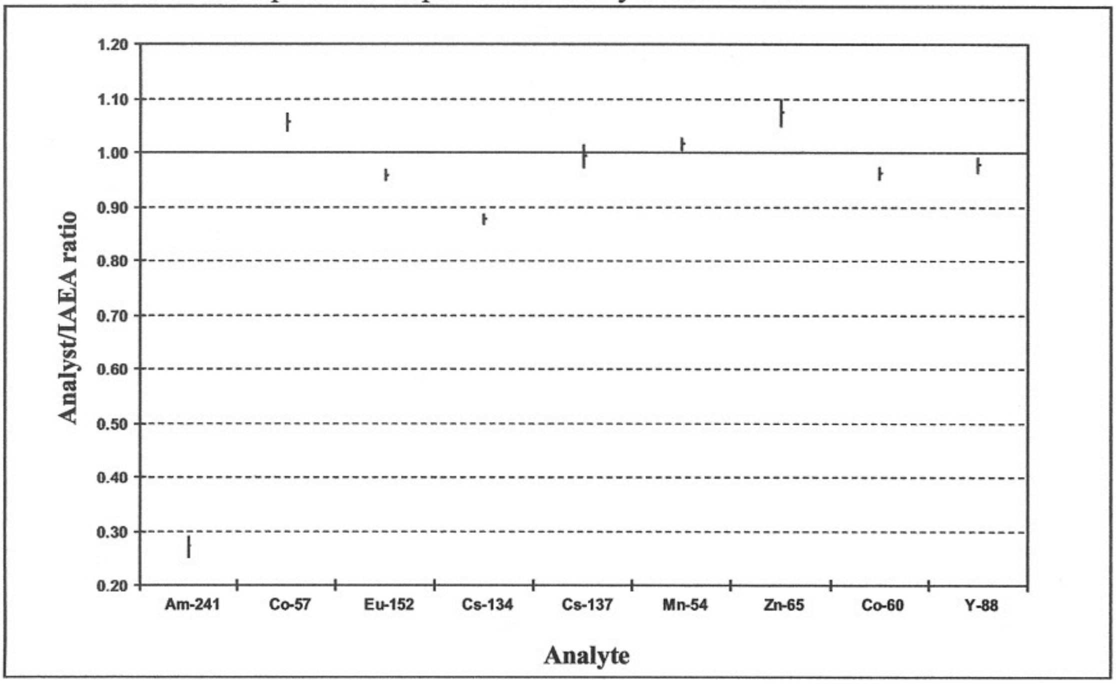



Figure 3 Results for sample 017B expressed as Analyst/IAEA ratio




*Note: Eu-152 was present in sample 017B only.*

## 4. Description of the materials used and participation requirements

| | |
|---|---|
| Matrix origin: | Coal fly ash collected from Kufstein (Austria). |
| Matrix characterization: | A number of samples were pre-screened for man-made γ-emitting radionuclides prior to spiking. The results indicated that the material was free from anthropogenic γ-emitting radionuclides. |
| Sample preparation: | *A) Mineral matrix spiked with γ-emitting radionuclides*<br>The coal fly ash was dispensed in 100.0 ± 0.1 g aliquots into plastic containers and each was spiked with known amounts of a certified standard solution containing a mixture of gamma-emitting radionuclides ($^{54}$Mn, $^{57}$Co, $^{60}$Co, $^{65}$Zn, $^{88}$Y, $^{134}$Cs, $^{137}$Cs and $^{241}$Am). After spiking the samples were thoroughly shaken for approx. 30 min. Each 100 g sample was measured to ensure that the material could be considered homogeneous for the purpose of this exercise.<br><br>*B) Standard solution for γ-emitting radionuclides*<br>The ampoule contained 2.5 ml of a solution comprised of $^{54}$Mn, $^{57}$Co, $^{60}$Co, $^{65}$Zn, $^{88}$Y, $^{134}$Cs, $^{137}$Cs, $^{152}$Eu and $^{241}$Am in 2 mol/L HCl and included 25 µg of relevant carriers. A suitable, weighed aliquot (or several aliquots) of the solution could be used for analysis. |
| Analytes of interest: | Each participant was requested to analyse both samples for all γ-emitting radionuclides present in the following list of possible candidate γ-emitting anthropogenic radionuclides: $^{54}$Mn, $^{57}$Co, $^{58}$Co, $^{59}$Fe, $^{60}$Co, $^{65}$Zn, $^{88}$Y, $^{95}$Zr/$^{95}$Nb, $^{99}$Mo/$^{99m}$Tc, $^{106}$Ru, $^{109}$Cd, $^{110m}$Ag, $^{113}$Sn, $^{125}$Sb, $^{133}$Ba, $^{134}$Cs, $^{137}$Cs, $^{140}$La/$^{140}$Ba, $^{144}$Ce, $^{152}$Eu, $^{154}$Eu, $^{155}$Eu, $^{203}$Hg and $^{241}$Am. Participants were informed that only some of the radionuclides listed were present in the samples. The activity levels of the radionuclides were such that they could be measured within a 24-hour measurement period using a conventional HPGe γ-spectrometer with a 20 % relative efficiency. |
| Choice of method/procedure: | Each participant could use any routine method of their choice, however the samples should not have been used to test a new procedure. |
| Reporting requirements: | A) All results should have been decay corrected to the reference date 2002-01-01, 00:00 GMT.<br><br>B) The deadline for submission of results was set to 1 March 2002. |