IAEA-TEL-2021-03 WWOPT

Proficiency Test on determination of anthropogenic and natural radionuclides in water, Japanese bamboo and simulated swipe samples

Important - before you start to analyse these samples.

Please kindly check the inventory of the package for completeness (Table 1) and ensure that the samples are not damaged.

Should any items be missing or broken, please send an email to: Proficiency-Tests.Contact-Point@iaea.org.
Instructions to Participants

1. Choice of method/procedure

Any routine method may be used; however, the participants should not report the results obtained by testing a newly introduced procedure.

2. Description of the samples

The amount of radioactive material in the samples is less than the exemption level, both in terms of radioactive concentrations and absolute activity values. However please take care to avoid any cross contamination.

The package contains 9 samples, as detailed in Table 1:

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sample Matrix</th>
<th>Weight (Approx. in grams)</th>
<th>Radionuclide analysis required</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Spiked water</td>
<td>500</td>
<td>Anthropogenic gamma and alpha emitting radionuclides, gross alpha and beta (GAB)</td>
</tr>
<tr>
<td>02</td>
<td>Spiked water</td>
<td>500</td>
<td>Anthropogenic gamma emitting radionuclides, H-3 (for intercomparison only), Sr-90, and GAB</td>
</tr>
<tr>
<td>03</td>
<td>Spiked water</td>
<td>500</td>
<td>Quality control (QC) with known activity concentrations of radionuclides</td>
</tr>
<tr>
<td>04</td>
<td>Japanese bamboo</td>
<td>150</td>
<td>Anthropogenic gamma emitting radionuclides</td>
</tr>
<tr>
<td>05</td>
<td>Spiked water</td>
<td>500</td>
<td>Gamma emitters, and transuranic radionuclides (TRU), GAB</td>
</tr>
<tr>
<td>06</td>
<td>Spiked water</td>
<td>50</td>
<td>QC sample for TRU determination</td>
</tr>
<tr>
<td>07a/07b</td>
<td>Simulated swipe samples</td>
<td>2 pcs</td>
<td>Gamma emitters, TRU, GAB (identical samples)</td>
</tr>
<tr>
<td>08</td>
<td>QC swipe sample</td>
<td>1 pc</td>
<td>QC sample with gamma emitters, TRU</td>
</tr>
<tr>
<td>09</td>
<td>Blank swipe sample</td>
<td>1 pc</td>
<td>Blank sample for the swipe samples</td>
</tr>
</tbody>
</table>

2.1. Spiked water - Samples 01, 02, 03, 05 & 06

Matrix origin:
Drinking water sourced from Seibersdorf, Austria.

Sample preparation:
The raw water was gravimetrically spiked with known amounts of prepared standard solution, containing a mixture of certified radionuclides and acidified (~0.05M HNO₃) for stability. The stability of the samples will be tested and ensured during the PT reporting period only.

Sample 01, Sample 02 and Sample 05 were spiked with several radionuclides. The identification of gamma emitting radionuclides is one of the tasks of this proficiency test, they are therefore not specified in advance.

As usual, Sample 03 is the QC sample and its radionuclide content is specified in Table 2:
Table 2. Radionuclide content of Water QC (Sample 03)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity concentration, Bq/kg</th>
<th>Uncertainty*, Bq/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>55.1</td>
<td>0.5</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>88.0</td>
<td>0.8</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td>58.7</td>
<td>0.4</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>115.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Note: Uncertainty is expressed as a combined standard uncertainty with k=1 coverage factor. Reference date is 2021-01-01.

The additional water samples, Sample 05 and Sample 06 contain transuranic isotopes. These were prepared the same way as Samples 01 to 03. The acid concentration in Sample 06 is approximately 0.5 M HNO$_3$ and the radionuclide content is listed in Table 3.

Table 3. Radionuclide content of Sample 06

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity concentration, Bq/g</th>
<th>Uncertainty*, Bq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{242}$Pu</td>
<td>0.110</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Note: Uncertainty is expressed as a combined standard uncertainty with k=1 coverage factor. Reference date is 2021-01-01.

2.2. Japanese Bamboo - Sample 04

Matrix origin:
The material was sampled by experts of the Tsukuba and Fukushima University (Japan). The raw material was dried and milled in Japan, then transferred to the Radioanalytical Laboratory of the Food Chain Safety Directorate (Hungary) for further treatment. After sieving into different grain size fractions, the 2-4 mm part was homogenised and bottled for PT purposes. The bottled samples were sterilised (25 kGy gamma dose) and the related certificate is available on the PT website.

Sample characterisation:
The determination of target values and associated uncertainties of the anthropogenic and natural radionuclides has been carried out by measurements in one laboratory and confirmed by measurements in another laboratory. The samples are characterised for gamma emitting radionuclides only.

2.3. Swipe samples – Samples 07a, 07b, 08 & 09

As suggested by the members of ALMERA, three different types of swipe samples have been included in this proficiency test. All samples were prepared using a printing technique.

Sample 07a and 07b are identical samples. A real swipe sample surface captured by autoradiography was printed on a 100% cotton carrier material. The original picture is shown in Figure 1.

The shape of the original sample is not a perfect circle which is slightly visible on the printed surface.

Figure 1. The original swipe pattern
3. Test sample handling

3.1. Spiked water samples:

Thoroughly mix the sample before transferring the contents to your standard sample counting container for gamma-ray spectrometry. It is recommended that any subsamples for analysis are measured by weight.

3.2. Japanese bamboo sample:

The recommended minimum sample size is 50 g for gamma ray spectrometry and 5 g for alpha spectrometry.

Determine dry content of the bamboo sample by drying an aliquot (approx. 5 g) of the sample immediately after opening the secure box. It is recommended to dry the material at 105°C overnight (minimum 8 hours) in a drying oven, without air circulation or until the mass of the sample is constant.

3.3. Swipe samples:

The three swipe samples and the blank are distributed in one piece of printed cotton carrier; therefore, the user should cut them carefully. To ensure the integrity of the samples, the printed surface should not be moistened by un-gloved or wet hands.

The transuranic content of these samples is higher than the normal environmental level, for this reason countermeasures against possible cross contamination are very important. The activity of the samples is below the exemption level, so there is no health hazard in handling these samples. The radionuclide content of the QC Sample 08 is detailed in Table 4.

Table 4. Radionuclide content of Sample 08

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity concentration, Bq/sample</th>
<th>Uncertainty*, Bq/sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{137}$Cs</td>
<td>8.0</td>
<td>0.3</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>6.05</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Note: Uncertainty is expressed as combined standard uncertainty with $k=1$ coverage factor.
Reference date is 2021-01-01.

4. Reporting requirements

All results should be reported online by October 15, 2021 in the reporting form on the website as detailed in the cover letter.

The reference date for decay correction for all samples is January 1, 2021. The decay correction is not required or applicable for the GAB measurements. The GAB measurements will be evaluated according to the intercomparison rules, and the target values and uncertainties will be derived from the reported results.

The determined activity concentration and its combined standard uncertainty ($k=1$) must be expressed in Bq/kg dry mass for Sample 04 (Japanese bamboo), and as Bq/kg for all water samples.

The measurement results for the simulated swipe samples should be reported in absolute activity as Bq/sample ± uncertainty (Bq/sample).
The uncertainty of the measurement results should be reported as a combined standard uncertainty at coverage factor $k=1$, taking into account all known uncertainty components, including at least the applicable contributors listed:

- uncertainty of the calibration source (specified by the metrological institute);
- uncertainty of the efficiency calibration (due to the efficiency curve fitting and transfer);
- uncertainty of the peak area;
- uncertainty of any applied corrections (self-attenuation, true-coincidence correction, etc.);
- uncertainty coming from the long-term stability of the gamma-ray spectrometer (by control chart if it is conducted);
- uncertainty from the background subtraction;
- uncertainty from the reproducibility of the geometry (positioning);
- uncertainty of the dry content determination (powder samples); and
- uncertainty due to the sample preparation and chemical recovery (for radiochemistry methods).

5. Evaluation of the reported results

The data will be evaluated according to the following steps:

- The relative bias between the reported and the target value (the best estimation of the true value) is expressed by the following equation:

$$\text{Bias}_{relative} = \frac{\text{Value}_{reported} - \text{Value}_{target}}{\text{Value}_{target}} \times 100\%$$

- The relative bias will be compared to the Maximum Acceptable Relative Bias (MARB) which is determined for each analyte, considering the radioanalytical methods, the level of radioactivity and the complexity of the analysis.

- If the $\text{Bias}_{relative} \leq \text{MARB}$ value, the result will be "Accepted" for accuracy.

- Based on fit for purpose and good laboratory practice principles, the expanded relative combined uncertainty should cover the relative bias:

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

$$\text{Bias}_{relative} \leq k \times P$$

- Where $k$ is the coverage factor, for the 99% confidential level. If the reported result is within the $\pm$ MARB value, but not overlapping with the target value within the uncertainty, this equation helps to decide whether or not it is significantly different.

- The $P$ value will be compared to the MARB also. If both the $P \leq \text{MARB}$ and $\text{Bias}_{relative} \leq k \times P$ are fulfilled, the reported result will be "Accepted" for precision. If one of them is insufficient, the result will be assigned "Not Accepted" for precision.
• The final score according to the above detailed evaluation:
  □ "Accepted" when both accuracy and precision achieve "Accepted" status,
  □ "Not Accepted" when the accuracy is "Not Accepted" and
  □ "Warning" when accuracy is “Accepted”, but the precision is "Not Accepted”.

• In this evaluation method the MARB is a "hard" criterion to emphasise the importance of the measurement accuracy, while a “Warning” score indicates either an under- or overestimated uncertainty. According to the above, a “Warning” score means that the result is good in terms of accuracy, however the uncertainty estimation should be revised.

6. Evaluation of Z-scores

The Z-scores were derived by the following equation:

\[ Z = \frac{Value_{Reported} - Value_{Target}}{s^*} \]

Where \( s^* \) the robust standard deviation without refinement, calculated by the following formula:

\[ s^* = 1.483 \cdot \text{median of } |Value_{Reported} - Value_{Target}| \]

It should be emphasized that the Z-score is a relative parameter, because the value of the robust standard deviation is derived from the reported results and is thus influenced by the performance of the participants.