CCRI(II) Supplementary Comparison on $^{40}$K, $^{137}$Cs and $^{90}$Sr activity content in dried bilberry material

Background information

A CCRI(II) Supplementary Comparison for the determination of the activity concentration (massic activity) of three radionuclides in dried bilberry material: $^{40}$K, $^{137}$Cs and $^{90}$Sr, is proposed. This material is intended to become a certified reference material (CRM) of the IRMM, under the assigned number IRMM-426. The results of the supplementary comparison (SCRV) would establish the certified values of the CRM.

The material has elevated levels of $^{137}$Cs and in particular of $^{90}$Sr. However, these are below the exemption levels so that it can be transported freely and handled in the laboratory without any radiological restrictions. Due to natural uptake from elevated levels in the environment (Chernobyl region) the radionuclides were metabolised by the plants. No spiking was applied.

The material has been processed by oven-drying (55 °C) and cryo-milled to a free-flowing powder with top grain size of 1.4 mm Ø and median of 300 μm Ø. It was sieved, homogenized and bottled in units of approximately 100 g. The water content of the material after bottling was 3.6 % (mass of water per mass of material).

The material has been sterilized by gamma-irradiation to enhance its long-term stability and to facilitate its transport across borders.

According to ISO Guides 34 and 35 on reference material production and certification, the homogeneity and stability of (the analytes in) the material must be positively demonstrated. This implies a shelf-life and minimum sample intake for the analysis of the material and the corresponding propagation of numerical estimates of homogeneity and stability into the uncertainty of the batch property values (certified values). In principle, this corresponds to

$$U_{CRM} = k \cdot u_{CRM} = k \cdot \sqrt{u_{\text{char}}^2 + u_{wb}^2 + u_{wb}^2 + u_{lts}^2 + u_{sts}^2}$$

where

- $U_{CRM}$ : expanded uncertainty of certified value
- $u_{\text{char}}$ : standard uncertainty of characterization study (here $u_{\text{SCRV}}$)
- $u_{wb}$ : standard uncertainty for "between-bottle" homogeneity
- $u_{lts}$ : standard uncertainty for long-term stability
- $u_{sts}$ : standard uncertainty for short-term stability – negligible for this material

The homogeneity, short- and long-term stability studies were completed at the IRMM.

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1 IRMM is the pilot laboratory for the comparison and has prepared the material.
Protocol for the comparison

1. Each participant will receive six units (of about 100 g each) of the material issued by the IRMM (pilot laboratory).

2. The activity concentration (massic activity) of each of the radionuclides, $^{40}$K, $^{137}$Cs and $^{90}$Sr is to be determined.

3. Traceability to the SI units and the SIR should be established using gravimetric determinations and standardized radionuclide solutions or certified standards for calibrations, and as tracers.

4. At least 6 samples need to be fully analysed (in other words: at least 6 complete individual determinations from sample preparation to measurement).

5. All results are to be reported normalized to dry mass.

6. Water/moisture content is to be determined by the participant for each of the six units on small aliquots that will NOT be used for the radionuclide determination.

7. Water/moisture content should be determined by Karl-Fischer-titration or oven-drying (the detailed procedure is attached to this protocol).

8. The minimum sample intake for radionuclide analysis is 50 g (which is also the maximum on the basis of 6 supplied units - 6 x 50 g for $^{90}$Sr, 6 x 50 g for gamma-spec)

9. For gamma-spec a smaller sample intake (but at least 20 g) is possible, if a correspondingly higher number of samples is analysed.

10. The reference date to be used is 1 Jan 2009.

11. Timing and deadlines:
   i. Material distribution: November 2009 July/August 2010
   ii. Deadline for submitting results: 6 months after reception of samples -> end of January 2011

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Oven-drying procedure for bilberry material

SCOPE

As already stated in the protocol for the CCRI(II) supplementary comparison, all results are to be reported normalized to dry mass. The water content should be determined by Karl-Fischer titration. Alternatively, oven drying at a temperature of \( (105 \pm 2) ^\circ C \) to constant weight at atmospheric pressure can be used.

The water content of a given material is defined as the ratio, expressed as a percentage, of the mass of the water to the total mass of the (undried) bilberry material.

EQUIPMENT

1. Weighing device: A balance or scale sensitive to 0.1 % of the mass of the test sample, and having a capacity equal to, or greater than, the wet mass of the sample to be tested.
2. Drying device: An oven or other suitable thermostatically controlled heating chamber capable of maintaining a temperature of \( (105 \pm 2) ^\circ C \).
3. Container that will not be affected by the drying temperature and is suitable for retaining the test sample without loss while permitting the water to evaporate.

PROCEDURE

1. Prepare a representative portion of the bilberry material to be tested for water content at the same time as the sample(s) for radionuclide determination. The water content is to be determined for each of the six units (bottles) on one or two small aliquots that will NOT be used for the radionuclide determination. To our experience, aliquots of 0.5 g are sufficient for the water determination.
2. The sample preparation from six bottles (samples for radionuclide determination as well as samples for water) must be distributed over AT LEAST two days.
3. Determine the mass of the test sample and record this mass as the “Wet mass”.
   a. The most convenient procedure for determining the mass of the sample before and after drying is to place it in a container where it will remain throughout the test. The mass of the container and sample are determined and the mass of the container subtracted.
   b. It is recommended to determine the mass of the test sample immediately after preparation, as a moisture-tight cover on the container does not completely prevent evaporation or absorption of water.
   c. Clause b. also applies to the sample(s) for radionuclide determination.
4. Dry to constant mass at \((105 \pm 2)\) °C.
   a. The drying time required to achieve constant mass will vary depending on the quantity and condition of the material. In most cases, an overnight drying period is sufficient.
   b. Please keep in mind the possible volatilization of some radionuclides at elevated temperatures.
   c. To reduce the drying time, position the containers in the drying device to allow the maximum air circulation and exhaust of the moisture laden air.
   d. Constant mass has been achieved when less than 0.1 % of the test sample wet mass is lost during an additional exposure to the drying process. Subsequent drying periods to verify constant mass shall be of at least 1 h duration.

5. Remove the sample from the drying device and cool to room temperature. It is recommended to determine the mass of the test sample immediately after cooling, as a moisture-tight cover on the container does not completely prevent absorption of moisture from the air.

6. Determine the mass of the test sample and record this weight as the “Dry mass”.

**CALCULATION**

Determine the water content as follows:

\[
\text{Water content (\%)} = \frac{\text{Wet mass} - \text{Dry mass}}{\text{Dry mass}} \times 100
\]

**PRECAUTIONS**

The drying rate of test samples will be affected by the moisture conditions and number of samples in the drying device. Avoid placing of wet samples in the drying device together with nearly dry samples, since absorption of moisture into the dry samples may occur.