Activity concentration measurements of $^{137}$Cs, $^{90}$Sr and $^{40}$K in a wild food matrix reference material (Wild Berries) CCRI(II)-S8

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Abstract

In 2009, the CCRI approved a supplementary comparison to be organized by the IRMM as pilot laboratory for the activity concentrations of $^{137}$Cs, $^{90}$Sr and $^{40}$K in a matrix material of dried bilberries. The organization of this comparison and the material and measurement methods used are described. The supplementary comparison reference value (SCRV) for each of the three radionuclides are given together with the degrees of equivalence of each participating laboratory with the SCRV for the specific radionuclide. The results of this supplementary comparison allow the participating NMIs/designated institutes to declare calibration and measurement capabilities (CMCs) for the given radionuclides in a similar type of food matrix, an important aspect seen the relatively few supplementary comparisons for activity in matrix materials organized so far.

1. Introduction

National metrology institutes (NMIs) and designated institutes (DIs) in the field measurement of radionuclides have vast experience in performing primary measurements of activity and participating in the corresponding key comparisons of CCRI(II), as shown in the list of key and supplementary comparisons [1] and reflected also in the list of calibration and measurement capabilities (CMCs [2]) of the key comparison data base (KCDB). Whereas the capability to perform primary measurements of usually mono-nuclidic aqueous solutions demonstrates mastering their specific difficulties and has its particular merits as being the means to realize the unit of the becquerel for a specific radionuclide, that capability does not necessarily reflect

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the ability to determine the same radionuclide in a matrix material. Problems of how to prepare a sample ready for measurement, in particular how to quantitatively extract radionuclides from the given matrix, present a different kind of difficulty and need to be considered. Only a few CCRI(II) supplementary comparisons (SCs) for measurement of radionuclides have been performed with matrix materials so far [1].

The results of this SC CCRI(II)-S8 for the activity determination of $^{137}$Cs, $^{90}$Sr and $^{40}$K in a dried bilberries matrix demonstrated the capability of the participating NMIs and DIs to determine these radionuclides in this matrix material, and thus allow the participants to claim corresponding CMCs in Appendix C of the KCDB [2] for these nuclides in a similar type of food matrix. IRMM as pilot laboratory which provided the material will use the results to establish the certified values of the new reference material IRMM-426.

The accident of 2011 in the Fukushima Daiichi nuclear power plant, after the Great Eastern Japan Earthquake of 11 March and subsequent Tsunami, underlined the importance of reliable measurements of radionuclides in food as a basis for taking decisions on radiological protection. Also fast screening methods should be based on sound metrological principles to be fit for purpose. Since certified reference materials (CRMs) are an excellent tool to validate radioactivity measurement methods in matrix materials, the decision to develop such a CRM at IRMM was taken earlier based on growing concern with the radioactivity found in wild food products, when assessing the total exposure of particular groups of a population living in regions of increased radioactive fallout such as deposited after the Chernobyl reactor accident.

Some of the data on the measurement of gamma-ray emitters in this comparison have been published earlier [3]. Where necessary, they are reproduced here in order to present a comprehensive report of the whole comparison CCRI(II)-S8.

2. Participants

Seven NMIs/DIs and two international organizations participated in CCRI(II)-S8 and reported results for the two gamma-ray emitting nuclides $^{40}$K and $^{137}$Cs. Five of these also provided results for the pure beta-emitter $^{90}$Sr. IRMM was the pilot laboratory. Details of the laboratories are given in Table 1 together with a brief indication (acronym) of the determination methods used.

3. Material used in comparison

In collaboration with the Ecomonitor Center for Monitoring Studies & Environmental Technologies (CMSET) in Kiev, Ukraine, a forested region with an increased ratio between $^{90}$Sr and $^{137}$Cs in the deposition from the radioactive fallout of the Chernobyl reactor accident could be identified [4]. In the summer of 2005, the CMSET collected bilberry samples from this so-called “strontium hot spot” region close to Chernobyl. Since the elevated levels of $^{90}$Sr and $^{137}$Cs in the berries were below the exemption levels, the material could be transported freely and handled safely in the laboratory without radiological concerns.

In order to avoid fermentation and decomposition, the berries were air-dried in ventilation dryers in the sampling region. After transport to IRMM, the material was processed by oven-drying (55 °C) and cryo-milled to a free-flowing powder with top grain size of $\Theta$ 1.4 mm and a median $\Theta$ 300 μm. It was sieved, homogenized and bottled in units of approximately 100 g into 280 mL amber glass jars. The water content of the material after bottling was 3.6 % (mass of water per mass of total material). The material was sterilized by gamma-irradiation to enhance its long-term stability and to facilitate its transport across borders. [3]

In a matrix material, source heterogeneity may influence the results obtained from different (sub-)samples, also in a supplementary comparison. Therefore, the (in)homogeneity of the three radionuclides was determined for the comparison material: 0.9 % ($^{137}$Cs), 2.1 % ($^{40}$K), and 1.8 % ($^{90}$Sr) for an aliquot mass of 50 g [5]. Since the homogeneity measurements were
performed in 16 randomly chosen bottles of the whole batch of material, the same values hold for the intended use of the material as CRM [6].

4. Organizational aspects of the supplementary comparison

Whereas in other CCRI(II) comparisons usually only one sample is distributed to each participant, IRMM sent six bottles of the bilberries material to each laboratory in order to comply with general principles of reference material certification [6]. Each laboratory was asked to submit individual results of the activity concentration normalized to dry mass for the 6 samples and the corresponding mean value. A sample mass of 50 g was recommended for the radionuclide determinations. If a smaller sample mass was used (minimum 20 g), a correspondingly higher number of samples was to be analyzed. The reference date for all results was 1 January 2009, 00h00 UTC. It was recommended not to measure radionuclides in dried samples, but to determine the water content for the required dry mass correction factor in separate, small aliquots of only 1 g to 3 g. Karl-Fischer titration was recommended for the water determination, but only the pilot laboratory, IRMM, was able to use it. The initially provided alternative drying method turned out to degrade the material beyond mere water evaporation. Therefore, two new oven-drying methods were worked out at IRMM which render moisture results in agreement with the results of Karl-Fischer titration: drying at 90 °C for 40 min or, alternatively, drying at 60 °C for 12 h [3].

The samples were distributed between July and September 2010, the altered oven-drying instructions followed by end of November 2010. Due to this delay, the deadline for submitting results for the gamma-ray emitters was extended – in agreement with all participants - to 24 February 2011 and that for 90Sr to 22 April 2011.

5. Methods used in comparison

5.1 Gamma-ray spectrometry

Whereas the preparation of measurement samples, the methods for efficiency calibration, the traceability of calibration standards, and the methods used for corrections are described in detail in Wätjen et al. [3], the main characteristics of the used methods are summarized here.

All nine laboratories prepared cylindrical sources of the undried bilberry powder. Most prepared one sample with a mass between 50 g and 90 g per bottle of material. CENTIS-DMR and MKEH prepared two samples of about 20 g each per bottle. Some applied “tapping” of the source or slight pressing in order to achieve a better delineation of the volume and a higher density. The density of the prepared powder samples was between 0.58 g·cm⁻³ and 0.68 g·cm⁻³; one laboratory (MKEH) reported a density as high as 0.82 g·cm⁻³.

The source containers varied in material and wall thickness. Seven laboratories used plastic containers with bottom thickness between 1 mm and 2 mm, NIST used a plexiglass container with a 5 mm thick bottom, and MKEH a glass container having a 1 mm thick wall.

The challenge and major source of uncertainty in gamma-ray spectrometry of volume sources is to preserve the traceability link when transferring efficiency values from standard solutions or point standard sources to the measurement parameters of the volume sources (differences in geometry and density). Since the comparison protocol did not prescribe a certain measurement method, a large variety of methods was applied to establish the counting efficiency for the cylindrical sources of bilberry powder.

- Two of these were completely experimental: the addition method of aliquots of primary-standardized solutions, which represents a kind of efficiency tracing; and the use of volume standard sources of similar density in the same geometry.
- The standard addition method (or efficiency tracing) provides the most direct traceability link to primary standards, if problems related to liquid spiking of solid materials, namely the
possibly heterogeneous distribution of the spike can be controlled. The standard addition method was applied by CENTIS-DMR, MKEH, and NIST (for $^{137}$Cs only); CENTIS-DMR explicitly stated the drying and re-homogenizing step after spiking.

- Volume standard sources of similar density in same geometry were applied by IFIN-HH and NIST, the latter for $^{40}$K only. IFIN-HH used a zeolite matrix (density $\sim 0.7$ g cm$^{-3}$) with aliquots of primary-standardized solutions [7], NIST used potassium hydrogen (acid) phthalate (KAP 99.9 % pure) to prepare a standard source of calculated natural $^{40}$K content which was “tapped” until a density very similar to the bilberry matrix was obtained. IAEA spiked a silicone resin matrix (density $\sim 1.0$ g cm$^{-3}$) with a multi-nuclide standard solution (traceable to CMI primary standards). The correction for differences in density and sample height (different source geometry) was done using LABSOCS calculations, confirmed by ETNA [8] and EFFTRAN [9]. It is obvious that the directness of traceability link varies between NIST and IFIN-HH on one hand and IAEA on the other. Heterogeneity of the volume standard sources may be an issue for IFIN-HH and IAEA.

- Two laboratories determined experimentally the self-attenuation in the prepared powder sources with point sources on top of filled and empty containers. These sample-specific linear attenuation coefficients were then used in density correction algorithms for the efficiency determined from multiple-nuclide standard solutions in the same geometry: LNE-LNHB integrated the experimental linear attenuation coefficients in Monte Carlo simulations for efficiency transfer in density, and TAEK used them with the correction formula by Debertin and Helmer [10].

- PTB and IRMM combined an experimental efficiency calibration from point standard sources and/or standard solutions in measurement geometry with Monte Carlo simulations for efficiency transfer in density and geometry. For $^{40}$K, IRMM used a standard source of calculated natural $^{40}$K in a KCl solution in measurement geometry plus Monte Carlo simulation for efficiency transfer in density only.

Details of the methods used to establish the efficiency calibration and efficiency transfer together with the used radionuclides are given in [3]. Traceability of the used standards was either established in-house by primary standardization of solutions, or by purchasing primary-standardized solutions from another NMI (these were NIST in the case of TAEK, CMI in case of IAEA, and, for $^{40}$K only, MKEH in case of CENTIS-DMR). Since NIST and MKEH used themselves, in this comparison, different approaches to establish efficiency than the laboratories using their standards, all calibrations are independent of each other. When cascade gamma-ray emitters were used for efficiency calibration, true coincidence summing corrections were applied, or, in case of TAEK, a large source-detector distance to minimize the effect. All laboratories applied decay corrections to the reference times of used standards and, for the calculation of the activity concentration in the bilberry samples, to the reference date of this comparison.

5.2 Determination of $^{90}$Sr

Initially, nine laboratories participated in the $^{90}$Sr part of the supplementary comparison. Before the deadline for submission of results, two laboratories withdrew; LNE-LNHB because of inconsistent results probably due to too small sample masses (about 4 g) in the analysis procedure, and MKEH. After the remaining 7 laboratories had submitted their results, a visual inspection of the data by the pilot laboratory indicated three possible outliers, the results of CENTIS-DMR, IFIN-HH and NPL. The double Grubb’s test corroborated the results of IFIN-HH and NPL to be statistical outliers at a significance level $\alpha = 0.05$, after the single Grubb’s test failed to detect any outlier due to masking effects. Moreover, the method used at IFIN-HH (gross-beta counting with numerical subtraction of beta emission coming from $^{137}$Cs and $^{40}$K) did not fulfill the criteria of a method producing traceable results to be included in the evaluation of the $^{90}$Sr activity. Therefore, IFIN-HH withdrew its submitted results on technical grounds. The two other laboratories were contacted and invited – corresponding to the CIPM guidelines for key comparisons [11] – to check their results for possible numerical errors. The CENTIS-DMR
responded with a corrected result, based on an improved background value, important in view of the low counting rates obtained with these samples. The NPL withdrew its result because they observed an as yet unexplained bias in a recent proficiency test they participated in, possibly affecting also the present results.

Finally, five laboratories remained to contribute to the determination of $^{90}$Sr in the supplementary comparison CCRI(II)-S8 (Table 1). In analogy to the different approaches used in gamma-ray spectrometry, the determination of $^{90}$Sr was achieved with very different radiochemical separation methods and counting techniques. Table 2 gives a summary of the methods used by the five laboratories. Whereas the ashing of the sample material varied only by temperature and time (400 °C to 650 °C, 16 h to 36 h), the dissolution of ash residues and intermediate precipitates during the separation steps was done with different mineral acids, depending on the precipitation and separation procedures applied further on. The separation of Sr and its purification, however, were performed using widely varying procedures. [12]

Co-precipitation of Sr as carbonate, followed by Fe(OH)$_3$ and BaCrO$_4$ scavenge precipitations (for Ba, Ra, Pb), were used in the CENTIS-DMR. Further purification was accomplished in this procedure by sequential Sr precipitations as chromate and finally carbonate. The IAEA and IRMM applied co-precipitation as oxalate or nitrate, respectively, followed by extraction chromatography with Eichrom Sr resin. The NIST used extraction chromatography on Eichrom Sr resin as primary separation method. It applied a BaCrO$_4$ scavenge precipitation to remove Ra and Pb and two hydroxide scavenge precipitates for further purification. TAEK followed an alternative route, extracted yttrium with HDEHP, followed by back extraction of Y into nitric acid, in order to determine $^{90}$Sr via its daughter $^{90}$Y alone.

The latter laboratory used stable yttrium carrier solution (Y$_2$O$_3$ dissolved in HNO$_3$), added after dissolution of the ash residue, to determine the chemical recovery by titration with Titriplex III, relative to the titre of the yttrium carrier solution. Furthermore, the TAEK verified the recovery for the bilberry matrix by spiking 10 dried bilberry samples with known amounts of $^{90}$Sr and applying the whole radiochemical procedure. In three laboratories, the chemical recovery was determined gravimetrically by adding stable Sr carrier solution to the sample at different steps in the analysis procedure (see Table 2). In these three cases, the natural Sr content of the berry material was corrected for, namely by determination of Sr with GF-AAS at the IAEA or ICP-MS at the IRMM. The NIST corrected for natural Sr with an estimation based on literature values. This estimate, \((0.266 \pm 0.143) \text{ mg Sr per g of ash}\), agrees very well with the value actually determined by ICP-MS at IRMM, namely \((0.25 \pm 0.03) \text{ mg Sr per g of ash}\). The CENTIS-DMR determined the chemical recovery using a $^{88}$Sr tracer solution, which was added to the weighed sample before ashing. The tracer solution had been standardised with a Ge spectrometer, calibrated in turn with point standard sources of MKEH. The same spectrometer was used for the recovery measurements.

The final source preparation was just as varied, where the first step consisted of a last purification: stripping Sr from Sr Spec resin, precipitation of oxalate or carbonate, or precipitation of Y(OH)$_3$ (see Table 2, column 6). The dissolved precipitates or the strip solution were then transferred to scintillation vials for measurement in liquid scintillation (LS) counters (CENTIS-DMR, IAEA, IRMM, TAEK) or filtered and dried in vacuo for gross beta counting in a flow proportional counter (NIST). Two laboratories using liquid scintillation counting as measurement method added liquid scintillation cocktail (Insta-Gel Plus) to the vials. [12]

Although four laboratories measured the samples in LS counters, their measurement approach was completely different. Of the two laboratories using liquid scintillation counting, the IAEA applied a relative method with a calibration source of $^{95}$Sr/$^{90}$Y made, following the same radiochemical procedure, from the same stable Sr carrier solution with a $^{90}$Sr/$^{90}$Y standard of NIST added. The IRMM used the CIEMAT/NIST method (LSC-C/N) of efficiency tracing with tritium. The two other laboratories using LS counters were measuring Cherenkov radiation, in one case (CENTIS-DMR) from $^{90}$Y during ingrowth in the strontium sample (and corrected for...
the $^{85}$Sr contribution to the gross Cherenkov radiation), the TAEK measured Cherenkov radiation from the previously extracted yttrium only.

6. Results

6.1 Dry mass correction

In order to determine the water content of the samples, one laboratory used Karl-Fischer titration, 6 used oven-drying at 90 °C for 40 min and 3 oven-drying at 60 °C for 12 h (one laboratory, TAEK, used both methods). The mean value of water content determined by the 9 laboratories was $3.6 \times 10^{-2}$ g·g$^{-1}$ (mass of water per mass of total material) with a variation of $0.5 \times 10^{-2}$ g·g$^{-1}$ corresponding to 12 %. The variation within any laboratory was of the order of $0.05 \times 10^{-2}$ g·g$^{-1}$ to $0.3 \times 10^{-2}$ g·g$^{-1}$ (1 % to 8 %), and the stated combined uncertainties, $u$, had similar values. These results confirm that the new oven-drying methods are suitable rendering consistent results in agreement with Karl-Fischer titration.

Each laboratory used its own moisture results determined for small sample aliquots between 0.5 g and 10 g to correct the mass of the samples for radionuclide determination to dry mass. 5 laboratories used individual correction factors per bottle, 4 a common correction for all samples. Given the small effective correction by 3.6 % on average, its uncertainty (up to 8 % in relative terms) has only a marginal effect on the corrected activity concentration in dry matter.

6.2 Calculation of the supplementary comparison reference values and their uncertainty

According to the CIPM guidelines [11], laboratories with results flagged for an anomaly after visual inspection or outlier tests were invited to check their results for possible numerical errors, without knowing any other participant’s result. Whereas four laboratories withdrew from the comparison in the $^{90}$Sr part before or after submitting results (cf. section 5.2), all nine laboratories maintained their participation for the gamma-spectrometric part, albeit after correction of numerical errors (cf. section 6.3).

The calculation of the SCRV and its associated standard uncertainty for each of the three radionuclides was performed by using the power-moderated weighted mean [13], following a decision of the CCRI(II) in its meeting of May 2013. This approach provides a robust result intermediate between weighted and arithmetic mean, depending on the quality of the data. It is judged “a good compromise between efficiency and robustness, while providing also a reliable uncertainty” [13].

6.3 $^{137}$Cs and $^{40}$K

After all participating laboratories had submitted their results, a visual inspection of the data by the pilot laboratory indicated three possible outliers among the $^{40}$K results (IAEA, IFIN-HH, MKEH), and one for $^{137}$Cs (IAEA). The Nalimov modified t-test corroborated only the $^{137}$Cs result of the IAEA to be a statistical outlier at a significance level $\alpha = 0.05$. Nonetheless, the three laboratories were contacted to review their corresponding results. Whereas IFIN-HH responded with a significant correction of its $^{40}$K result, due to an error in the determination of the peak efficiency at 1460.8 keV [3], the IAEA corrected a small error in parameter settings of the efficiency transfer code effecting both nuclides only marginally (by 1 % and 4 %). The MKEH reported an insignificant rounding error only. The IAEA, however, discovered later that the used calibration standard had an activity that was higher than stated in the certificate, which rendered the contribution of the IAEA to this comparison too low by about 10 % [14, 12].

Individual results for the 6 samples measured by each laboratory are presented in Figs. 1 and 2 for $^{40}$K and $^{137}$Cs, respectively. The close proximity of most laboratories’ results of its six individual samples, randomly selected from the whole batch of reference material, indicates that
the observed variation between laboratories is a laboratory-specific bias and not due to any unaccounted heterogeneity of the samples [3].

The mean values and their associated combined standard uncertainties, as reported by each laboratory, are presented in Table 3, columns 2 to 5. The SCRV and its associated uncertainty for both radionuclides was calculated as a power-moderated weighted mean [13], using software developed by S. Pommé. Since the IAEA had, meanwhile, discovered that the calibration standard used was not correct, its gamma-spectrometric results were excluded from the calculation of the SCRV for technical reasons. The results are (normalised to dry mass)

\[
\begin{align*}
40^kK & \quad (250.8 \pm 3.4) \text{ Bq kg}^{-1} \quad \text{(with a power } \alpha = 1.63), \\
137^Cs & \quad (780.7 \pm 9.4) \text{ Bq kg}^{-1} \quad \text{(with a power } \alpha = 1.63),
\end{align*}
\]

and are reproduced, together with the mean values of each laboratory, in figures 4 and 5.

6.4 \(^{90}Sr\)

Individual results for the 6 samples measured by each laboratory (3 samples in the case of IAEA due to a failure of laboratory equipment and consequent loss of samples) are presented in Fig.3. The reported mean values and their associated combined standard uncertainties are given in columns 6 and 7 of Table 3. The SCRV and its associated uncertainty for \(^{90}Sr\) was calculated as \((153.7 \pm 3.1) \text{ Bq kg}^{-1}\) (with power \(\alpha = 1.4\)) (reproduced in Fig. 6).

6.5 Degrees of equivalence

The degree of equivalence, \(\text{DoE}_i\), of the result \(A_i\) of a particular laboratory \(i\) with the CRV is defined as the difference \(D_i\) between the values together with the expanded uncertainty \((k = 2)\) of this difference, \(U_i\), hence

\[ \text{DoE}_i = D_i \pm U_i = A_i - \text{CRV} \pm U_i, \]

where \(U_i = 2u(D_i)\). For laboratory results included in the CRV with a weight \(w_i\)

\[ u^2(D_i) = (1-2w_i) u^2 + u^2(\text{CRV}). \]

If the result of a laboratory \(i\) is not included in the CRV\(^2\), then

\[ u^2(D_i) = u^2 + u^2(\text{CRV}). \] [15, 13]

The degrees of equivalence for the results of the laboratories participating in this comparison are given in Table 4.

7. Conclusions

An international supplementary comparison, CCRI(II)-S8, for the determination of activity concentration of \(^{40}K\), \(^{137}Cs\) and \(^{90}Sr\) in a fruit matrix was successfully completed. After withdrawal of some laboratories’ results on technical grounds and correction for numerical errors (without knowledge of other results) in five cases, 8 and 5 laboratories were retained as contributing to the SCRV of the gamma-emitting radionuclides and of \(^{90}Sr\), respectively. Following the conceptual decision of the CCRI(II) in its 2013 meeting, the SCRVs and their uncertainties were calculated using the power-moderated weighted mean: \((250.8 \pm 3.4) \text{ Bq kg}^{-1}\) for \(^{40}K\), \((780.7 \pm 9.4) \text{ Bq kg}^{-1}\) for \(^{137}Cs\) and \((153.7 \pm 3.1) \text{ Bq kg}^{-1}\) for \(^{90}Sr\). Most of the laboratories submitted values that fall within 5 % of the SCRVs. Whereas such degrees of equivalence are much worse than what is usually obtained in key comparisons, the added complexity of measurement due to the nature of matrix samples and the use of secondary standardization methods in this supplementary comparison must be taken into account.

\(^2\) In this comparison, the results of IAEA for \(^{137}Cs\) and \(^{40}K\).
Acknowledgement

The authors are indebted to Stefaan Pommé who kindly made a spreadsheet available containing ‘macros’ with all formulae required to calculate the reference values, using the power-moderated weighted mean, their associated standard uncertainties, and the degrees of equivalence of each laboratory’s results with respect to the reference values.

References


Table 1.
Laboratories participating in CCRI(II)-S8 supplementary comparison "Wild Berries" and acronyms of methods used for the determination of $^{40}$K and $^{137}$Cs or $^{90}$Sr. Partially reproduced from [3].

<table>
<thead>
<tr>
<th>Laboratory name</th>
<th>Acronym</th>
<th>Country</th>
<th>Regional metrology organisation</th>
<th>Method acronym ($^{40}$K and $^{137}$Cs)</th>
<th>Method acronym ($^{90}$Sr)</th>
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Table 2.
Radiochemical methods and counting techniques used in the determination of $^{90}$Sr by the five laboratories submitting results to the CCRI(II) supplementary comparison. Reproduced from [12].

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Preconcentration</th>
<th>Sample dissolution</th>
<th>Purification, separation</th>
<th>Tracer used</th>
<th>Source preparation</th>
<th>Counting method</th>
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<td>CENTIS-DMR</td>
<td>tracer added; ashing at 400 °C, 16 h</td>
<td>dissolution using mineral acids</td>
<td>co-precipitation of Sr as carbonate; Fe(OH)$_3$ and BaCrO$_4$ scavenges; Sr precipitation as chromate and then carbonate; extraction chromatography (Eichrom Sr resin)</td>
<td>$^{90}$Sr, added before ashing, gamma-ray spectrometry; calibrated by point standard sources from MKEH</td>
<td>strip of Sr from Eichrom Sr resin; transferred to glass scintillation vial</td>
<td>4π Cherenkov counting of ingrowing $^{90}$Y in LS counter; $\varepsilon$ of Cherenkov counting by $^{90}$Sr/$^{90}$Y ref. sources (LSC C/N)</td>
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<tr>
<td>IAEA</td>
<td>ashing at 600 °C; Sr carrier added</td>
<td>sequential dissolutions in HNO$_3$, H$_2$O$_2$, HCl</td>
<td>co-precipitation with CaC$_2$O$_4$; extraction chromatography with Eichrom Sr resin</td>
<td>10 mg stable Sr carrier, gravimetrical; nat. Sr of sample with GF-AAS</td>
<td>precipitate of SrC$_2$O$_4$·H$_2$O, filtered, dissolved in HNO$_3$; Insta-Gel Plus added</td>
<td>LSC, $^{90}$Sr/$^{90}$Y in secular equilibrium; calibration sources of same Sr carrier and $^{90}$Sr standard</td>
</tr>
<tr>
<td>IRMM</td>
<td>ashing at 650 °C, 36 h in muffle furnace</td>
<td>predigestion (HNO$_3$+H$_2$O$_2$) over night; Sr carrier added; microwave digestion</td>
<td>Sr-Ca precipitation with fuming HNO$_3$; extraction chromatography (Eichrom Sr resin)</td>
<td>10 mg stable Sr carrier, gravimetrical; nat. Sr of sample with ICP-MS</td>
<td>oxalate precipitate, filtered, dissolved in HNO$_3$; Insta-Gel Plus added</td>
<td>LSC-C/N $^3$H efficiency tracing; $^{90}$Sr/$^{90}$Y in equilibrium</td>
</tr>
<tr>
<td>NIST</td>
<td>ashing at 600 °C, 16 h in muffle furnace; Sr carrier added</td>
<td>dissolution in HNO$_3$; MnO$_2$ dissolved in H$_2$O$_2$</td>
<td>primary separation with Eichrom Sr resin; scavenges precipitation (for Ra, $^{210}$Pb) as BaCrO$_4$; Cr(III), Fe(III) hydroxide scavenges</td>
<td>18 mg stable Sr carrier, gravimetrical; nat. Sr of sample estimated with literature values</td>
<td>carbonate precipitate, filtered, dried in vacuo</td>
<td>gross beta counting, $^{90}$Sr/$^{90}$Y in equilibrium, end-window, gas-flow proportional counter</td>
</tr>
<tr>
<td>TAEK</td>
<td>ashing in 5 steps up to 600 °C, 16 h in microwave furnace</td>
<td>dissolution in boiling HCl; Y carrier added</td>
<td>HDEHP extraction of yttrium, back extraction of Y into HNO$_3$</td>
<td>stable Y carrier, titrated; recovery of Sr from matrix also determined with $^{90}$Sr spikes</td>
<td>yttrium hydroxide precipitate, dissolved in HNO$_3$; transferred to PE scintillation vial</td>
<td>4π Cherenkov counting of $^{90}$Y in LS counter</td>
</tr>
</tbody>
</table>
**Fig. 1.** Individual results for the activity concentration of $^{40}\text{K}$ in the 6 samples measured by each laboratory (normalised to dry mass). The solid and dashed lines represent the arithmetic mean and standard deviation of the 9 laboratories' mean values.

**Fig. 2.** Individual results for the activity concentration of $^{137}\text{Cs}$ in the 6 samples measured by each laboratory (normalised to dry mass). The solid and dashed lines represent the arithmetic mean and standard deviation of the 9 laboratories' mean values.
Fig. 3. Individual results for the activity concentration of $^{90}\text{Sr}$ in the 6 samples measured by each laboratory (3 samples in case of IAEA, see text), normalised to dry mass. The solid and dashed lines represent the arithmetic mean and standard deviation of the 5 laboratories’ mean values.
Table 3.
Activity concentrations of $^{40}$K, $^{137}$Cs and $^{90}$Sr in the bilberry powder matrix of IRMM-426, normalised to dry mass, at reference time 1 January 2009, 00h00 UTC. All mean values, $A_i$, and their combined standard uncertainties, $u_i (k = 1)$, are given as reported by each participant.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>$^{40}$K</th>
<th></th>
<th>$^{137}$Cs</th>
<th></th>
<th>$^{90}$Sr</th>
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<tbody>
<tr>
<td></td>
<td>$A_i$ (Bq·kg$^{-1}$)</td>
<td>$u_i$ (Bq·kg$^{-1}$)</td>
<td>$A_i$ (Bq·kg$^{-1}$)</td>
<td>$u_i$ (Bq·kg$^{-1}$)</td>
<td>$A_i$ (Bq·kg$^{-1}$)</td>
<td>$u_i$ (Bq·kg$^{-1}$)</td>
</tr>
<tr>
<td>CENTIS-DMR</td>
<td>238.3</td>
<td>8.4</td>
<td>749</td>
<td>19</td>
<td>145</td>
<td>11</td>
</tr>
<tr>
<td>IAEA</td>
<td>224.5</td>
<td>4.5</td>
<td>715.2</td>
<td>9.3</td>
<td>150.8</td>
<td>5.3</td>
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<tr>
<td>IFIN-HH</td>
<td>250</td>
<td>16</td>
<td>760</td>
<td>21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IRMM</td>
<td>259</td>
<td>8</td>
<td>816</td>
<td>21</td>
<td>151</td>
<td>4</td>
</tr>
<tr>
<td>LNE-LNHB</td>
<td>251</td>
<td>30</td>
<td>778</td>
<td>47</td>
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<tr>
<td>MKEH</td>
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<td>763</td>
<td>17.6</td>
<td>-</td>
<td>-</td>
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<tr>
<td>NIST</td>
<td>237</td>
<td>10</td>
<td>774</td>
<td>33</td>
<td>165.3</td>
<td>5.5</td>
</tr>
<tr>
<td>PTB</td>
<td>251</td>
<td>5</td>
<td>816</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TAEK$^3$</td>
<td>253</td>
<td>3</td>
<td>775</td>
<td>3</td>
<td>153</td>
<td>4</td>
</tr>
</tbody>
</table>

$^3$ TAEK removed one sample from contributing to its mean value for $^{40}$K and $^{137}$Cs, as it produced outlying results.
Fig. 4. Activity concentration (normalised to dry mass) of $^{40}$K reported by the participants in this comparison, CCR(II)-S8. The uncertainty bars represent the combined standard uncertainty of each laboratory’s value. The solid line represents the SCRV, calculated as power-moderated weighted mean, and the dashed lines correspond to the associated (power-moderated) standard uncertainty of the SCRV.

Fig. 5. Activity concentration (normalised to dry mass) of $^{137}$Cs reported by the participants. The uncertainty bars represent the combined standard uncertainty on these values. The solid line represents the SCRV, calculated as power-moderated weighted mean, and the dashed lines correspond to its associated (power-moderated) standard uncertainty.
Fig. 6. Activity concentration (normalised to dry mass) of $^{90}\text{Sr}$ reported by the participants. The uncertainty bars represent the combined standard uncertainty on these values. The solid line represents the SCRV, calculated as power-moderated weighted mean, and the dashed lines correspond to its associated (power-moderated) standard uncertainty.
Table 4.
Degrees of equivalence, \( DoE_i = D_i \pm U_i \), for the determination of the activity concentration of \(^{40}\text{K}\), \(^{137}\text{Cs}\) and \(^{90}\text{Sr}\) in the bilberry powder matrix of IRMM-426 for all comparison participants.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>(^{40}\text{K})</th>
<th></th>
<th></th>
<th>(^{137}\text{Cs})</th>
<th></th>
<th></th>
<th>(^{90}\text{Sr})</th>
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<tbody>
<tr>
<td></td>
<td>(D_i) (Bq·kg(^{-1}))</td>
<td>(U_i) (Bq·kg(^{-1}))</td>
<td>(D_i) (Bq·kg(^{-1}))</td>
<td>(U_i) (Bq·kg(^{-1}))</td>
<td>(D_i) (Bq·kg(^{-1}))</td>
<td>(U_i) (Bq·kg(^{-1}))</td>
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<td>CENTIS-DMR</td>
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<tr>
<td>IAEA</td>
<td>-26.3</td>
<td>11.3</td>
<td>-65.5</td>
<td>26.4</td>
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<tr>
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<tr>
<td>MKEH</td>
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<td>35.5</td>
<td>-</td>
<td>-</td>
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<td>10.6</td>
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<tr>
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<td>-0.7</td>
<td>8.3</td>
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</table>