

Manuscript Title

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Abstract

Text of abstract, **maximum 80 words**. Example: A new reference material for the activity concentration of ^{137}Cs , ^{40}K and ^{90}Sr in a wild berry was certified from a batch of bilberries collected in the vicinity of the Chernobyl nuclear power plant. Radionuclides in this material were metabolised by the plants, therefore no spiking had to be performed. The material was processed at IRMM and homogeneity and stability were demonstrated. The certified property values for ^{137}Cs , ^{40}K and ^{90}Sr were determined through a supplementary comparison, CCRI(II)-S8. *(The example text is an incomplete excerpt taken from a publication of U. Wätjen et al. (Wätjen et al., 2012))*

Keywords: Radioactivity in food; ^{90}Sr ; ^{137}Cs ; ^{40}K ; Certified reference material; Bilberry

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I. Introduction

In recent years, radioactivity in wild food stuffs found increased interest in the assessment of the exposure of the population to ionizing radiation. This has been particularly so for groups living in regions of increased radioactive fallout, for example after the Chernobyl reactor accident. For this reason, and because of a general lack of certified reference materials (CRMs) for radionuclides in food stuffs, IRMM has been developing a CRM for the activity concentration of ^{40}K and the anthropogenic radionuclides ^{90}Sr and ^{137}Cs in a dried bilberry matrix. The accident of March 2011 in the nuclear power plant Fukushima Daiichi, after the Great Eastern Japan Earthquake of 11 March and the subsequent Tsunami, underlined the need for CRMs of radionuclides in food. The large-scale screening programme for radioactivity in food stuffs, established by the authorities in Japan and many other countries, accentuated the need in order to validate methods providing reliable measurements as a basis for taking undisputable decisions on radiological protection. Although these measurement capabilities are needed for all types of potentially contaminated food, dried bilberry material may be taken as representative for vegetables and fruits in particular. This paper describes the certification of the IRMM reference material IRMM-426 Wild Berries for activity concentrations of the natural radionuclide ^{40}K and the anthropogenic nuclides ^{90}Sr and ^{137}Cs , metabolised by the plants due to natural uptake from elevated levels in the environment.

II. Material

As described in (Wätjen *et al.*, 2012), bilberry samples were collected in the summer of 2005 in a woodland region of so-called “strontium hot spots” close to the Chernobyl reactor site. This region in the Chernihivska oblast was selected by the Ecomonitor Center for Monitoring Studies & Environmental Technologies (CMSET, Kiev) because, due to weather conditions (wind direction, rainout, washout) and core temperature during the Chernobyl reactor accident, the radioactive deposition in this area is characterized by an increased ratio between ^{90}Sr and ^{137}Cs compared to other areas of the region (Voitsekhovich, 2005). The collected berries have a ^{90}Sr activity concentration high enough to be determined with sufficiently small uncertainty, whereas both radionuclides are below the exemption levels to ensure free transport of the material and safe handling in the laboratory. In order to avoid degradation of the berries, the samples were air-dried in ventilation dryers before transport

Table I Uncertainty components for ^{137}Cs and ^{40}K homogeneity measurements.

Uncertainty component	^{137}Cs (%)	^{40}K (%)
Moisture content	0.1	0.1
Weighing	0.1	0.1
Counting statistics (incl. background)	0.23	1.8
Sample positioning	0.2	0.2
Combined standard uncertainty	0.4	1.8

to IRMM. The batch of 130 kg raw material received by IRMM was oven-dried, cryo-milled, sieved, homogenised and bottled in units of about 100 g in 280 mL amber glass jars (Wätjen *et al.*, 2012). A batch of 1186 jars was produced. The water content after bottling was determined by Karl-Fischer titration to be 3.6 % (m/m) . The material was sterilised by γ -irradiation to enhance its long-term stability and to facilitate its transport across borders.

III. Homogeneity and stability studies

A homogeneity study was performed in order to assess the potential contribution of material heterogeneity to the uncertainty of the reference values valid for the whole batch. Sixteen bottles were randomly selected and analysed for one aliquot each of 50 g (11 bottles) or two aliquots of 25 g (5 bottles). The determination procedures applied for ^{137}Cs , ^{40}K and ^{90}Sr were the same as those used by IRMM in the characterization study, but applied here under repeatability conditions using relative measurement results only, thereby eliminating the contribution of intermediate precision from the analytical method. This approach results in a lower measurement uncertainty and small differences in heterogeneity between the sample units are more easily detected (Table I). Table II presents the results of homogeneity measurements for the γ -emitters. The standard deviation s_{bb} of measurement results is taken as a conservative estimate of the uncertainty u_{bb} (or u_{hom}) associated with the material heterogeneity; conservative, since $u_{\text{bb}} = s_{\text{bb}}$ comprises also the intrinsic measurement variation. These values are valid for a minimum sample mass of 50 g.

Table II Homogeneity measurement results for γ -emitters, counting rates normalised to sample mass of 50.0 g (dry mass).

Sample ID	^{137}Cs (cps)	^{40}K (10^{-3} cps)
39	0.455	8.123
78	0.457	8.296
176	0.455	8.073
247	0.452	7.939
358	0.458	8.365
407	0.455	8.159
519	0.456	8.006
585	0.454	8.193
604	0.458	8.276
660	0.460	8.584
744	0.450	8.153
836	0.456	7.928
905	0.451	8.123
1002	0.454	8.408
1041	0.443	8.206
1145	0.456	8.286
mean x	0.454	8.195
st. dev. s	0.0040	0.174
$u_{\text{bb}} = \text{rel. st. dev.}$		
$= s/x$ (%)	0.88 %	2.1 %

An isochronous long-term stability study was carried out with a total of 16 samples of aliquot mass 50 g. In an isochronous stability study, randomly chosen bottles of the material are stored at different temperatures for different periods of time. After the assigned storage period, bottles are removed from the testing temperature environment and stored until the moment of analysis at a reference temperature assumed not degrade the material (in this case, at -18 °C). An isochronous study has the advantage that all samples of the study

can be analysed at the same moment under repeatability conditions, with much smaller measurement uncertainties (Lamberty *et al.*, 1998). In the case of IRMM-426, 6 of the measured samples each were stored for up to one year at temperatures of 4 °C and 18 °C, while 4 samples were kept constantly at the reference temperature of -18 °C. For both temperatures, the slopes of the regression lines versus storage time for the three radionuclides do not differ significantly from zero. In accordance with (ISO Guide 35:2006(E), 2006), the isochronous storage scheme is continued with different bottles than those measured here in order to allow for future monitoring of the material, so called post-certification monitoring.

An isochronous short-term stability study was carried out with a total of an additional 16 samples, stored over a period of 6 weeks at 18 °C and 60 °C in order to simulate transport conditions of the CRM. No significant change in the activity concentration for any of the radionuclides at 18 °C was observed, but a decrease of about 3.5 % (still within overlapping uncertainties) was measured for ^{137}Cs and ^{40}K in samples, kept at 60 °C for 6 weeks. Taking into consideration that the shipping period of the material normally would not take more than 1 week, such very high hypothetical transport temperature would lead to a 0.4 % additional uncertainty contribution for ^{137}Cs and ^{40}K and 0.2 % for ^{90}Sr .

In summary, the standard uncertainties due to the possible heterogeneity of ^{137}Cs , ^{40}K and ^{90}Sr in the material for an aliquot mass of 50 g were determined to be 0.9 %, 2.1 % and 1.8 %, respectively. The standard uncertainties for the long term stability, over a period of one year, are 1.0 %, 1.2 % and 2.0 % for ^{137}Cs , ^{40}K and ^{90}Sr , respectively. In comparison to these uncertainty contributions to the combined uncertainty of the CRM property values, the standard uncertainty attributable to transport conditions, u_{sts} , is negligible.

IV. Characterisation study

A. Determination of γ -ray emitting radionuclides

Seven national metrology institutes (NMIs) or designated institutes (DIs) and two international organisations took part in the characterisation study, organised as a supplementary comparison of the Consultative Committee for Ionizing Radiation Section II (Measurement of Radionuclides) under the designation CCRI(II)-S8 “bilberry”. Each laboratory obtained 6 samples of the dried bilberry powder, and had to submit 6 individual results of the activity concentrations normalised to dry mass and a corresponding mean value. The results for

the two gamma-emitters in this supplementary comparison were published already in much detail by Wätjen *et al.* (Wätjen *et al.*, 2012), but one laboratory, IAEA, found that the calibration standard used in their contribution to CCRI(II)-S8 had an activity that was higher than stated in the certificate. Consequently, the experimental efficiency of the detector system was determined too large, which rendered the results of IAEA in the supplementary comparison too low by about 10 %. Therefore, whereas the original values of the supplementary comparison are kept, the results of IAEA are not taken into account for the reference material certification since they were incorrect. The mean values and standard deviations of the eight retained laboratories' results for the activity concentration of ^{137}Cs and ^{40}K in IRMM-426 Wild Berries are $(779 \pm 25) \text{ Bq}\cdot\text{kg}^{-1}$ and $(253 \pm 15) \text{ Bq}\cdot\text{kg}^{-1}$ (dry mass), respectively. As shown by Wätjen *et al.* (Wätjen *et al.*, 2012), the large variety of efficiency calibration and geometry and density transfer methods used in the eight laboratories renders the arithmetic means of the characterisation campaign very robust.

B. Determination of ^{90}Sr

Five laboratories participated in the determination of ^{90}Sr in the supplementary comparison CCRI(II)-S8. As with the different approaches used in γ -ray spectrometry, the determination of ^{90}Sr was achieved with very different radiochemical separation methods and counting techniques. 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, was performed using widely varying procedures. Co-precipitation of Sr as carbonate, oxalate or nitrate were first steps in the procedure, followed by (sequential) scavenge precipitations such as $\text{Fe}(\text{OH})_3$, BaCrO_4 or carbonate, or, alternatively, followed directly by extraction chromatography on Sr resin. The NIST applied several scavenge precipitations for further purification after extraction chromatography. 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 only.

The latter laboratory used stable yttrium carrier solution, added after dissolution of the ash residue, to determine the chemical recovery by titration. Furthermore, 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 points in the analysis procedure. The CENTIS-DMR determined the chemical recovery using a standardised ^{85}Sr tracer solution, added before ashing, and γ -ray spectrometry.

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 $\text{Y}(\text{OH})_3$). The dissolved precipitates or the strip solution were then transferred to scintillation vials for measurement in liquid scintillation (LS) counters (four laboratories) or filtered and dried in vacuo for gross beta counting in an end-window, gas-flow proportional counter. Although four laboratories measured the samples in LS counters, their approach was completely different. Of the two laboratories using liquid scintillation counting, both of which added Insta-Gel Plus as scintillation cocktail, one applied a relative method with a calibration source of $^{90}\text{Sr}/^{90}\text{Y}$ whereas the other relied on the CIEMAT/NIST efficiency tracing method (LSC-C/N). The two other laboratories using LS counters were measuring Cherenkov radiation (in one case, from the ingrowing ^{90}Y in the strontium sample, in the other, from the previously extracted yttrium).

The results of the five laboratories contributing to the ^{90}Sr property value of IRMM-426 are shown in Figure 1, together with their combined standard uncertainties, $u_{c,i}$, and the certified property value with its expanded uncertainty U_{CRM} .

V. Certified property values

All three property values of IRMM-426 Wild Berries and their combined standard uncertainty and uncertainty contributions u_{char} , u_{hom} , u_{lbs} and u_{sts} are given in Table III. The uncertainties are propagated following the well-known equation

$$u_{\text{CRM}} = \sqrt{u_{\text{char}}^2 + u_{\text{hom}}^2 + u_{\text{lbs}}^2 + u_{\text{sts}}^2} \quad (1)$$

to estimate the combined standard uncertainty u_{CRM} of the property values according to ISO Guide 35 (ISO Guide 35:2006(E), 2006), taking the demonstrated homogeneity (assessed as between-unit heterogeneity) and stability (within their limits, expressed as standard uncertainties) of the CRM into account. With the values found for the short-term stability, u_{sts} can be set to zero. The standard uncertainty, u_{char} , of determining the property values from

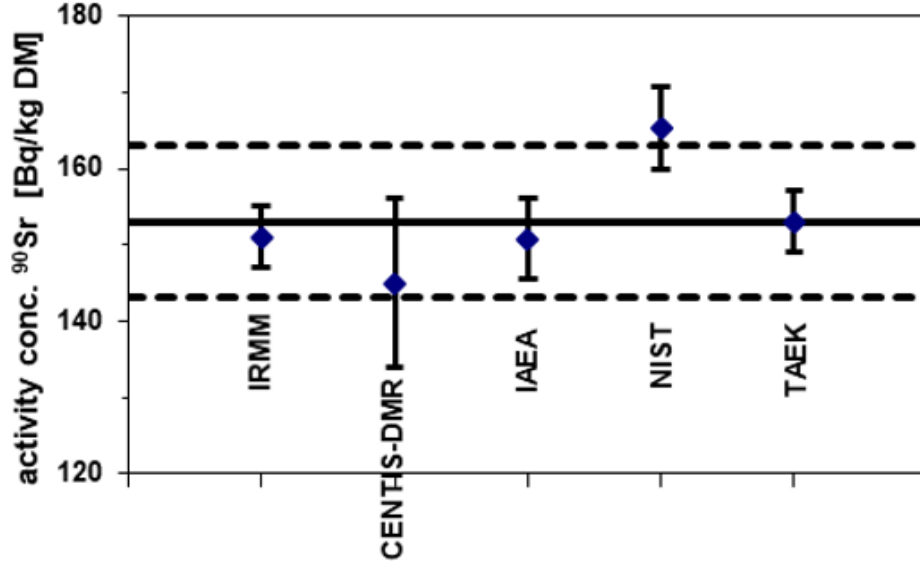


Figure 1 Results of laboratories in the characterisation study and certified reference value for ^{90}Sr in IRMM-426, given as arithmetic mean (solid line) and expanded uncertainty $U_{CRM} = k \cdot u_{CRM}$ ($k = 2$) (dotted). Laboratory means shown with their combined standard uncertainties $u_{c,i}$ (error bars). DM denotes dry mass.

the characterisation study is derived from (Pauwels *et al.*, 1998), provided that the results of all laboratories are independent of each other:

$$u_{\text{char}}^2 = \frac{\sum_{i=1}^n u_{c,i}^2}{n^2} \quad (2)$$

where $u_{c,i}$ is the combined standard uncertainty of the measurement result reported by each of the n laboratories in the characterisation study.

The certified property values, corrected to dry mass and their expanded uncertainties $U_{CRM} = k \cdot u_{CRM}$ (coverage factor $k = 2$) are as follows:

$$\begin{aligned} ^{137}\text{Cs}: & \quad 779 \pm 28 \text{Bq} \cdot \text{kg}^{-1} \\ ^{40}\text{K}: & \quad 253 \pm 16 \text{Bq} \cdot \text{kg}^{-1} \\ ^{90}\text{Sr}: & \quad 153 \pm 10 \text{Bq} \cdot \text{kg}^{-1} \end{aligned}$$

VI. Conclusion

A new reference material, IRMM-426, for the two most important anthropogenic radionuclides ^{137}Cs and ^{90}Sr (and the natural ^{40}K) in a dried berry matrix was certified following

Table III Certified property values of IRMM-426 Wild Berries, their combined standard uncertainty u_{CRM} and uncertainty components (all values in Bq·kg⁻¹ dry mass).

Nuclide	Property value	Comb. std. unc. u_{CRM}	u_{char}	u_{hom}	u_{lts}	u_{sts}
¹³⁷ Cs	779	14	8.8	7.0	7.8	3.2
⁴⁰ K	253	8	5.4	5.3	3.0	1.0
⁹⁰ Sr	153	5	2.9	2.8	3.1	0.31

the requirements of ISO Guide 35 (ISO Guide 35:2006(E), 2006). Homogeneity and stability studies were carried out at IRMM, whereas the measurement results of nine national and international standard laboratories in the CCRI(II)-S8 supplementary comparison “bilberry” were used for the characterisation study of the new CRM. The wide range of approaches to efficiency calibration in gamma-ray spectrometry and of radiochemical procedures and counting methods applied in ⁹⁰Sr determination renders the certified property values robust with low associated uncertainties. The new CRM IRMM-426 can be used to validate radionuclide measurement methods in research and monitoring laboratories. It will contribute to more reliable measurements of radionuclides in food and improved food screening for radioactivity as a basis for taking informed decisions on radiological protection.

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