**Title: Times New Roman (TNR), 14 point, bold**

**Author1a, author2b\*, author3a, author4c, etc. (Times New Roman, 12 point, bold)**

a Institution a (Times New Roman, 9 point)
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**Abstract *(in TNR 9 bold)***

Text of abstract, maximum 80 words, Times New Roman, 9 point. Left and right 1 cm additional margin, left and right aligned. Example: A new reference material for the activity concentration of 137Cs, 40K and 90Sr 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 137Cs, 40K and 90Sr 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.)*

**Keywords:** radioactivity in food; Sr-90; Cs-137; K-40; certified reference material; bilberry

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1. **Introduction *(all section headings in TNR 9 bold)***

*(all text in TNR 9, single line, insert free lines at headings/ figures/tables/equations as given here)* 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 40K and the anthropogenic radionuclides 90Sr and 137Cs 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 40K and the anthropogenic nuclides 90Sr and 137Cs, metabolised by the plants due to natural uptake from elevated levels in the environment.

1. **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 90Sr and 137Cs compared to other areas of the region (Voitsekhovych, 2005). The collected berries have a 90Sr 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 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 gamma-irradiation to enhance its long-term stability and to facilitate its transport across borders.

1. **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 137Cs, 40K and 90Sr 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 1). Table 2 presents the results of homogeneity measurements for the gamma-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*bb = *s*bb comprises also the intrinsic measurement variation. These values are valid for a minimum sample mass of 50 g.

**Table 1:** Uncertainty components for 137Cs and 40K homogeneity measurements. *(end of table/figure caption with half row extra)*

Uncertainty component 137Cs (%) 40K (%)

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

**Table 2:** Homogeneity measurement results for gamma-emitters, counting rates normalised to sample mass of 50.0 g (dry mass).[[1]](#footnote-1)

Sample ID 137Cs (cps) 40K (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

std. dev. *s* 0.0040 0.174

*u*bb = rel. std. 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 (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 137Cs and 40K 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 137Cs and 40K and 0.2 % for 90Sr.

In summary, the standard uncertainties due to the possible heterogeneity of 137Cs, 40K and 90Sr 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 137Cs, 40K and 90Sr, respectively. In comparison to these uncertainty contributions to the combined uncertainty of the CRM property values, the standard uncertainty attributable to transport conditions, usts, is negligible.

1. **Characterisation study**
	1. *Determination of gamma-ray emiting 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. (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 137Cs and 40K in IRMM-426 Wild Berries are (779 ± 25) Bq·kg–1 and (253 ± 15) Bq·kg–1 (dry mass), respectively. As shown by 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.

* 1. *Determination of 90Sr*

Five laboratories participated in the determination of 90Sr in the supplementary comparison CCRI(II)-S8. As with the different approaches used in gamma-ray spectrometry, the determination of 90Sr 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 Fe(OH)3, BaCrO4 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 90Sr via its daughter 90Y 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 90Sr 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 85Sr tracer solution, added before ashing, and gamma-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 Y(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 90Sr/90Y 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 90Y in the strontium sample, in the other, from the previously extracted yttrium).

**Fig. 1:** Results of laboratories in the characterisation study and certified reference value for 90Sr in IRMM-426, given as arithmetic mean (solid line) and expanded uncertainty *U*CRM = *k*·*u*CRM (*k* = 2) (dotted). Laboratory means shown with their combined standard uncertainties *u*c,i (error bars). DM denotes dry mass.

The results of the five laboratories contributing to the 90Sr property value of IRMM-426 are shown in Fig. 1, together with their combined standard uncertainties, *u*c,i, and the certified property value with its expanded uncertainty *U*CRM.

1. **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*lts and *u*sts are given in Table 3. The uncertainties are propagated following the well-known equation

to estimate the combined standard uncertainty *u*CRM of the property values according to ISO Guide 35 (ISO, 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 the characterisation study is derived from Pauwels et al. (1998), provided that the results of all laboratories are independent of each other:

where *u*c,i is the combined standard uncertainty of the measurement result reported by each of the *n* laboratories in the characterisation study.

**Table 3:** 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).

 comb.std.

nuclide property uncert. *u*char *u*hom *u*lts *u*sts

 value *u*CRM

137Cs 779 14 8.8 7.0 7.8 3.2

40K 253 8 5.4 5.3 3.0 1.0

90Sr 153 5 2.9 2.8 3.1 0.31

The certified property values, corrected to dry mass and their expanded uncertainties *U*CRM = *k*·*u*CRM (coverage factor *k* = 2) are as follows:

137Cs : 779 ± 28 Bq·kg-1

40K : 253 ± 16 Bq·kg-1

90Sr : 153 ± 10 Bq·kg-1

1. **Conclusions**

A new reference material, IRMM-426, for the two most important anthropogenic radionuclides 137Cs and 90Sr (and the natural 40K) in a dried berry matrix was certified following the requirements of ISO Guide 35 (ISO, 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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1. *See note on page 4 concerning large tables/figures* [↑](#footnote-ref-1)