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Results of an EC laboratory comparison on ^{40}K, ^{90}Sr and ^{137}Cs in dried bilberry powder

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HIGHLIGHTS

- New CRM IRMM-426 Wild Berries was used as test material.
- Only 91% and 83% of ^{137}Cs and ^{40}K results within 20% of reference values.
- Good performance for ^{90}Sr: 88% within 30% of reference values.
- For many labs, discrepant evaluation to E_n criterion and relative deviations.
- Many laboratories cannot estimate realistic uncertainties (^{137}Cs, ^{90}Sr).

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ABSTRACT

The evaluation is presented of a laboratory comparison (LC) on ^{90}Sr, ^{40}K and ^{137}Cs in dried bilberries organised in 2011 by the IRMM. The activity concentrations reported by 88 participant laboratories are compared to the reference values of the new reference material IRMM-426 Wild Berries. Nine per cent and 17% of activity concentration results for ^{137}Cs and ^{40}K, respectively, deviate more than 20% from the reference values, a result worse than that obtained in previous LCs. For ^{90}Sr, about 88% of results lie within 30% of the reference value, better than observed in previous LCs. But only 58% of ^{90}Sr results are satisfactory in terms of the E_n criterion, indicating difficulties with a complete uncertainty estimation.

1. Introduction

Member States of the European Union are obliged by the Euratom Treaty and derived European legislation to perform measurements of radioactivity and to report the results to the European Commission. Regular European comparisons are conducted in order to verify the performance of monitoring laboratories and ensure comparability of reported results. Since 2003, these laboratory comparisons (LCs) have been organised by the Institute for Reference Materials and Measurements (IRMM). The accident in the nuclear power plant at Fukushima Daiichi in 2011, resulting from the Great Eastern Japan Earthquake and subsequent Tsunami, underlined the importance of radioactivity monitoring in food stuff and the use of comparisons/proficiency tests to provide confidence in measurement results.

In 2011, IRMM organised an LC on the activity concentrations of three radionuclides (^{40}K, ^{90}Sr, ^{137}Cs) in dried bilberry powder. Participants were nominated by the national representatives in the expert group according to the Euratom Treaty articles 35/36. Moreover, several laboratories from EU (pre-)accession and other European countries were invited to participate. In total, 88 laboratories reported measurement results. A robust evaluation of the performance of the individual laboratories was done using relative deviations and the E_n criterion.

2. The reference values

The candidate reference material IRMM-426 Wild Berries was used as the testing material. The collection of the berries in a region affected by the Chernobyl NPP accident, their processing at IRMM, and the CCRI(II) supplementary comparison used to determine reference values for the gamma-ray emitters were described previously (Wätjen et al., 2012). The certification of IRMM-426, including its characterisation for ^{90}Sr, is presented elsewhere in these proceedings (Wätjen et al., 2014). The reference values for the three radionuclides are reproduced in Table 1. The use of a large variety of sample processing, radiochemical separation and source preparation techniques, tracers and counting methods (Wätjen et al., 2014) ensured the reference values are robust and reliable.

The timing of the LC was chosen to ensure the anonymity of the reference values. The LC reporting deadline was 3 days before

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Table 1
Activity concentrations A_{ref} with expanded uncertainties U_{ref} ($k=2$) in the certified reference material IRMM-426 Wild Berries at reference date 1 January 2009.

Radionuclide	$A_{ref} \pm U_{ref}$ (Bq kg^{-1})
^{40}K	253 ± 16
^{90}Sr	153 ± 10
^{137}Cs	779 ± 28

the ICRM 2011 conference, where the results of the CCRI(II) supplementary comparison were first presented.

3. Methods used by the laboratories participating in the comparison

Each laboratory received about 100 g of the testing material (one bottle). Participants used measurement methods of their own choice, preferably the routine procedures of their laboratories. This choice did not apply to the material drying needed to report results corrected for dry mass. The laboratories were requested to use one of the two drying procedures provided by IRMM (Wätjen et al., 2012). Depending on their capabilities, they were asked to determine activity concentrations of ^{40}K, ^{90}Sr, and ^{137}Cs. Activity concentrations of ^{137}Cs and ^{40}K were determined (with one exception) by direct gamma-ray spectrometry. One laboratory measured the ^{137}Cs activity via beta counting after radiochemical separation and the ^{40}K activity using flame spectrophotometry.

Most often, strontium and yttrium were separated from the sample by several consecutive precipitation (mainly oxalate) steps. Extraction with di-(2-ethylhexyl)phosphoric acid (HDEHP) in toluene was applied in eight laboratories. Sr Resin, often in combination with precipitation, was used by seven participants, other unspecified extraction chromatography in five laboratories. One of these laboratories used home-made resin. Separation based on isolation of strontium from calcium with fuming nitric acid was applied in two laboratories. Five different counting methods were applied for the strontium determination. The majority of laboratories used gas flow proportional counting. Others employed liquid scintillation counting (LSC), Cherenkov counting, plastic scintillation and Geiger-Müller (GM) counters.

4. Scoring criteria

As in previous LCs, the results were evaluated against the reference values using two approaches (Wätjen, 2008), viz. by relative deviation D_{rel}

$$D_{rel} = \frac{A_{lab} - A_{ref}}{A_{ref}} \cdot 100$$

where A_{lab} is the participant's result for mean activity concentration, A_{ref} is the reference value, and by the performance statistic "E_n number" (ISO, 2005)

$$E_n = \frac{A_{lab} - A_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

where U_{lab} is the expanded uncertainty ($k=2$) of the participant's result, and U_{ref} is that of the reference value. The E_n numbers are interpreted in the following way:

$|E_n| \le 1$, satisfactory, the laboratory values are compatible with the reference value;
$|E_n| > 1$, unsatisfactory, "warning signal"; the laboratory values differ significantly from the reference value, sources of deviation should be investigated and corrected; a second level of critical value can be defined:
$|E_n| > 1.5$, "action signal", there is an urgent need to investigate and find the sources of the large deviation.

5. Results of the comparison and discussion

Out of 88 participants, 84 and 86 reported results for ^{40}K and ^{137}Cs, respectively. For ^{90}Sr, 52 participants submitted results. Table 2 presents the percentage of results within ±20% of the reference values and the performance of laboratories expressed in terms of the E_n criterion. The 20% criterion is an arbitrarily chosen level based on a perception that routine gamma-spectrometric analysis is achievable within this level of deviation.

Only 83% and 91% of the results for the gamma-ray emitters ^{40}K and ^{137}Cs, respectively, were deviating less than 20% from the reference values. Among the 12 laboratories reporting too high values for ^{40}K (Fig. 1), four laboratories had also too high results for ^{137}Cs (Fig. 2, the four highest values). Apparently, for these four laboratories, there are sources of error in their general gamma-spectrometric procedures, rendering too high results for both radionuclides. The result of one of these laboratories deviated for ^{40}K by 110% from the reference value. The laboratory using beta counting for ^{137}Cs after radiochemical separation reported a result which is only 10% of the reference value and this might suggest that the method is not fit for purpose. It is particularly disturbing that the results for gamma-ray emitters in the present LC are worse than those in previous ones, especially as the activity concentrations were somewhat similar. The soil LC (Merešová et al., 2012) and the milk LC (Wätjen, et al., 2008) had 93% and

Table 2
Overview of the laboratory performances regarding relative deviation and E_n criterion for ^{40}K, ^{137}Cs and ^{90}Sr. The numbers in parentheses indicate number of laboratories.

	^{40}K (84)	^{137}Cs (86)	^{90}Sr (52)
Within ± 20%	83% (70)	91% (78)	77% (40)
Outside ± 20%	17% (14)	9% (8)	23% (12)
Satisfactory $\|E_n\| \le 1$	81% (68)	72% (62)	58% (30)
Warning $\|E_n\| > 1$	7% (6)	6% (5)	15% (8)
Action $\|E_n\| > 1.5$	12% (10)	22% (19)	27% (14)

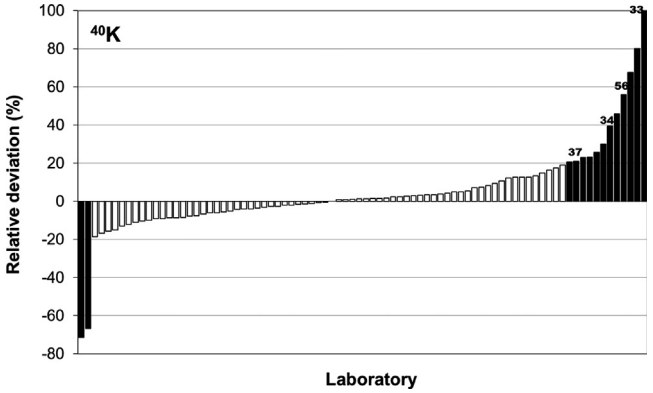

Fig. 1. Deviation chart of the participants' results of ^{40}K plotted in ascending order. White histogram bars indicate results within the range ±20% from the reference value and black indicate results outside this range.

98% of laboratories reporting results within 20% for ^{40}K and ^{137}Cs, respectively. The reference to previous LCs serves as an overall comparison of results. The individual laboratories are for a large part different, about half of the laboratories in the present LC did not participate in the previous ones referred to.

The evaluation in terms of the E_n criterion corroborates the findings only for ^{40}K. Eighty-one per cent of the ^{40}K results are compatible with the reference value, 7% of results trigger a warning signal and 12% an action signal. Interestingly, for ^{137}Cs, the numbers are worse: 72%, 6% and 22% respectively (Fig. 3). This discrepancy in performance between E_n criterion and deviation from the reference value of around 20% of the laboratories can only be explained by an underestimation of uncertainties. Sixteen per cent of all laboratories claim combined standard uncertainties for the determination of ^{137}Cs of less than 1.5%, most of which (11 laboratories or 13%) declare uncertainty in efficiency calibration either as dominant (at such low values) or non-existent compared to counting uncertainty.

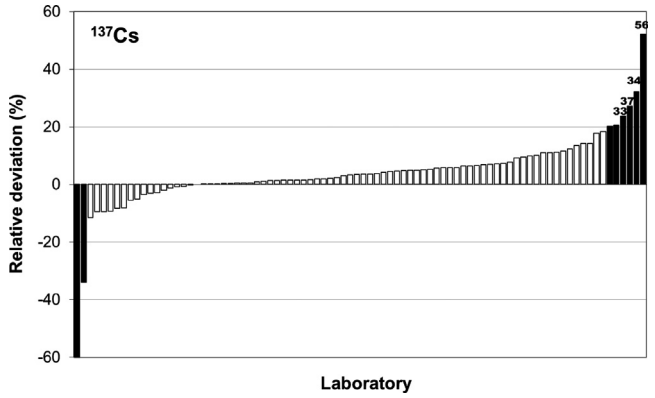

Fig. 2. Deviation chart of the participants' results of ^{137}Cs plotted in ascending order. White bars indicate results within the range ± 20% from the reference value and black indicate results outside this range.

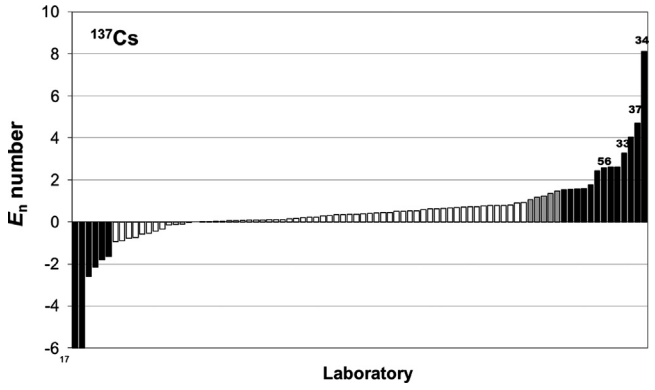

Fig. 3. E_n numbers of laboratory results for ^{137}Cs activity concentrations plotted in ascending order. White bars indicate compatible results, grey indicate warning signal and black indicate action signal.

In terms of relative deviation, unsatisfactory results can probably be attributed to the difficulties in dealing with the matrix material, its density and the sample-detector geometry. The efficiency calibration for such volume sources requires correction and efficiency transfer methods from standard sources to the geometry and density of the bilberry powder samples. These corrections (or their omission) may be underestimated in terms of uncertainty (or bias). Moreover, the high number of results above 20% from the reference value in the case of ^{40}K also suggests difficulties with the background correction or efficiency calibration in that energy region.

In evaluating the determination of ^{90}Sr, a less strict criterion (30%) is often used, taking into account the high complexity of these measurements. Whereas 77% of results fall within the 20% criterion, it is found that 88% of the results lie within 30% from the reference value. This good performance is remarkable in itself and much better than that observed in the previous LCs, where about 23% and 35% of laboratories deviated more than 30% from the reference value for the milk LC (Spasova et al., 2008) and the soil LC (Merešová et al., 2012), respectively. Contrary to this, based on the E_n criterion, only 58% of reported values are satisfactory. Warning and action signals are triggered by 15% and 27% of results, respectively. These results are somewhat worse than the overall results of the milk LC (68% satisfactory) and better in comparison to the soil LC (only 35% satisfactory), indicating – by comparison to the favourable results based on relative deviations – that, in ^{90}Sr determination, difficulties with a correct estimation of measurement uncertainties are even larger than in gamma-ray spectrometry.

The activity concentration of ^{90}Sr was determined by a large number of different analysis procedures. An attempt was made to group and compare the results by separation method as far as information was given (Table 3). With one exception, no significant difference between the results obtained by using different

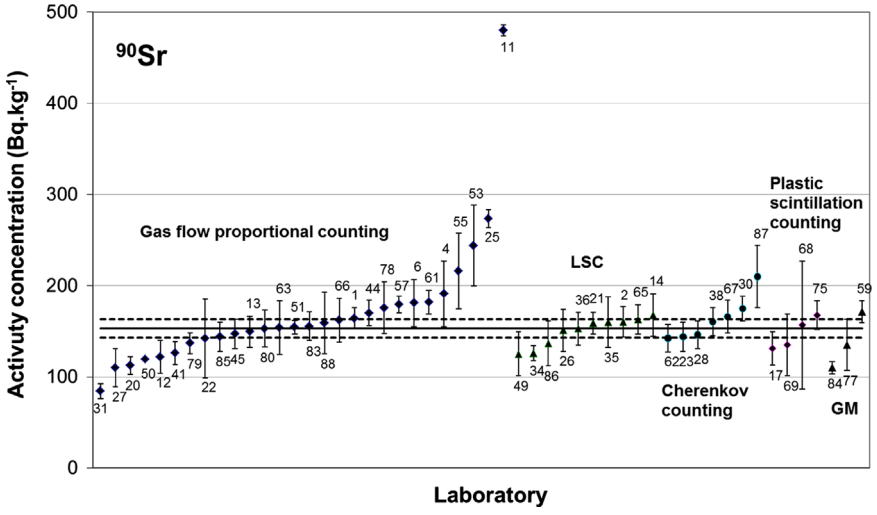

Fig. 4. Activity concentrations of ^{90}Sr determined by the laboratories, sorted according to counting technique. Solid and dashed lines indicate reference value and expanded uncertainty ($A_{ref} \pm U_{ref}$), error bars are expanded uncertainties reported by the laboratories.

Table 3
Overview of the laboratory performances regarding relative deviation and E_n criterion sorted according to separation methods of ^{90}Sr. The numbers in parentheses indicate number of laboratories. Eighteen laboratories did not provide relevant information.

	Precipitation (11)	HDEHP (8)	Extraction chromatography		Fuming
			Unspecified (6)	Sr resin (7)	Nitric acid (2)
Within ± 20%	82% (9)	100% (8)	50% (3)	100% (7)	100% (2)
> 20%, < 30%	9% (1)	0% (0)	17% (1)	0% (0)	0
Outside ± 30%	9% (1)	0% (0)	33% (2)	0% (0)	0
Compatible $\|E_n\| \leq 1$	55% (6)	88% (7)	17% (1)	86% (6)	100% (2)
Warning $\|E_n\| > 1$	27% (3)	12% (1)	0	0	0
Action $\|E_n\| > 1.5$	18% (2)	0	83% (5)	14% (1)	0

Table 4
Overview of the laboratory performances regarding relative deviation and E_n criterion sorted according to counting methods for ^{90}Sr. The numbers in parentheses indicate number of laboratories.

	Gas flow proportional counter (28)	LSC (10)	Cherenkov counting (7)	Plastic scintillation counting (4)	Geiger Müller counting (3)
Within ± 20%	64% (18)	100% (10)	86% (6)	100% (4)	67% (2)
> 20%, < 30%	18% (5)	0% (0)	0% (0)	0% (0)	33% (1)
Outside ± 30%	18% (5)	0% (0)	14% (1)	0% (0)	0% (0)
Compatible $\|E_n\| \leq 1$	46% (13)	80% (8)	71% (5)	75% (3)	33% (1)
Warning $\|E_n\| > 1$	14% (4)	10% (1)	14% (1)	25% (1)	33% (1)
Action $\|E_n\| > 1.5$	39% (11)	10% (1)	14% (1)	0	33% (1)

separation methods is observed. Only extraction chromatography where the details were not specified provided the most discrepant results with half of them deviating more than 20% from the reference value and triggering a warning or action signal for three laboratories. On the other hand, extraction chromatography with Sr resin proved very successful, 100% of results within 20% of the reference value. A similar comparison was done for the counting methods (Table 4). The most frequently used counting method was gas proportional counting (28 participants). In spite of the small number of laboratories involved, not allowing to draw definite conclusions, there is evidence that LSC and plastic scintillation counting and also Cherenkov counting (with only one laboratory of 7 off) render better results than gas flow proportional and Geiger Müller counting, where one-third of results exceeds the 20% criterion (Fig. 4).

6. Conclusions

An LC for radionuclide activity concentration in a food matrix was organised with a new IRMM reference material, unknown to the participants at the time of the LC. Nine per cent and 17% of the results for activity concentration of ^{137}Cs and ^{40}K, respectively, deviated by more than 20% from the reference values. These results are worse in comparison to previous LCs organised by IRMM. This result may be due to the special character of the food matrix and inappropriate use or neglect of necessary corrections such as for density and/or geometry differences between calibration standards and LC test samples, but there is no direct evidence to support these conjectures. Further investigations would be needed to draw any definite conclusions. This comparison demonstrates that 10–20% of laboratories had difficulties to determine activity concentrations of ^{137}Cs and ^{40}K in this particular food sample.

The performance in the determination of ^{90}Sr, seen the complexity of radiochemical procedures, is remarkable with only 12% of results lying outside ± 30% from the reference value, and significantly better than that observed in previous exercises. The bad evaluation results with respect to the E_n criterion (42% not compatible), however, demonstrate the challenges of realistic uncertainty estimations. Separation of strontium by extraction chromatography without specified details was performing significantly worse than all other methods used, including extraction chromatography on Sr resin with 100% success rate. Among the counting methods, there is evidence (albeit with small numbers) that gas flow proportional and Geiger Müller counting perform worse than the other detection methods.

The use of two fundamentally different performance criteria in the same laboratory comparison, leading to discrepant evaluation results depending on the criterion, revealed the enormous difficulties that many laboratories have with correct uncertainty estimations, in particular for ^{137}Cs and ^{90}Sr in this comparison. All laboratories with unsatisfactory results with respect to relative deviation or the E_n criterion, whether in gamma-ray spectrometry or in the determination of ^{90}Sr, are urged to investigate and improve their analysis procedures and/or their estimation of uncertainties.

Acknowledgements

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