

JRC REFERENCE MATERIALS REPORT



The certification of the activity concentration of the radionuclides ^{137}Cs , ^{90}Sr and ^{40}K in wild berries: IRMM-426

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Abstract

This report describes the production of CRM IRMM-426, a dried bilberry material certified for the radionuclide activity concentrations of ^{137}Cs , ^{90}Sr and ^{40}K . The material was produced following ISO Guide 34:2009. Bilberry samples were collected in a woodland region of so-called "strontium hot spots" close to the Chernobyl reactor site. The samples were air-dried at the sampling site before transport to IRMM, where the raw material was oven-dried, cryo-milled, sieved, homogenised and bottled. The bottled material was sterilised by gamma-irradiation. Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006. The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only. Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity and instability and to characterisation. The material is intended for the assessment of method performance and quality control. As any reference material, it can also be used for control charts or validation studies. The CRM is available in amber glass jars containing about 100 g of dried bilberry powder. The minimum amount of sample to be used for analysis is 50 g for ^{90}Sr and 18 g for ^{137}Cs and ^{40}K .

CERTIFICATION REPORT

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Summary

This report describes the production of CRM IRMM-426, a dried bilberry material certified for the radionuclide activity concentrations of ^{137}Cs , ^{90}Sr and ^{40}K . The material was produced following ISO Guide 34:2009 [1].

Bilberry samples were collected in a woodland region of so-called “strontium hot spots” close to the Chernobyl reactor site. The samples were air-dried at the sampling site before transport to IRMM, where the raw material was oven-dried, cryo-milled, sieved, homogenised and bottled. The bottled material was sterilised by gamma-irradiation.

Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006 [2].

The material was characterised by an intercomparison¹ among laboratories of demonstrated competence and adhering to ISO/IEC 17025 [3]. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4] and include uncertainties related to possible inhomogeneity and instability and to characterisation.

The material is intended for the assessment of method performance and quality control. As any reference material, it can also be used for control charts or validation studies. The CRM is available in amber glass jars containing about 100 g of dried bilberry powder. The minimum amount of sample to be used for analysis is 50 g for ^{90}Sr and 18 g for ^{137}Cs and ^{40}K .

The following values were assigned (at reference date 1 January 2009, 00h00 UTC):

	Radionuclide activity concentration at reference date 1 January 2009, 00h00 UTC	
	Certified value ^{1) 2)} [Bq kg ⁻¹]	Uncertainty ^{1) 3)} [Bq kg ⁻¹]
^{137}Cs	780	70
^{90}Sr	153	29
^{40}K	253	25

1) Certified values and uncertainty at time of measurement (decay correction) to be calculated by using only the Recommended decay data: http://www.nucleide.org/DDEP_WG/DDEPdata.htm.

2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and with a different or largely differing (^{137}Cs and ^{40}K) method of determination. The certified value and its uncertainty are traceable to the International System of Units (SI). All values are stated on dry mass basis.

3) The uncertainty is the expanded uncertainty with a coverage factor $k = 2$ (2.2 in case of ^{90}Sr) corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

¹ CCRI(II) supplementary comparison CCRI(II)-S8 “wild berries”

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Glossary

A	Activity of a radionuclide
A_m	Massic activity or Activity concentration $A_m = A / m$
ANOVA	Analysis of variance
BIPM	Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
CCRI	Comité Consultatif des Rayonnements Ionisants (Consultative Committee for Ionising Radiation)
CENTIS-DMR	Centro de Isótopos – Metrología de Radionúclidos (Center of Isotopes – Radionuclide Metrology Department) (Cuba)
CIPM	CIPM Comité International des Poids et Mesures (International Committee of Weights and Measures)
CIPM MRA	Mutual Recognition Arrangement of the International Committee of Weights and Measures
CMSET	Center for Monitoring Studies and Environmental Technologies, Kiev (Ukraine)
CRM	Certified reference material
EU	European Union
ET-AAS	Electrothermal atomic absorption spectrometry
GUM	Guide to the Expression of Uncertainty in Measurements
HDEHP	Bis(2-ethylhexyl) hydrogen phosphate
/	Net counting rate expressed in counts per second (s^{-1})
IAEA	International Atomic Energy Agency
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
IEC	International Electrotechnical Commission
IFIN-HH	Institutul Național de C&D pentru Fizică și Inginerie Nucleară Horia Hulubei (Horia Hulubei National Institute of Physics and Nuclear Engineering) (Romania)
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
LNE-LNHB	Laboratoire National de métrologie et d'Essais – Laboratoire National Henri Becquerel (France)
LSC	Liquid scintillation counting
LSC-C/N	LSC with CIEMAT/NIST efficiency tracing method
LTST	Index denoting homogeneity results using data of the long-term stability

	study
<i>m</i>	Mass
MKEH	Hungarian Trade Licensing Office
MS_{within}	Mean of squares within-unit from an ANOVA
<i>N</i>	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
NIST	National Institute of Standards and Technology (USA)
NMI	National metrology institute
PE	Polyethylene
PTB	Physikalisch-Technische Bundesanstalt (Germany)
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
RSD	Relative standard deviation
R^2	Coefficient of determination of a linear regression
<i>s</i>	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when appropriate
s_{between}	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate
SI	International System of Units
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
<i>T</i>	Temperature
<i>t</i>	Time
t_i	Time point for each replicate
TAEK	Turkish Atomic Energy Authority
<i>u</i>	Standard uncertainty
<i>U</i>	Expanded uncertainty
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
u_c	Combined standard uncertainty; an additional index "rel" is added as appropriate
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate

u_Δ	Combined standard uncertainty of measurement result and certified value
u_{its}	Standard uncertainty of the long-term stability; an additional index "rel" is added as appropriate
u_{meas}	Standard measurement uncertainty
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate
UTC	Coordinated Universal Time
\bar{x}	Arithmetic mean
α	Significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value

1 Introduction

1.1 Background

There is a general lack of certified reference materials (CRMs) for radionuclides in food-stuffs. The accident of March 2011 in the nuclear power plant Fukushima Daiichi, resulting from 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 foodstuffs, 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. Also fast screening methods should be based on sound metrological principles to be fit for purpose. In the European Union, Council Regulation (EURATOM) No 3954/87 of 22 December 1987 specifies maximum permitted levels of radioactive contamination of food- and feedstuffs following a nuclear accident or any other case of radiological emergency [5]. In the immediate aftermath of the Fukushima accident, the European Commission adopted, as a precautionary measure, Implementing Regulation (EU) N° 297/2011 [6] imposing special conditions governing the import of feed and food originating in or consigned from Japan following the accident. This Regulation provided for the requirement of a pre-export check carried out by Japanese authorities on all exported feed and food from the affected zone, combined with random controls at the point of entry into the EU to confirm the compliance with the levels set out in Council Regulation No 3954/87. In the following weeks and months, the implementation regulation was amended several times, taking into account the development of the situation in Japan with respect to release of radionuclides from the damaged reactors and the affected zones, seasonal variations in harvesting and fishing in Japan, but also aligning, on a provisional basis, the applicable maximum levels on feed and food imported from Japan to the lower action levels applied in Japan [7].

1.2 Choice of the material

In recent years, radioactivity found in wild food products has been of growing concern when assessing the total exposure of the population as a whole. This is due to the increased dose taken up by particular groups of a population living in regions with comparatively high deposition of radioactive fallout, such as after the Chernobyl reactor accident, and possibly having particular patterns of food intake. For this reason, IRMM developed this reference material for the activity concentration of ^{40}K and the anthropogenic radionuclides ^{90}Sr and ^{137}Cs in dried bilberries. Reference materials and demonstrated measurement capabilities are needed, in principle, for all types of potentially contaminated food, but dried bilberry material may be taken as a representative matrix for vegetables and fruits in particular.

Bilberry samples were collected in a region close to the Chernobyl reactor site, but outside the exclusion zone. Due to natural uptake from elevated levels in the environment, the radionuclides ^{90}Sr and ^{137}Cs were metabolised by the plants; therefore, no spiking was required. The resulting activity concentration levels are of the order of the maximum permitted levels for food as provided for in the EU and Japanese legislation and international recommendations. Moreover, the elevated levels of ^{137}Cs and, in particular, ^{90}Sr are below the exemption levels such that the material can be transported without restrictions and handled safely in the laboratory without radiological concerns.

1.3 Design of the project

The radionuclide activity concentrations of ^{137}Cs , ^{90}Sr and ^{40}K in the dried bilberry powder were characterised by intercomparison, namely the CIPM-CCRI(II) supplementary comparison CCRI(II)-S8 "wild berries". Seven national metrology institutes (NMIs) and designated institutes in the field measurement of radionuclides and two international organisations 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 . All participating laboratories are signatories to the Mutual Recognition Arrangement of the International Committee of Weights and Measures (CIPM MRA) and are, in their daily work, familiar with and adhering to the concepts of metrological traceability and measurement uncertainty estimation.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.3 Homogeneity and stability study

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM; measurements under a self-declared quality management system compliant with the requirements of ISO/IEC 17025)

2.4 Characterisation

CEA Saclay, LIST, Laboratoire National de métrologie et d'Essais – Laboratoire National Henri Becquerel (LNE-LNHB), Gif-sur-Yvette Cedex, FR
(measurements performed under a self-declared and externally peer-reviewed quality management system compliant with the requirements of ISO/IEC 17025)

Centro de Isótopos – Metrología de Radionúclidos (CENTIS-DMR), La Habana, CU
(measurements performed under a self-declared and externally peer-reviewed quality management system compliant with the requirements of ISO/IEC 17025)

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM; measurements under a self-declared quality management system compliant with the requirements of ISO/IEC 17025)

Institutul Național de C&D pentru Fizică și Inginerie Nucleară Horia Hulubei (IFIN-HH), Magurele, RO
(measurements under the scope of ISO/IEC 17025 accreditation, RENAR No. LI 804/22.07.2009)

International Atomic Energy Agency (IAEA), Department of Nuclear Sciences and Applications, Terrestrial Environment Laboratory, Seibersdorf, AT
(measurements under a self-declared quality management system compliant with the requirements of ISO/IEC 17025, to be presented in the frame of the accreditation process undertaken by the laboratory in 2014)

Magyar Kereskedelmi Engedélyezési Hivatal (MKEH), Budapest, HU
(measurements under a self-declared quality management system compliant with the requirements of ISO/IEC 17025)

National Institute of Standards and Technology (NIST), Physical Measurement Laboratory, Gaithersburg, US
(measurements under a self-declared quality management system compliant with the requirements of ISO/IEC 17025)

Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, DE

(measurements under a self-declared and externally peer-reviewed quality management system compliant with the requirements of ISO/IEC 17025)

Türkiye Atom Enerji Kurumu (TAEK), Sarayköy Nükleer Araştırma ve Eğitim Merkezi, Kazan, Ankara, TR

(gamma-spectrometric measurements under the scope of ISO/IEC 17025 accreditation, TÜRKAK No. AB-0218-T; ^{90}Sr determination under a self-declared quality management system with same apparatus and work instructions adapted from the accredited ^3H analysis in drinking water, same TÜRKAK no.)

3 Material processing and process control

3.1 Origin of the starting material

The material of this CRM with the generic name wild berries consists of bilberries (botanical name *Vaccinium myrtillus*, family of the *Ericaceae*) also known as European blueberry, blaeberry, myrtle blueberry, or whortleberry. 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, but outside the exclusion zone. This region in the Chernihivska oblast was selected by the Center for Monitoring Studies and Environmental Technologies (CMSET, Kiev) because, due to weather conditions (wind direction, rainout, washout) and core temperatures during the Chernobyl reactor accident, the radioactive deposition in this area is characterised by an increased activity ratio $A(^{90}\text{Sr})/A(^{137}\text{Cs})$ between ^{90}Sr and ^{137}Cs compared to other areas of the region. Due to natural uptake from the elevated levels in the environment, the anthropogenic radionuclides ^{90}Sr and ^{137}Cs were metabolised by the plants (just like the natural ^{40}K). 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 levels² to ensure transport of the material without restrictions and safe handling in the laboratory.

The actual harvesting was conducted from 14 to 20 July 2005 in the Gatka and Zavod forest districts south of the villages Vasyleva Guta, Borovyky, and Budysche in the Chernihivska oblast. Control measurements, performed by CMSET, revealed that the radionuclide activity concentrations of the berries collected in the two different districts were very close to each other. In order to avoid fermentation and decomposition of the berries, the samples were air-dried in ventilation dryers close to the sampling locations for 24 h at 70 °C. Dried berries were screened according to their integrity conditions and dry leaves and other impurities were removed. The remaining dried berries were combined in one lot and mixed. Before transport to IRMM, CMSET performed another series of control measurements to confirm that the radionuclide activity concentrations were around the target values of the CRM raw material and below exemption levels for transport. ^{90}Sr was found between 40 Bq kg⁻¹ to 100 Bq kg⁻¹, and ^{137}Cs around 900 Bq kg⁻¹.

3.2 Processing

The batch of 130 kg raw material was received by IRMM in white plastic crates and stored at 18 °C in a ventilated storage place awaiting further processing. The material was dried in an oven at 55 °C and then cryo-milled to a free-flowing powder with top grain size of 1.4 mm and a median grain size of 300 µm (as measured with laser diffraction). It was sieved, homogenised and bottled in units of approximately 100 g into 280 mL amber glass jars. A batch of 1186 units was produced. The material was sterilised by gamma-irradiation to

² In samples from other areas of the Chernobyl region, ^{137}Cs levels may be above the exemption level, once ^{90}Sr reaches activity concentrations allowing its determination with low uncertainty.

reduce bacterial growth, enhancing its long-term stability and facilitating its transport across borders.

3.3 Process control

Particle size analysis with a laser diffraction instrument, sieve analysis and optical microscopy were performed to characterise the powder size and morphology. Due to the small sample intake with laser diffraction instruments, most measurements resulted in unimodal size distributions where all particles were within the measurement range $< 1750 \mu\text{m}$ (Fig. 1), whereas some results also showed bimodal distributions with some particles above $1750 \mu\text{m}$. Given these results and the micrographs following sieving through a 1 mm sieve (Fig. 2), one can conclude that very few particles are present in the material which are $> 2 \text{ mm}$ in diameter. A sieve analysis was performed with 10 g of material, which confirmed the particle size distributions found with laser diffraction: Only one particle was present on the $1400 \mu\text{m}$ sieve; the median size, X_{50} , is around $300 \mu\text{m}$ for both techniques and the mass fraction below $50 \mu\text{m}$ is very small.

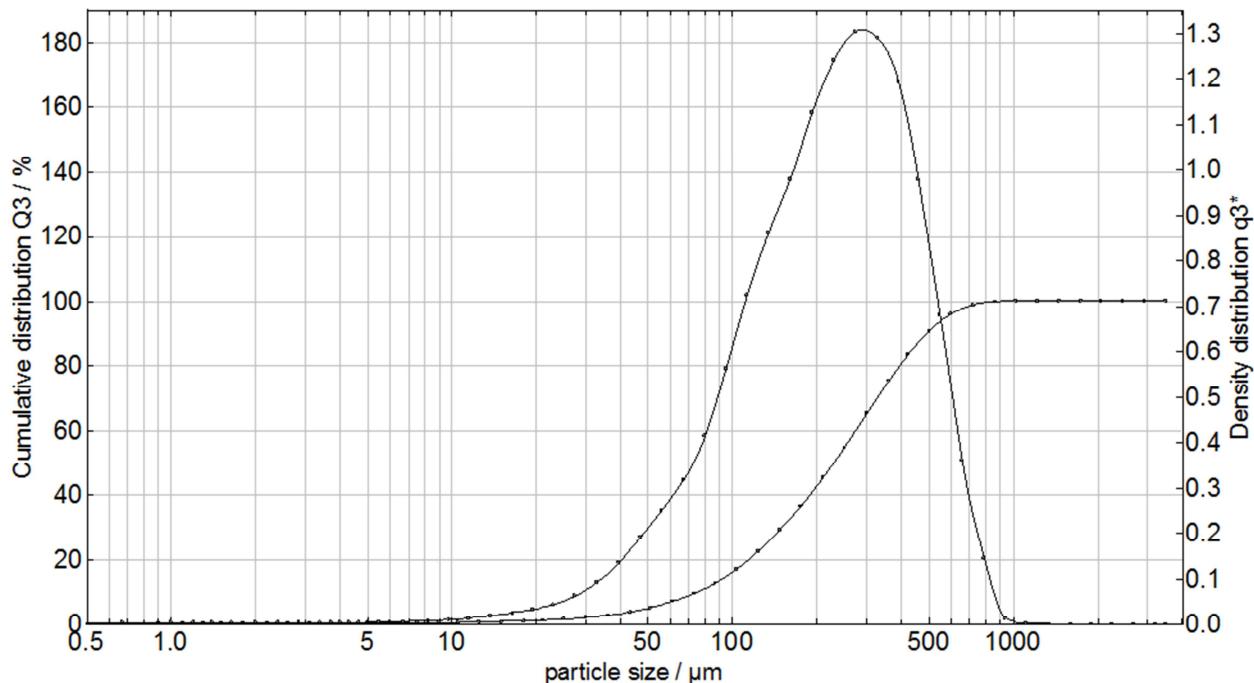


Fig. 1: Particle size distribution for dried berries powder (unit 0325), showing a unimodal distribution with a median particle size of $300 \mu\text{m}$.

It should be noted that the radioanalytical methods to be used on this material rely on sample preparation such as dry ashing and total digestion or direct γ -ray measurements, methods which are not sensitive to the presence of these few relatively large particles.

The water content of the material after bottling was determined by volumetric Karl-Fischer titration as $(3.63 \pm 0.04) \%$ (mass of water per mass of total material, given as mean \pm standard deviation), based on analysis of 3 samples each from 5 randomly chosen units.

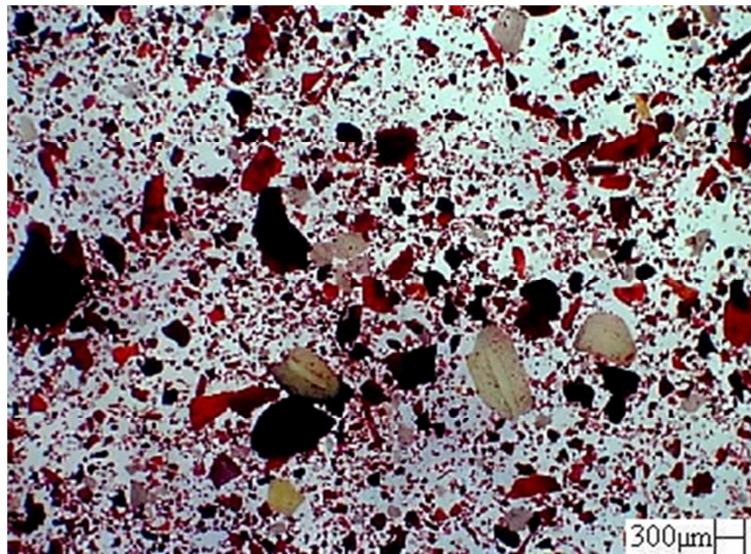


Fig. 2: Micrograph of the dried berries powder, indicating very few large particles of around 1 mm size. The pale parts are likely to be kernel material and the larger flakes are probably from the peel.

4 Homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value. In contrast to that it is not relevant if this variation between units is significant compared to the analytical variation. Consequently, ISO Guide 34 requires RM producers to quantify the between-unit variation. This aspect is covered in between-unit homogeneity studies.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all units of the material, within the stated uncertainty.

The number of selected units is larger than the cubic root of the total number of produced units ($n = 1186$). The 16 units were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. From each selected bottle, one sample was measured by γ -ray spectrometry for determination of ^{137}Cs and ^{40}K and a second one for ^{90}Sr by radiochemical separation and subsequent liquid scintillation counting (sample aliquots of 50 g). Another, limited homogeneity study was performed with five sub-samples of 18 g from each unit for the gamma-emitting radionuclides and two sub-samples of 50 g from each unit for ^{90}Sr . This study, however, could not be used for the quantification of between-unit inhomogeneity (albeit for its corroboration, see Table 2 below) of the whole batch of produced CRM by analysis of variance for two reasons: the number of bottles used was too small ($N = 5$ for gamma-emitters, $N = 8$ for ^{90}Sr) to be representative for the whole batch, and all involved bottles were taken from only half of the batch.

The determination procedures applied for ^{137}Cs , ^{40}K and ^{90}Sr were the same as those used by IRMM in the characterisation study, but applied here under repeatability conditions using relative measurement results only, thereby eliminating a number of uncertainty contributions

for absolute values such as the contribution from calibration. In particular in γ -ray spectrometry, this approach results in a small measurement uncertainty (Table 1), and small differences between the sample units (heterogeneity) are more easily detected. Moreover, corrections for the different filling height and density of the material in the measurement containers for γ -ray spectrometry were evaluated for each individual sample by Monte Carlo simulation. The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results were corrected for the mean water content determined in five units for two aliquots each. The results are shown as tables in Annex A.

Regression analyses were performed with SoftCRM to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence or the analytical sequence were found statistically nor graphically, for any of the three radionuclides.

Table 1: Uncertainty components for homogeneity measurements [14].

Uncertainty component	^{137}Cs [%]	^{40}K [%]	^{90}Sr [%]
Moisture content	0.1	0.1	0.1
Weighing	0.1	0.1	0.1
Counting statistics (incl. background)	0.3	1.8	0.5
Sample positioning	0.2	0.2	---
Loss in ash transfer	---	---	1
Chemical recovery	---	---	4
Combined relative standard uncertainty, $u_{\text{meas,rel}}$	0.4	1.8	4.2

The dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and, in case of the limited homogeneity study, on the unit means. No outlying individual results or outlying unit means were detected.

Quantification of between-unit inhomogeneity was then accomplished by taking, in a first step, the standard deviation, s_{bb} , of the individual results (see Annex A) as a conservative estimate of u_{bb} . Since this estimate comprises also the intrinsic measurement variation, expressed as measurement uncertainty u_{meas} , the overestimation of inhomogeneity was removed in a second step, considering the measurement uncertainty [8]. Thus, the between-bottle inhomogeneity, u_{bb} , is calculated as:

$$u_{bb} = \sqrt{(s_{bb})^2 - (u_{\text{meas}})^2} \quad (1)$$

The results of this evaluation of the between-unit variation are summarised in Table 2. The resulting values from the above equation were converted into relative uncertainties.

These results are corroborated by using an alternative approach: analysis of variance (ANOVA) of the limited homogeneity study, which can separate the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}), where the latter is equivalent to the method

Table 2: Results of the dedicated homogeneity studies.

Analyte	$s_{bb,rel}$ [%]	$u_{meas,rel}$ [%]	$u_{bb,rel}$ [%]	$s_{wb,rel}$ [%]	corroborative $u_{bb,rel}$ [%] (using $s_{wb,rel}$)
¹³⁷ Cs	0.88	0.4	0.8	0.97	n.c. ¹⁾
⁹⁰ Sr	4.0	4.2	n.c. ¹⁾	4.2	n.c. ¹⁾
⁴⁰ K	2.1	1.8	1.1	1.7	1.23

¹⁾ n.c.: cannot be calculated as $s_{bb} < u_{meas}$ or $s_{bb} < s_{wb}$

repeatability. Due to the limitation discussed above, only the method repeatability, s_{wb} , is used here, replacing u_{meas} in equation (1).

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \quad (2)$$

where

MS_{within} mean square within a unit from an ANOVA

\bar{y} mean of the results of the limited homogeneity study

The result for ⁴⁰K (last column of Table 2) corroborates the result of the between-unit variation ($u_{bb,rel}$ in column 4) which was evaluated using measurement uncertainty u_{meas} (taken from Table 1) in equation (1).

The determination procedure of ⁹⁰Sr was improved with time, in particular a smaller variation and standard uncertainty of the chemical recovery could be accomplished. By the time of the long-term stability measurements, the measurement uncertainty, u_{meas} (⁹⁰Sr), was reduced by almost one half (see Table 5). Consequently, the results of the long-term stability study for ⁹⁰Sr, in spite of being inter-twined with possible effects of storage under different temperatures, show a smaller variation than the earlier homogeneity experiments. Since the number of samples in the long-term stability study ($N = 16$) is large enough and covers the whole batch of the CRM, these results can also be considered for the homogeneity assessment (for individual results, see Annex A). The results are summarised in Table 3.

Table 3: Homogeneity results based on measurements of the long-term stability study, and final results for the between-unit variation.

Analyte	$s_{bb(LTST),rel}$ [%]	$u_{meas(LTST),rel}$ [%]	$u_{bb(LTST),rel}$ [%]	final $u_{bb,rel}$ [%]
¹³⁷ Cs	1.2	1.3	n.c. ¹⁾	0.8
⁹⁰ Sr	2.0	2.4	n.c. ¹⁾	2.0
⁴⁰ K	1.3	2.2	n.c. ¹⁾	1.1

¹⁾ n.c.: cannot be calculated as $s_{bb} < u_{meas}$

For the gamma-emitting nuclides, the conservative estimates $s_{bb(LTST)}$ corroborate the results of the dedicated homogeneity study (Table 2). A net $u_{bb(LTST)}$ corrected for measurement uncertainty cannot be calculated for any of the 3 nuclides. In the ⁹⁰Sr determination, however, the improved chemical recovery renders a much better $s_{bb(LTST)}$ than the s_{bb} of the dedicated homogeneity experiments. Therefore, for ⁹⁰Sr, $s_{bb(LTST)}$ is taken as an improved conservative estimate of the between-unit inhomogeneity u_{bb} .

In summary, the homogeneity study showed no outlying unit means or trends in the filling sequence. Therefore, for the gamma-emitting radionuclides, the between-unit standard deviation after consideration of measurement uncertainty can be used as a best estimate of u_{bb} . In the case of ^{90}Sr , the improved analysis procedure during the long-term stability study rendered a smaller variation among all tested units. Hence, the between-unit standard deviation $s_{bb(\text{LTST})}$ derived from the long-term stability experiments can be used as a best estimate of u_{bb} .

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake for analysis. Due to within-unit homogeneity, individual aliquots of a material will not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

The minimum sample intake was derived from measurements for the homogeneity and stability studies, no dedicated minimum sample intake study was performed.

Homogeneity and stability experiments were performed using a 50 g sample intake. This sample intake resulted in good repeatability for all three certified radionuclides, demonstrating that the within-unit inhomogeneity does no longer contribute to analytical variation at this sample intake. For the gamma-emitting radionuclides, ^{137}Cs and ^{40}K , within-unit homogeneity experiments limited to half of the batch were also performed using a sample intake of 18 g and rendering a repeatability (s_{wb} , see Table 2, second to last column) as good as with 50 g sample intake. Therefore, a minimum sample intake of 50 g is recommended for ^{90}Sr , whereas a minimum sample intake of 18 g is sufficient for analysis of ^{137}Cs and ^{40}K .

5 Stability

Time, temperature, radiation and water content were regarded as the most relevant influence quantities on stability of the materials. The influence of ultraviolet or visible radiation was minimised by the choice of the containment (amber glass bottles) which eliminates most of the incoming light. In addition, materials are stored and dispatched in the dark, thus eliminating practically the possibility of degradation by ultraviolet light. The water content was adjusted to an optimum during processing. Additionally the material was sterilized by γ -irradiation to eliminate microbial growth. Therefore, only the influences of time and temperature needed to be investigated.

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C could be reached and stability under these conditions must be demonstrated if transport at ambient temperature will be applied.

The stability studies were carried out using an isochronous design [9]. In that approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible (reference conditions). At the end of the isochronous storage, the samples are analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests.

It should be noted that the term stability in the context of a CRM does not refer to radioactive decay. It is self-evident that the radionuclides are decaying according to their half-lives, an “instability” which is quantitatively predictable using the Recommended decay data³.

5.1 Short-term stability study

For the short-term stability study, samples were stored at 18 °C and 60 °C for 0, 1, 2 and 6 weeks (at each temperature). The planned duration of the study was 4 weeks but the last samples were moved two weeks later to the reference temperature of -20 °C. Two units per storage time and temperature (and 4 units as reference at -20 °C) were selected using a random stratified sampling scheme. From each bottle, one sample of 50 g was measured by γ-ray spectrometry for determination of ¹³⁷Cs and ⁴⁰K and a second one of 50 g for ⁹⁰Sr by radiochemical separation and subsequent liquid scintillation counting. The determination procedures applied for ¹³⁷Cs, ⁴⁰K and ⁹⁰Sr were the same as those used by IRMM in the characterisation study, but applied here under repeatability conditions using relative measurement results only, thereby eliminating a number of uncertainty contributions for absolute values such as the contribution from calibration (Table 4). The main difference versus the homogeneity measurements (Section 4) lies in the fact that corrections for differences in filling height and material density in the measurement of the gamma-emitting radionuclides were not individually evaluated, but only the range of corrections known from the homogeneity measurements was used to add an additional uncertainty component for filling height and density (cf. with Table 1). The measurements were performed under repeatability conditions and in a randomised sequence to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the mean water content determined for the homogeneity study, performed in the same time period, in five units for two aliquots each.

Table 4: Uncertainty components for short-term stability measurements [14].

Uncertainty component	¹³⁷ Cs [%]	⁴⁰ K [%]	⁹⁰ Sr [%]
Moisture content	0.1	0.1	0.1
Weighing	0.1	0.1	0.1
Counting statistics (incl. background)	0.2	1.8	0.3
Filling height and density	1.2	1.2	---
Sample positioning	0.2	0.2	---
Loss in ash transfer	---	---	1
Chemical recovery	---	---	4
Combined relative standard uncertainty, $u_{\text{meas,rel}}$	1.3	2.2	4.2

³ http://www.nucleide.org/DDEP_WG/DDEPdata.htm

The obtained data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. Two outlying individual results were found, both for ^{90}Sr at 18 °C and only when using the double Grubbs test at the significance level $\alpha = 0.05$. As no technical reason for the outliers could be found all data were retained for statistical analysis.

Furthermore, the data were evaluated against storage time and regression lines of the normalised net counting rate (gamma-emitters) or activity concentration (^{90}Sr , respectively) versus time were calculated using SoftCRM. The slopes of the regression lines (loss/increase due to simulated shipping conditions) were tested for statistical significance. For all three radionuclides, the slopes of the regression lines were not significantly different from zero (at 99 % confidence level) at 18 °C. At 60 °C, however, a trend was observed for ^{137}Cs at 99 % confidence level (for ^{40}K only at 95 % confidence level), whereas no trend was observed for ^{90}Sr .

The detailed results of the measurements are shown in Annex B.

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. No change was measured for ^{90}Sr . 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 an additional uncertainty contribution of 0.6 % for ^{137}Cs and ^{40}K .

Taking the increased uncertainty contribution for transport conditions into account (see section 5.3), the material can be dispatched without further precautions under ambient conditions.

5.2 Long-term stability study

For the long-term stability study, samples were stored at 4 °C and 18 °C for 0, 4, 8 and 12 months (at each temperature). The reference temperature was set to -20 °C. Two samples per storage time and temperature (and 4 units as reference at -20 °C) were selected using a random stratified sampling scheme. From each unit, one sample was measured by γ-ray spectrometry for determination of ^{137}Cs and ^{40}K and another one by radiochemical separation and subsequent liquid scintillation counting for ^{90}Sr (all sample aliquots of 50 g). As with the short-term stability and homogeneity studies, the determination procedures applied were the same as those used by IRMM in the characterisation study, but applied under repeatability conditions using relative measurement results only, thereby eliminating a number of uncertainty contributions for absolute values such as the contribution from calibration. The measurement uncertainties valid for the long-term stability study are given in Table 5. Main difference versus the short-term stability measurements lies in the improved chemical recovery of Sr, resulting in less variation and smaller standard uncertainty. The measurements were performed under repeatability conditions, in a random sequence to be able to separate any potential analytical drift from a trend over storage time. The results were corrected for the mean water content determined in six units stored at different temperatures for different times, in two aliquots each.

The obtained data were evaluated individually for each storage temperature. The results were screened for outliers using the single and double Grubbs test. Two outlying individual results were found, one for ^{90}Sr in a reference sample stored at -20 °C for the study at 4 °C storage temperature (at a significance level of $\alpha = 0.05$, single Grubbs test), and the other one for ^{137}Cs , also in a reference sample in the study at 4 °C storage temperature ($\alpha = 0.05$). As no technical reason for the outliers could be found all data were retained for statistical analysis.

Table 5: Uncertainty components for long-term stability measurements [14].

Uncertainty component	^{137}Cs [%]	^{40}K [%]	^{90}Sr [%]
Moisture content	0.1	0.1	0.1
Weighing	0.1	0.1	0.1
Counting statistics (incl. background)	0.2	1.8	0.4
Filling height and density	1.2	1.2	---
Sample positioning	0.3	0.3	---
Loss in ash transfer	---	---	1
Chemical recovery	---	---	2.1
Combined relative standard uncertainty, $u_{\text{meas,rel}}$	1.3	2.2	2.4

Furthermore, the data were evaluated against storage time and linear regression lines of normalised peak intensity/activity concentration versus time were calculated using SoftCRM. The slopes of the regression lines (loss/increase due to storage conditions) were tested for statistical significance. For all three radionuclides, the slopes of the regression lines were not significantly different from zero (at 99 % confidence level) at both 4 °C and 18 °C.

The individual results of the long term stability measurements are shown in Annex C.

In summary, two statistical outliers were observed, but none of the trends for activity concentration with time was statistically significant on a 99 % confidence level for any of the temperatures. The material can therefore be stored at 18 °C.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is $0 \pm x\%$ per time".

Uncertainties of stability during dispatch and storage were estimated as described in [10] for each radionuclide. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contributions u_{sts} and u_{its} are calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{\text{sts,rel}} = \frac{\text{RSD}}{\sqrt{\sum(t_i - \bar{t})^2}} \cdot t_u \quad (3)$$

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \cdot t_{sl} \quad (4)$$

RSD	relative standard deviation of all results of the stability study at relevant temperature
t_i	time point i of measurement
\bar{t}	mean value of all time points
t_{tt}	chosen transport time (1 week at 60 °C)
t_{sl}	chosen shelf life (48 months at 18 °C)

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies. A possible degradation of 0.6 % per week observed for ^{137}Cs and ^{40}K was combined with the uncertainty of the slope. The resulting uncertainty describes the possible change during a dispatch at 60 °C lasting for one week.
- $u_{lts,rel}$, the stability during storage. This uncertainty contribution was estimated from the 18 °C studies. The uncertainty contribution describes the possible degradation during 48 months storage at 18 °C.

The results of these evaluations are summarised in Table 6:

Table 6: Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a temperature of 60 °C and $t_{tt} = 1$ week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and $t_{sl} = 4$ years.

Analyte	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
^{137}Cs	0.60	4.0
^{90}Sr	0.24	8.0
^{40}K	0.70	4.2

A limited degradation during hypothetical dispatch conditions at 60 °C was observed. Since the possible degradation was combined with the uncertainty of the regression line and taken into account in the uncertainty of the reference values, the material can be transported at ambient conditions without special precautions.

Since no trends were detected in the long-term stability study, the material can be stored at 18 °C.

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

6 Characterisation

The material characterisation is the process of determining the property values of a reference material.

The material characterisation was based on an intercomparison of expert laboratories, in the frame of the CIPM-CCRI(II) supplementary comparison CCRI(II)-S8 "wild berries" [11], i.e.

the radionuclide activity concentrations of the material were determined in different laboratories that applied different measurement procedures to demonstrate the absence of a measurement bias. Due to the nature of the analytes, however, all participants used gamma-ray spectrometry as measurement method for the gamma-ray emitting nuclides. Nevertheless, widely differing approaches to calibration of the same measurement method resulted in different procedures. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Selection of participants

Nine laboratories were selected among the member laboratories of the Consultative Committee for Ionising Radiation (CCRI(II)) at the CIPM/BIPM and signatories to the CIPM Mutual Recognition Arrangement (CIPM MRA), based on criteria that comprised both technical competence and quality management aspects. All selected laboratories belong either to the NMI or a Designated Institute (DI) for radioactivity measurements of their country or international organisation. Each of them is member of the International Committee for Radionuclide Metrology (ICRM). Documented evidence of the laboratory proficiency in the field of radionuclide measurements of 7 of the 9 participants is publicly available in the list of calibration and measurement capabilities (CMCs [12]) of the key comparison data base (KCDB). Of the remaining two laboratories, the International Atomic Energy Agency (IAEA) submitted a method validation report. The Turkish Atomic Energy Authority (TAEK) delivered documented evidence of its laboratory proficiency by submitting results for intercomparison exercises. Each participant was required to operate a quality system. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (Section 2).

6.2 Study setup

Each laboratory received six bottles of IRMM-426 and was requested to provide six independent results, one per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. Each laboratory was free to choose an analysis method of its own choice, with the requirement to ensure traceability of the measurement results to the International System of Units (SI). The sample preparations (if any) and measurements had to be spread over at least two days to ensure intermediate precision conditions. The water content had to be determined in each unit at least once and results were reported on dry mass basis, using one of the procedures given in Annex E.

Laboratories were also requested to give estimations of the combined standard uncertainties of the mean value and of the six results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

6.3 Methods used

All methods used during the characterisation study, for all three radionuclides, are summarised in Annex D. The laboratory code (e.g. L01) is a random number and does not correspond to the order of laboratories in Section 2.

6.3.1 Gamma-ray spectrometry

The methods used in the determination of the gamma-ray emitting nuclides, ^{137}Cs and ^{40}K , i.e. the preparation of measurement samples, the methods used for efficiency calibration, the traceability of calibration standards, and the methods used for corrections are described in [13] and [11]. Only their main characteristics are summarised here.

Cylindrical sources of the undried bilberry powder were prepared, usually one sample between 50 g and 90 g per bottle of material. Only two laboratories (L02 and L03) prepared

two samples of about 20 g each per bottle. “Tapping” of the source or slight pressing was applied in order to achieve a better delineation of the volume and a higher density (between 0.58 g·cm⁻³ and 0.68 g·cm⁻³; L03 reported a density as high as 0.82 g·cm⁻³). The source containers varied in material (glass, plexiglass® or plastic without further specification) and wall thickness (between 1 and 5 mm).

“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) [11]”. Since the participants had a free choice of methods, a variety of methods was applied to establish the counting efficiency for the cylindrical sources of the powder:

- The standard addition method (efficiency tracing in the terminology of radionuclide metrologists, using the same or different radionuclides with similar gamma-emission energy) was used by two laboratories plus one laboratory for ¹³⁷Cs only; it provides the most direct traceability link if problems related to the possible heterogeneity of an initially liquid spike in the solid sample can be controlled.
- Two laboratories (plus one for ⁴⁰K only) applied volume standard sources of similar density in the same geometry or similar (different by sample height). The differences in density and sample height were corrected by Monte Carlo simulations. The directness of the traceability link varies with increasing differences in density or geometry between standard source and sample, and heterogeneity of the standard source may be an issue.
- Two laboratories measured the self-attenuation in the prepared samples with point sources on top of filled and empty containers, using the sample-specific linear attenuation coefficients either in a correction formula or integrated in a Monte Carlo simulation for efficiency transfer in density.
- Two laboratories 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).

Table 16 in Annex D gives an overview of the variety of methods used. The combination of results from methods based on completely different approaches to efficiency calibration, using different calibration sources and correction principles mitigates undetected method bias. Traceability of the used standards was either established in-house by primary standardisation of solutions, or by purchasing primary-standardised solutions from another NMI. Since the participating NMIs, whose calibration sources were used by other participants, used themselves different approaches to establish efficiency than the laboratories using their standards, all calibrations are independent of each other [11].

6.3.2 Determination of ⁹⁰Sr

The details of the determination methods used for ⁹⁰Sr can be found in [14] and [11], and in Table 17 in Annex D. The main characteristics are summarised here.

Separation of Sr and its purification were performed using various procedures: precipitation of Sr-Ca with fuming nitric acid, co-precipitation as carbonate, oxalate or nitrate, followed by scavenge precipitations such as Fe(OH)₃, BaCrO₄ or carbonate, or, alternatively, followed directly by extraction chromatography on Sr resin (Eichrom Technologies LLC, IL, USA). One laboratory (L06) applied several scavenge precipitations for further purification after extraction chromatography. And laboratory L08 extracted yttrium with HDEHP, followed by back extraction of Y to determine ⁹⁰Sr via its daughter ⁹⁰Y only. Chemical recovery was determined by this laboratory by titration of a stable Y carrier used as tracer, and it verified the Sr recovery from the matrix after spiking with a ⁹⁰Sr standard. Three laboratories determined the chemical recovery gravimetrically by adding stable Sr carrier solution at different points in the analysis procedure. Laboratory L02 used a standardised ⁸⁵Sr tracer solution and gamma-ray spectrometry to determine the chemical recovery. In the final source

preparation, a last purification was done in various ways (stripping Sr from the resin, oxalate or carbonate precipitation, or precipitation of $\text{Y}(\text{OH})_3$), and the precipitates or strip solution were transferred to scintillation vials or a filter for proportional counting after drying (L06). Although four laboratories used liquid scintillation counters as measurement instrument, the methods applied were completely different: One of the two laboratories using LSC applied a relative method with a $^{90}\text{Sr}/^{90}\text{Y}$ calibration source, whereas the second laboratory relied on the LSC-C/N efficiency tracing method. Two other laboratories measured Cherenkov radiation in LS counters, one from the ingrowing ^{90}Y in the strontium sample, the other from the extracted yttrium.

This variety of sample dissolution/purification/separation/source preparation methods and different counting techniques (Cherenkov counting, liquid scintillation counting, gross beta counting) based on completely different principles mitigates undetected method bias.

6.4 Dry mass determination

For all measurements carried out during certification (homogeneity, stability and characterisation studies) the following protocols for dry mass determinations were applied:

- homogeneity and stability studies: Karl-Fischer titration,
- IRMM in the characterisation study: Karl-Fischer titration,
- six laboratories in the characterisation study: drying in an oven for a limited time (NOT to constant mass) at $90\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$ for 40 minutes,
- three laboratories (one used both methods) in the characterisation study: drying in an oven for a limited time (NOT to constant mass) at $60\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$ for 12 hours.

Dry mass determinations were carried out on a separate aliquot of at least 1 g, more details can be found in Annex E. Weighing of the samples for dry mass determination and weighing for the analyses were done at the same time to avoid differences due to possible take up of moisture by the material.

Both oven-drying methods were worked out at IRMM and found to render moisture results in agreement with results of Karl-Fischer titration on this material.

The water content determined by the laboratories was in the range of 30 g kg^{-1} to 42 g kg^{-1} . This is a variation of $< 5\text{ g kg}^{-1}$ among the laboratories, corresponding to a coefficient of variation of 12 % with a mean value of 36 g kg^{-1} . The variation within a laboratory was of the order of 0.5 g kg^{-1} to 3 g kg^{-1} (1 % – 8 %), and the reported combined uncertainties, u_{meas} , for water determination were of a similar order. Given the small effective correction of 3.6 % on average, its uncertainty up to 8 % has no significant effect on the corrected activity concentrations in dry matter [13]. Moreover, the consistent set of moisture results confirms the good sealing of the bottles and the relatively small hygroscopicity of the powder accomplished during processing (Section 3).

6.5 Evaluation of results

The characterisation campaign resulted in nine datasets per gamma-emitting radionuclide and seven datasets for ^{90}Sr . All individual results of the participants, grouped per radionuclide, are displayed in tabular and graphical form in Annex F.

6.5.1 Technical evaluation

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- appropriate validation of the measurement procedure
- compliance with the analysis protocol: sample preparations and measurements performed on at least two days, and water content determination

- absence of values given as below limit of detection or below limit of quantification
- method used is selective for the measurand and can produce results fulfilling the traceability criteria (Section 8.1)

Based on the above criteria, supported by a visual inspection of the data and outlier tests, the following datasets were rejected as not technically valid (Table 7).

Table 7: Datasets that showed non-compliances with the analysis protocol and technical specifications, and action taken.

Radionuclide	Laboratory code	Description of problem	Action taken
⁹⁰ Sr	L07	statistical outlier ($\alpha=0.05$), does not agree within uncertainties with mean of characterisation study; method used (gross-beta counting with numerical subtraction of beta emission coming from ¹³⁷ Cs and ⁴⁰ K) not selective for ⁹⁰ Sr, does not fulfil criteria of traceability; and method was not validated	not used for evaluation
¹³⁷ Cs, ⁴⁰ K	L09	statistical outlier (only ¹³⁷ Cs, $\alpha=0.05$), does not agree within uncertainties with mean of characterisation study; laboratory discovered that used calibration standard had an activity higher by about 10 % than stated in the certificate; this rendered validation obsolete, lab withdrew dataset	not used for evaluation

6.5.2 Statistical evaluation

The datasets accepted based on technical reasons were tested for normality of dataset means using kurtosis and skewness tests and were tested for outlying means using the Grubbs test and using the Cochran test for outlying standard deviations (both at a 99 % confidence level). Standard deviations within (s_{within}) and between (s_{between}) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 8.

Table 8: Statistical evaluation of the technically accepted datasets for IRMM-426. p : number of technically valid datasets.

Radio-nuclide	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [Bq kg ⁻¹]	s [Bq kg ⁻¹]	s_{between} [Bq kg ⁻¹]	s_{within} [Bq kg ⁻¹]
¹³⁷ Cs	8	none	none	yes	779.4	24.7	24.4	9.5
⁹⁰ Sr	5	none	none	n.a. ¹⁾	152.8	7.6	7.6	5.9
⁴⁰ K	8	none	one (L03)	yes	253.1	14.4	14.1	6.1

¹⁾ Insufficient data for tests with $p = 5$. In case of pooling measurement results for all individual samples (not allowed in the present case, however) skewness and kurtosis tests would show normality.

The laboratory means follow normal distributions. Due to the limited number of data sets ($p = 5$) in the case of ^{90}Sr , the usual tests cannot be applied. The measurement results for all individual samples, however, are normally distributed. One of the data sets exhibits an outlying variance (L03 for ^{40}K). However, it must be borne in mind that outlier tests do not take uncertainty information into consideration. The combined standard uncertainty evaluated by laboratory L03, in particular the contributions from counting statistics and background evaluation, fully account for its larger variance. This merely reflects different counting times, shielding conditions, etc. resulting in different variability. As all measurement methods were found technically sound, all results were retained.

For the gamma-emitting radionuclides, standard deviations between laboratories are considerably larger than the standard deviations within laboratories, showing that confidence intervals of replicate measurements are unsuitable as estimate of measurement uncertainty.

It should be borne in mind that the methods used in the characterisation are methods routinely applied for measuring ^{137}Cs , ^{40}K and ^{90}Sr in foodstuffs. The agreement of results from different methods demonstrates that the processing did not affect any properties relevant for these methods and that CRM IRMM-426 behaves like a real sample.

The uncertainty related to the characterisation is estimated by combining the standard uncertainties of each laboratory mean [15]. Since no common calibrants were used, and the analysis procedures were different due to the largely varying approaches to efficiency calibration in gamma-ray spectrometry or different radiochemical separation procedures and counting techniques for the determination of ^{90}Sr , the results of all laboratories are independent of each other. Thus, the combined standard uncertainties, $u_{c,i}$, of each mean result of the n laboratories are combined as

$$u_{char}^2 = \frac{\sum_{i=1}^n u_{c,i}^2}{n^2} \quad (5)$$

This corresponds to $u_c(l)$ or exclusively laboratory-dependent uncertainties in the terminology of [15].

Before doing so, however, the uncertainty budgets submitted by laboratory L08 for the gamma-emitting radionuclides ^{137}Cs and ^{40}K had to be corrected since they were obviously underestimating some contributions to the uncertainty. After critical examination of the submitted budgets, the contributions for interpolating the efficiency curve, influence of water content, and sample positioning (geometry effects) were increased. The corrected combined standard uncertainties of L08 for ^{137}Cs and ^{40}K , respectively, are then 2.1 % and 2.9 % instead of the submitted 0.32 % and 1.1 %.

The final results, standard deviations and combined standard uncertainties of the characterisation study are given in Table 9. Within the final evaluated uncertainty, the mean of laboratory means is a good estimate of the true value.

Table 9: Results, standard deviations and uncertainties of the characterisation study for IRMM-426 at reference date 1 January 2009, 00h00 UTC.

Radionuclide	p	Mean [Bq kg $^{-1}$]	s [Bq kg $^{-1}$]	u_{char} [Bq kg $^{-1}$]
^{137}Cs	8	779.4	24.7	9.4
^{90}Sr	5	152.8	7.6	3.1
^{40}K	8	253.1	14.4	5.6

7 Value Assignment

Certified and informative values were assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM require generally pooling of not less than 6 datasets to assign certified values. For ^{90}Sr , only 5 datasets were accepted but found sufficient for certification, since they were obtained with completely independent and different methods of determination. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [4] were established.

Indicative values are values where either the uncertainty is deemed too large or where too few independent datasets were available to allow certification. No indicative values were assigned.

Additional material information refers to values that were obtained in the course of the study.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 8 was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and potential degradation during transport (u_{sts}) and long-term storage, u_{lts} (Section 5). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{\text{CRM, rel}}$) with a coverage factor k as:

$$U_{\text{CRM, rel}} = k \cdot \sqrt{u_{\text{char, rel}}^2 + u_{\text{bb, rel}}^2 + u_{\text{sts, rel}}^2 + u_{\text{lts, rel}}^2} \quad (6)$$

- u_{char} was estimated as described in Section 6.5
- u_{bb} was estimated as described in Section 4.1
- u_{sts} was estimated as described in section 5.3
- u_{lts} was estimated as described in Section 5.3

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions to the determination of the gamma-emitting nuclides, ^{137}Cs and ^{40}K , a coverage factor k of 2 was applied to obtain the expanded uncertainties corresponding to a level of confidence of about 95 %. Even in the case of ^{90}Sr , with a dominant uncertainty contribution from the long-term stability study, the effective degrees of freedom v_{eff} calculated with the Welch-Satterwaite formula (Annex G.4 of [4]) result in a coverage factor k of 2.2, for the t -distribution at a level of confidence of 95 %.

The certified values and their uncertainties are summarised in Table 10.

Table 10: Certified values and their uncertainties for IRMM-426 at reference date 1 January 2009, 00h00 UTC.

Radio-nuclide	Certified value ¹⁾ [Bq kg ⁻¹]	$U_{\text{char, rel}}$ [%]	$U_{\text{bb, rel}}$ [%]	$U_{\text{sts, rel}}$ [%]	$U_{\text{ts, rel}}$ [%]	$U_{\text{CRM, rel}}$ [%]	U_{CRM} [Bq kg ⁻¹] ²⁾
¹³⁷ Cs	780	1.2	0.8	0.6	4.0	4.3	70
⁹⁰ Sr	153	2.0	2.0	0.24	8.0	8.5	29
⁴⁰ K	253	2.2	1.1	0.7	4.2	4.9	25

¹⁾ reported on dry mass basis (Section 6.4)

²⁾ expanded and rounded uncertainty, $k = 2$ for ¹³⁷Cs and ⁴⁰K, $k = 2.2$ for ⁹⁰Sr

7.2 Additional material information

The data provided in this section should be regarded as informative only on the general composition of the material in some elements and can not be, in any case, used as certified or indicative value. They are mean values of ICP-MS or ICP-OES determinations in two laboratories of samples taken from a total of 8 units of the batch (Sr determined in three laboratories).

Table 11: Mass content of some elements in IRMM-426, reported on dry mass basis.

Na [mg kg ⁻¹]	Mg [mg kg ⁻¹]	Al [mg kg ⁻¹]	K [g kg ⁻¹]	Ca [g kg ⁻¹]	Rb [mg kg ⁻¹]	Sr [mg kg ⁻¹]	Cs [mg kg ⁻¹]	Ba [mg kg ⁻¹]
27.2	720	59	8.6	1.3	55	5.1	0.30	15.1

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

¹³⁷Cs, ⁴⁰K and ⁹⁰Sr are chemically and physically clearly defined analytes. The successful participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias. The measurand is therefore structurally defined and independent of the measurement method.

Quantity value

Only validated methods were used for the determination of the assigned values. Different methods and different calibrants of specified traceability of their assigned values were used and all relevant input parameters were calibrated. The individual results are therefore traceable to the SI, as it is also confirmed by the agreement among the technically accepted datasets. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

8.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific analytes (or specific groups of analytes) from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CSLI Guideline C-53A [16] recommends the use of the following definition for the term *commutability*:

"The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant. For instance, CRMs intended to be used to establish or verify metrological traceability of routine radionuclide measurement procedures must be commutable for the routine radionuclide measurement procedures for which they are intended to be used.

The CRM IRMM-426 was produced from naturally grown bilberry material by drying, milling and mixing. Since the methods used in the characterisation of this CRM are methods routinely applied for measuring ^{137}Cs , ^{40}K and ^{90}Sr in foodstuffs, the agreement of results from these different methods demonstrates that the processing did not affect any properties relevant for these methods and that the analytical behaviour will be the same as for a routine sample of berry or any other milled fruit or vegetable material. Nevertheless, one has to bear in mind that, in gamma-ray spectrometry, sample density influences the gamma-ray transmission, and possibly different grain size of a sample milled in the user's laboratory does so as well. For other foodstuff of different major constituents than fruit or vegetable matrices or different density, the commutability, in gamma-ray spectrometry, has to be assessed.

For ^{90}Sr determination, provided the analytical procedures chosen are as aggressive as those used for this CRM in the characterisation study (e.g. mineralisation at high temperature), the analytical behaviour for samples in the user's laboratory, also of other foodstuff, will be the same as for this CRM. For foodstuff rich in fat, the commutability has to be assessed, and care must be taken when planning high temperature ashing or any other matrix destruction, since high fat materials may ignite or volatilise in an uncontrolled manner.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

The elevated levels of ^{137}Cs and, in particular, ^{90}Sr in this material are below the exemption levels so that the material can be transported freely and handled in the laboratory safely without radiological concerns. Nevertheless, since the material is a radioactive sample, external exposure should be kept to a minimum. Avoid dust inhalation or distribution of dust in the laboratory and laboratory equipment. Clean laboratory equipment after usage.

9.2 Storage conditions

The materials shall be stored at $18\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ in the dark. Care shall be taken to avoid change of the moisture content once the units are open, as the material is hygroscopic. The user is reminded to close bottles immediately after taking a sample.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened bottles.

9.3 Preparation and use of the material

The units shall be shaken by turning upside down for at least 2 min before opening to ensure material re-homogenisation.

9.4 Minimum sample intake

The minimum sample intake representative for a whole unit is 18 g for analysis of ^{137}Cs and ^{40}K . For analysis of ^{90}Sr , the minimum sample intake is 50 g.

9.5 Dry mass correction

Dry mass determination shall be carried out on a separate portion of at least 1 g, by drying in an oven for a limited time (NOT to constant mass) using one of the temperature-time parameter sets (more details can be found in Annex E):

- first alternative: dry at $90\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for 40 minutes,
- second alternative: dry at $60\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for 12 hours.

Weighing of the samples for dry mass determination and weighing for the analysis shall be done at the same time to avoid differences due to possible take up of moisture by the material.

9.6 Use of the certified value

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results/calibration. As any reference material, it can also be used for control charts or validation studies.

Use as a calibrant

It is not recommended to use this matrix material as calibrant. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [17]).

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{\text{meas}}^2 + u_{\text{CRM}}^2}$
- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty (u_{Δ}) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %

- If $\Delta_{\text{meas}} \leq U_{\Delta}$ no significant difference between the measurement result and the certified value exists, at a confidence level of about 95 %.

Use in quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same result as inhomogeneity was included in the uncertainties of the certified values.

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Annexes

Annex A: Results of the homogeneity measurements

The determination procedures applied here for ^{137}Cs , ^{40}K and ^{90}Sr were the same as those used by IRMM in the characterisation study, but applied here under repeatability conditions using relative measurement results only, thereby eliminating the uncertainty contributions for absolute values and calibrations. For gamma-emitting radionuclides, the decay-corrected and mass-normalised net counting rate I is used. Moreover, the counting rate was corrected (by Monte Carlo calculations) for filling height and density of the dried berry material in each individual measurement sample. Hence, uncertainty contributions for filling height and density were negligible. Each sample was measured once for 5 days. For ^{90}Sr , a nominal calibration factor was applied (lacking accuracy but carrying no uncertainty for the sole purpose of comparison). Mass of sample aliquots was 50 g in all cases, one sample per bottle used for γ -ray spectrometry, the other one for radiochemical separation and subsequent LSC determination of ^{90}Sr . Some individual samples, however, were lost in sample preparation and had to be replaced by other units (ID 250, 873, 975 and 1059) than used for γ -ray spectrometry. Combined measurement uncertainties $u_{\text{meas,rel}}$ for ^{137}Cs , ^{40}K and ^{90}Sr are 0.4 %, 1.8 %, and 4.2 %, respectively.

Table 12: Measurement results for all samples of the homogeneity study for the three radionuclides. Values I and A_m and their uncertainties u given as net counting rate or nominal activity concentration (the latter for ^{90}Sr only), to be used as relative values only.

Sample ID	^{137}Cs	^{40}K	Sample ID	^{90}Sr
	I [s^{-1}]	I [10^{-3}s^{-1}]		A_m [Bq kg^{-1}]
39	0.455	8.123	39	136.04
78	0.457	8.296	78	141.57
176	0.455	8.073	176	136.85
247	0.452	7.939	250	141.21
358	0.458	8.365	358	149.29
407	0.455	8.159	407	137.94
519	0.456	8.006	519	153.77
585	0.454	8.193	585	145.39
604	0.458	8.276	604	147.41
660	0.460	8.584	660	147.38
744	0.450	8.153	744	145.43
836	0.456	7.928	836	156.34
905	0.451	8.123	873	140.97
1002	0.454	8.408	975	143.33
1041	0.443	8.206	1002	140.72
1145	0.456	8.286	1059	147.44
mean	0.454	8.19		144.4
s_{bb}	0.0040	0.17		5.8
$s_{bb,\text{rel}} (\%)$	0.88 %	2.1 %		4.0 %

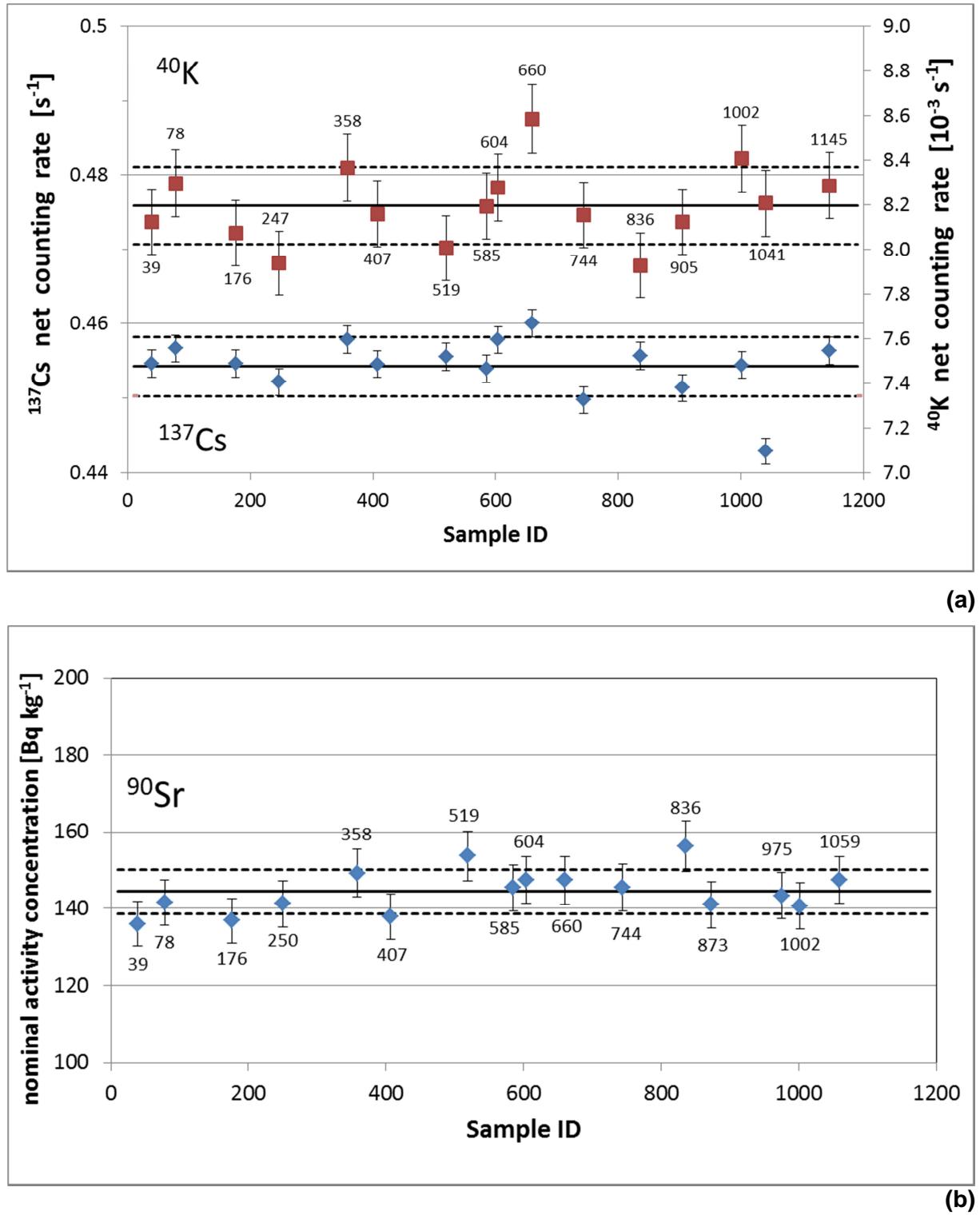


Fig. 3: Absence of trend in filling sequence, displayed (a) for gamma-emitters, (b) for ^{90}Sr . Means and standard deviations of homogeneity study measurement results are indicated by filled and dashed lines. Error bars indicate combined measurement uncertainty, u_{meas} .

Since by the time of the long-term stability measurements the determination procedure of ^{90}Sr had been improved with a reduced measurement uncertainty, $u_{\text{meas}}(^{90}\text{Sr})$, the results of the long-term stability study showed a smaller variation for ^{90}Sr than the results of the earlier

dedicated homogeneity experiments. And this in spite of being inter-twined with possible effects of storage under different temperatures.

Table 13: Measurement results of ^{90}Sr for all samples of the long-term stability study used for homogeneity assessment. Values A_m and their uncertainties u given as nominal activity concentration, to be used as relative values only. Combined measurement uncertainty, $u_{\text{meas,rel}}$, for ^{90}Sr is 2.4 %.

Sample ID	^{90}Sr
	A_m [Bq kg $^{-1}$]
14	148.8
28	151.2
174	146.2
322	151.4
365	150.2
420	149.0
469	147.8
525	144.8
618	146.3
643	150.3
652	147.7
812	153.2
846	153.2
911	156.1
987	150.6
1150	149.6
mean	149.8
$S_{\text{bb(LTST)}}$	2.93
$S_{\text{bb(LTST),rel}} (\%)$	2.0 %

Fig. 4 demonstrates that these results are free of a trend in analysis sequence, corroborating the statistical analysis results.

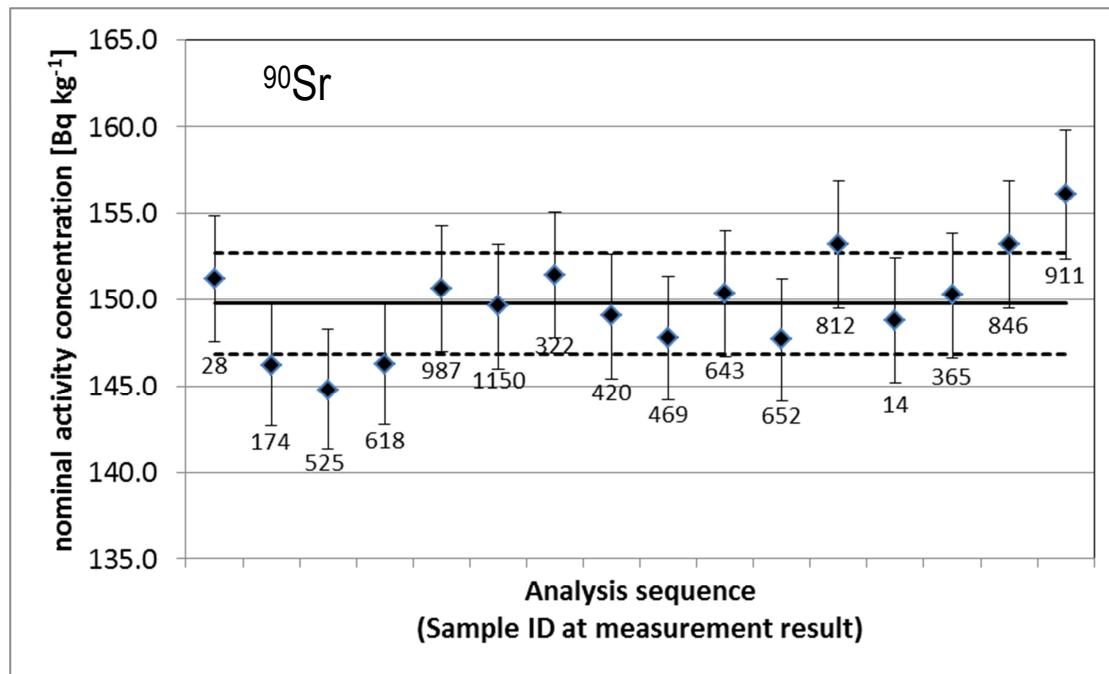


Fig. 4: Absence of trend in analysis sequence for ^{90}Sr . Error bars indicate combined measurement uncertainty, u_{meas} . Mean and standard deviation of the measurement results are indicated by filled and dashed lines.

Annex B: Results of the short-term stability measurements

The determination procedures applied for ^{137}Cs , ^{40}K and ^{90}Sr were the same as those used by IRMM in the characterisation study, but applied here under repeatability conditions using relative measurement results only, thereby eliminating the uncertainty contributions for absolute values and calibrations. For gamma-emitting radionuclides, the decay-corrected and mass-normalised net counting rate I is given. For ^{90}Sr , a nominal calibration factor was applied (lacking accuracy but carrying no uncertainty for the sole purpose of comparison). Mass of sample aliquots was 50 g in all cases, one sample per bottle used for γ -ray spectrometry, the other one for radiochemical separation and subsequent LSC determination of ^{90}Sr . Three measurements were performed for each sample, mean values of the three measurements are given in the table and figures below.

Table 14: Mean values of 3 measurement results each for all samples of the short-term stability study for the three radionuclides. Values I and A_m and their uncertainties u given as net counting rate or nominal activity concentration, to be used as relative values only.

Sample ID	^{137}Cs		^{40}K		^{90}Sr	
	I [s^{-1}]	u [s^{-1}]	I [10^{-3} s^{-1}]	u [10^{-3} s^{-1}]	A_m [Bq kg^{-1}]	u [Bq kg^{-1}]
-20 °C	Reference samples at -20 °C					
0045	1.073	0.0139	21.18	0.47	140.8	5.9
0315	1.072	0.0139	21.60	0.48	145.6	6.1
0612	1.094	0.0142	21.64	0.48	144.6	6.1
0892	1.092	0.0142	21.50	0.47	147.0	6.2
18 °C	1 week					
0094	1.056	0.0137	20.51	0.45	144.7	6.1
0943	1.094	0.0142	21.96	0.48	142.3	6.0
	2 weeks					
0702	1.079	0.0140	21.49	0.47	144.6	6.1
0413	1.069	0.0139	20.76	0.46	144.6	6.1
	6 weeks					
0188	1.088	0.0141	21.26	0.47	144.9	6.1
1056	1.073	0.0139	21.14	0.47	144.8	6.1
60 °C	1 week					
0220	1.057	0.0137	20.57	0.45	144.1	6.1
0806	1.080	0.0140	21.29	0.47	147.1	6.2
	2 weeks					
0553	1.063	0.0138	20.72	0.46	145.1	6.1
1116	1.060	0.0138	21.33	0.47	150.0	6.3
	6 weeks					
0277	1.042	0.0135	20.91	0.46	145.8	6.1
0565	1.052	0.0137	20.44	0.45	143.8	6.0

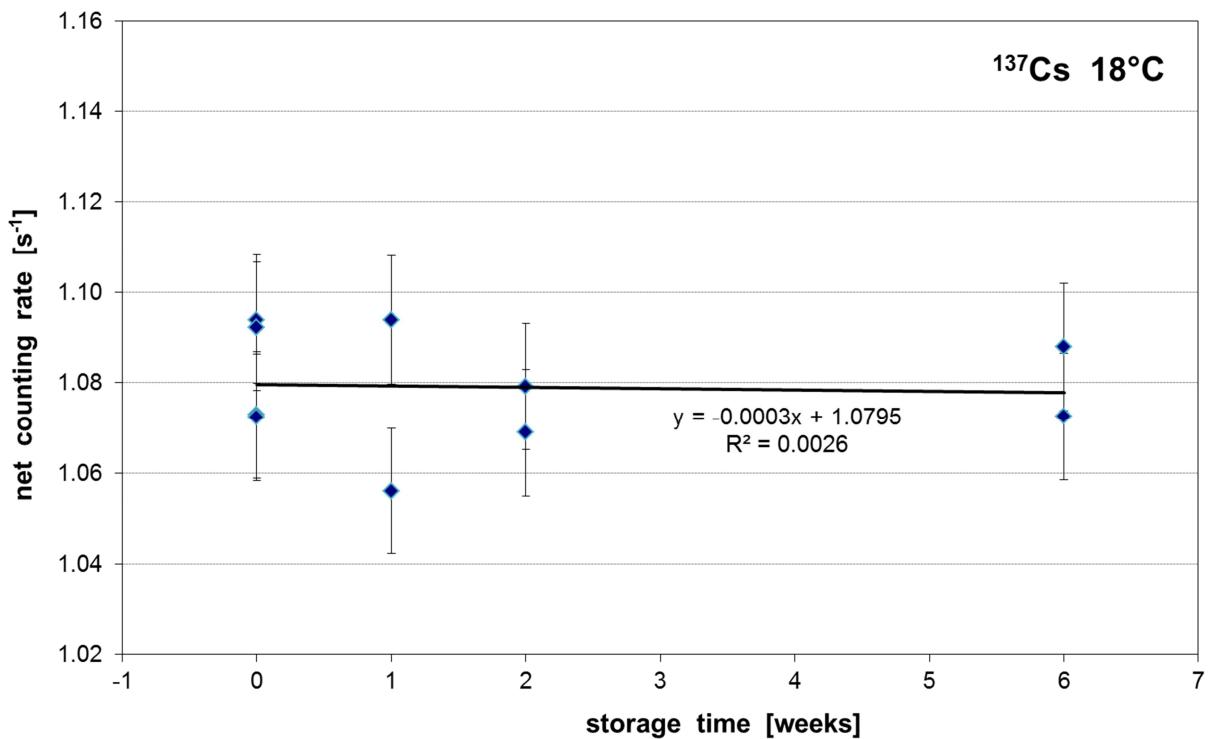


Fig. 5: ^{137}Cs results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 18 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

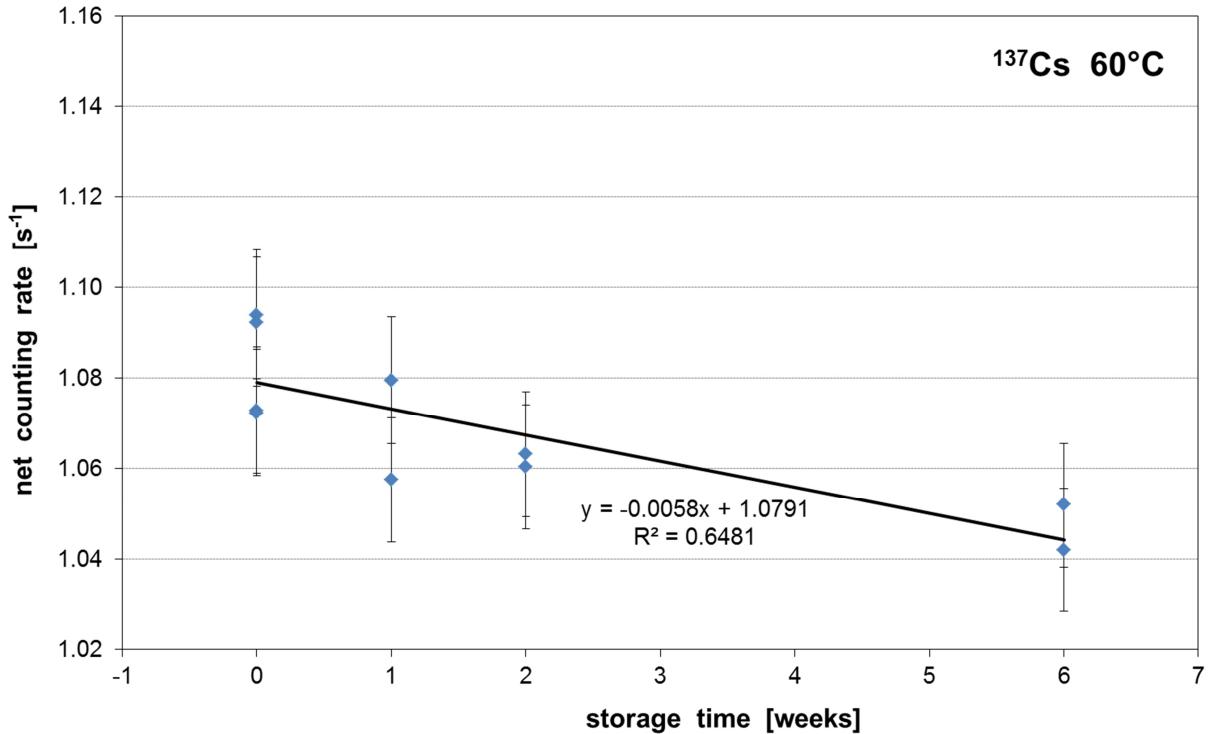


Fig. 6: ^{137}Cs results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 60 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

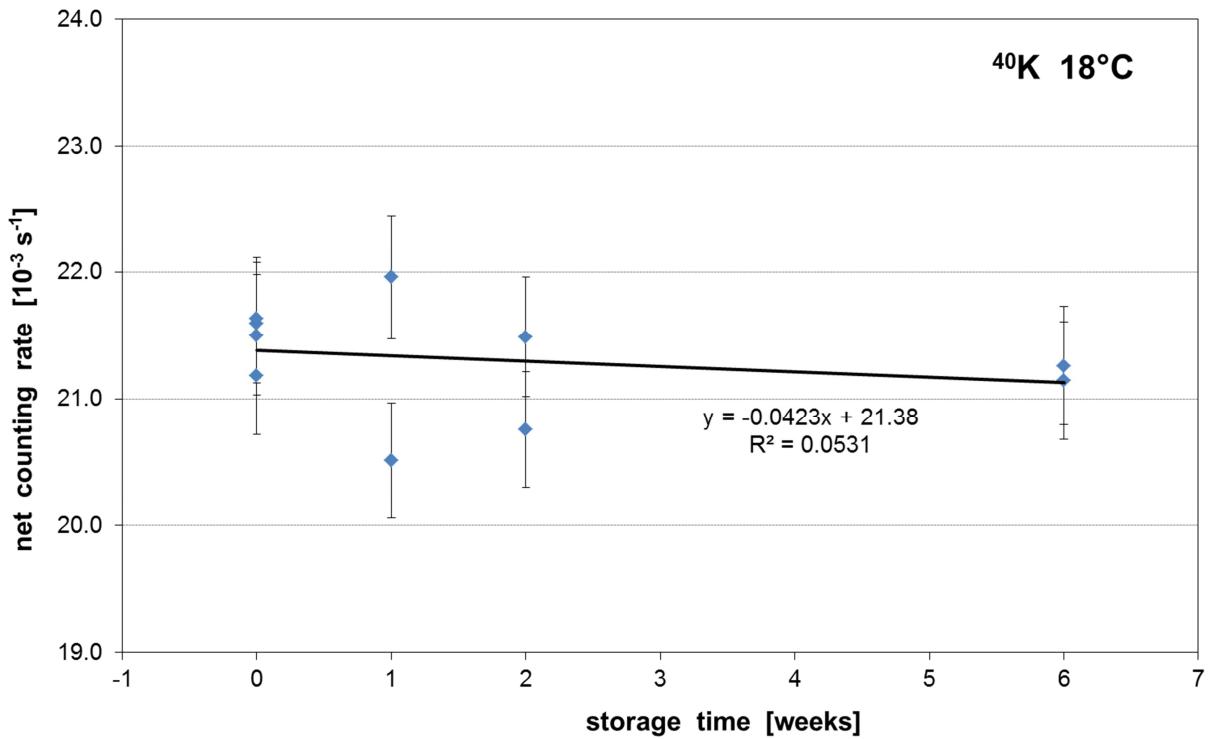


Fig. 7: ^{40}K results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 18°C . Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

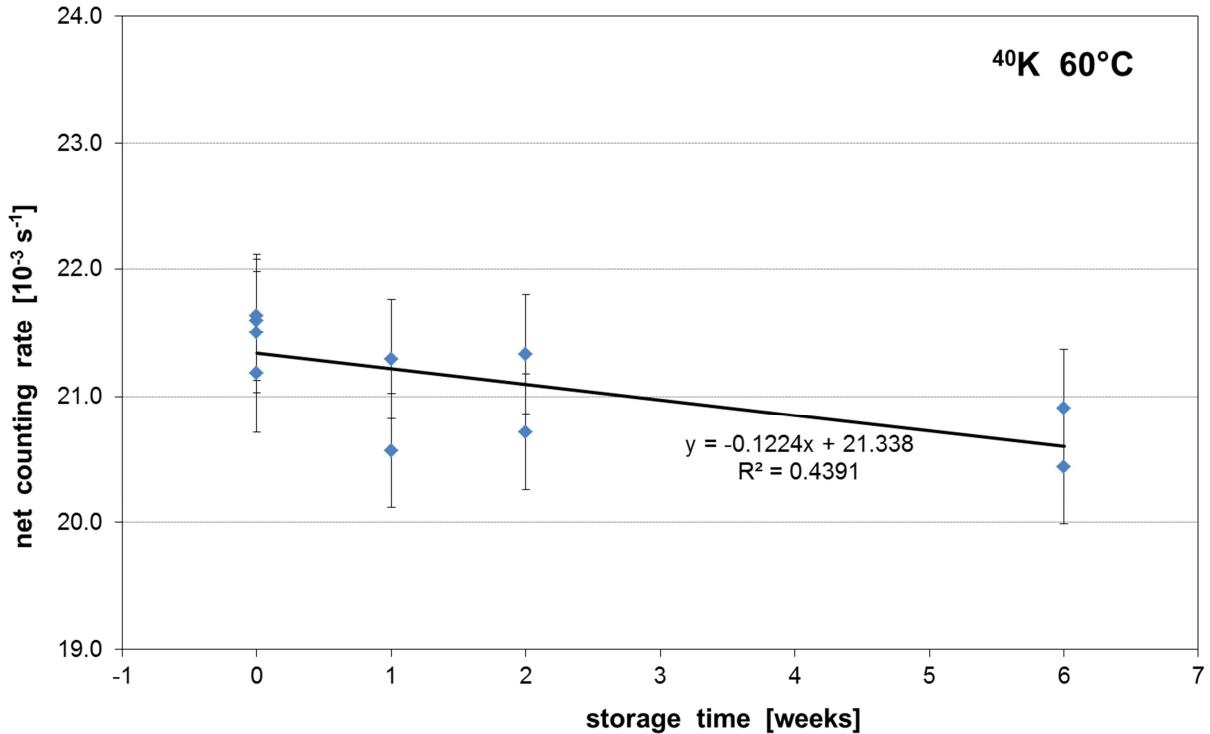


Fig. 8: ^{40}K results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 60°C . Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

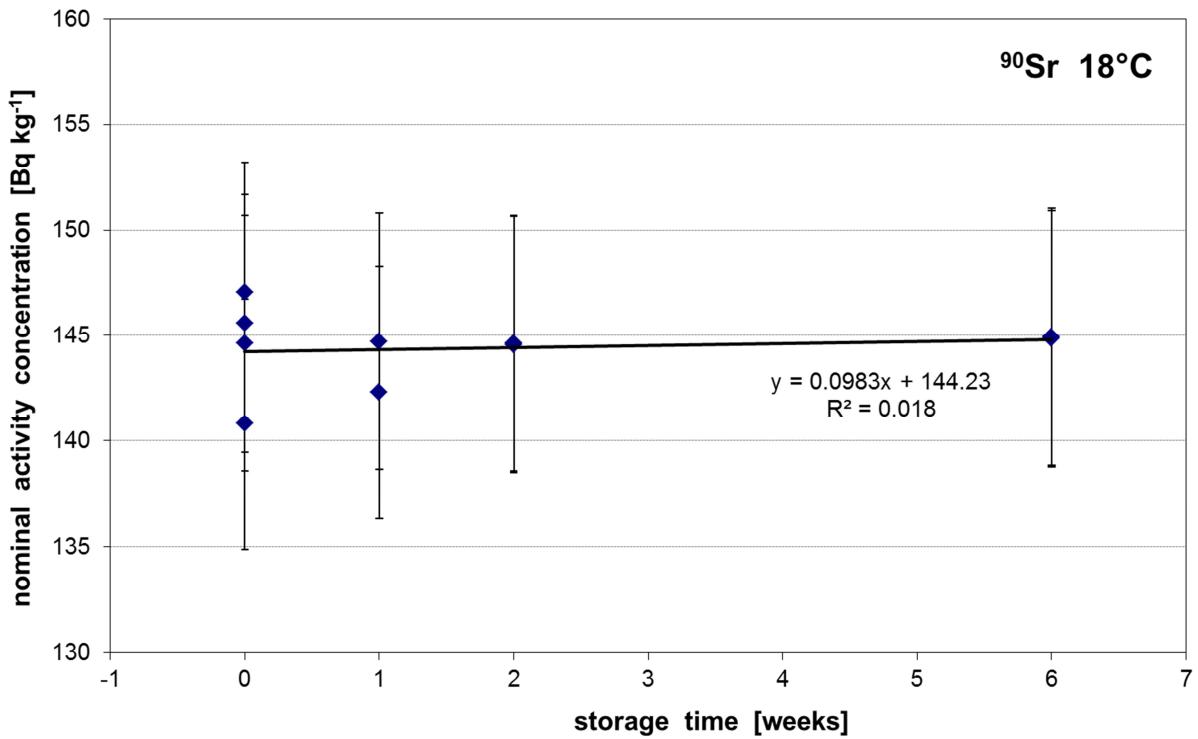


Fig. 9: ⁹⁰Sr results displayed as nominal activity concentrations A_m and regression line for samples stored at 18 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

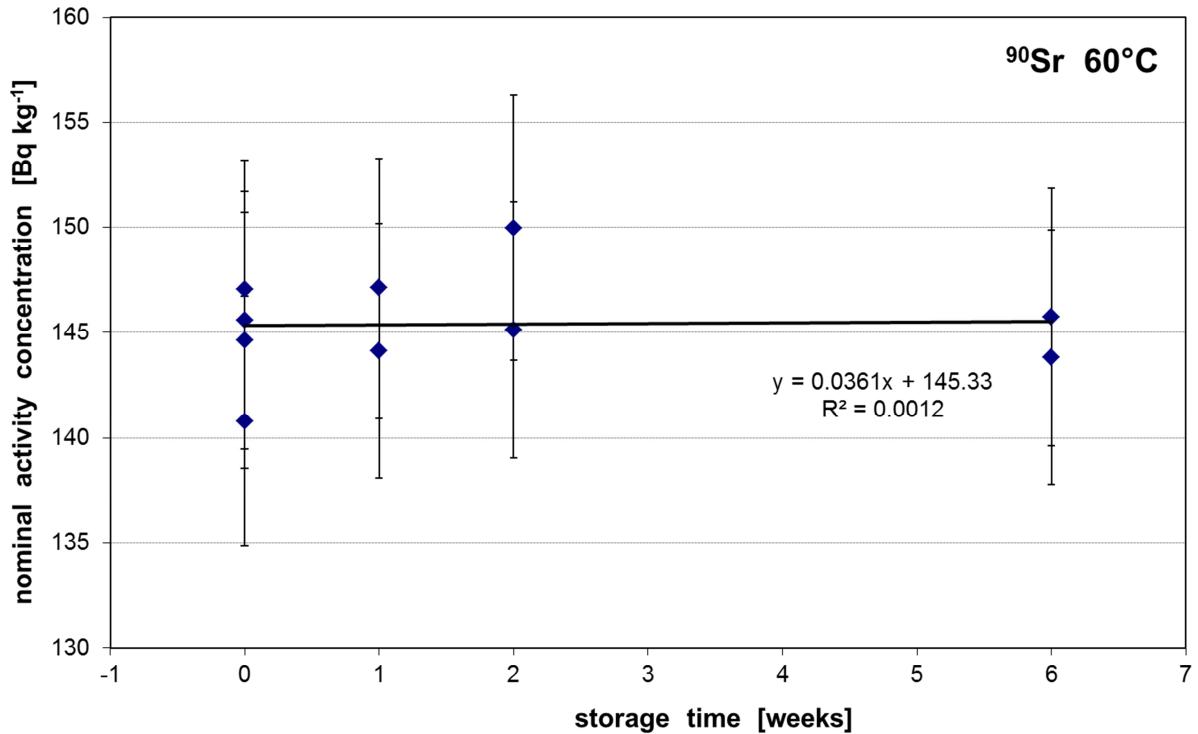


Fig. 10: ⁹⁰Sr results displayed as nominal activity concentrations A_m and regression line for samples stored at 60 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

Annex C: Results of the long-term stability measurements

As with the short-term stability measurements, the determination procedures applied for ^{137}Cs , ^{40}K and ^{90}Sr were the same as those used by IRMM in the characterisation study, but applied under repeatability conditions using relative measurement results only. Mass of sample aliquots was 50 g in all cases, one sample per bottle used for γ -ray spectrometry, the other one for radiochemical separation and subsequent LSC determination of ^{90}Sr . Three measurements were performed for each sample, mean values of the three measurements are given in the table and figures below.

Table 15: Mean values of 3 measurement results each for all samples of the long-term stability study for the three radionuclides. Values I and A_m and their uncertainties u given as net counting rate (gamma-emitters) or nominal activity concentration (^{90}Sr), to be used as relative values only.

Sample ID	^{137}Cs		^{40}K		^{90}Sr	
	I [s^{-1}]	u [s^{-1}]	I [10^{-3} s^{-1}]	u [10^{-3} s^{-1}]	A_m [Bq kg^{-1}]	u [Bq kg^{-1}]
-20 °C	Reference samples at -20 °C					
0014	1.026	0.0133	21.26	0.47	148.8	3.6
0322	1.053	0.0137	21.93	0.48	151.4	3.6
0618	1.056	0.0137	22.09	0.49	146.3	3.5
0911	1.050	0.0136	21.89	0.48	156.1	3.7
4 °C	4 months					
0028	1.043	0.0136	21.41	0.47	151.2	3.6
0643	1.066	0.0139	21.89	0.48	150.3	3.6
	8 months					
0365	1.049	0.0136	21.72	0.48	150.2	3.6
0652	1.065	0.0138	22.29	0.49	147.7	3.5
	12 months					
0420	1.049	0.0136	22.12	0.49	149.0	3.6
0987	1.055	0.0137	21.69	0.48	150.6	3.6
18 °C	4 months					
0174	1.041	0.0135	21.52	0.47	146.2	3.5
0469	1.026	0.0133	21.60	0.48	147.8	3.5
	8 months					
0525	1.051	0.0137	21.92	0.48	144.8	3.5
0812	1.063	0.0138	22.15	0.49	153.2	3.7
	12 months					
0846	1.034	0.0134	21.79	0.48	153.2	3.7
1150	1.054	0.0137	22.06	0.49	149.6	3.6

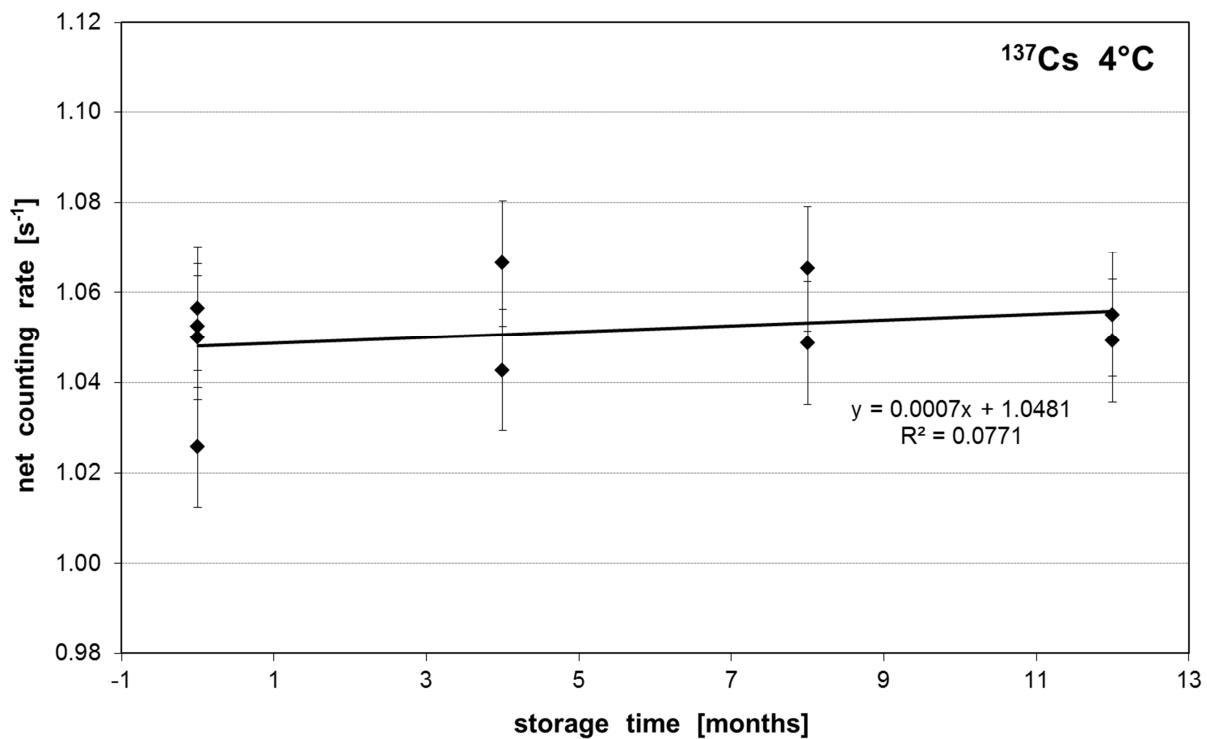


Fig. 11: ¹³⁷Cs results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 4 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

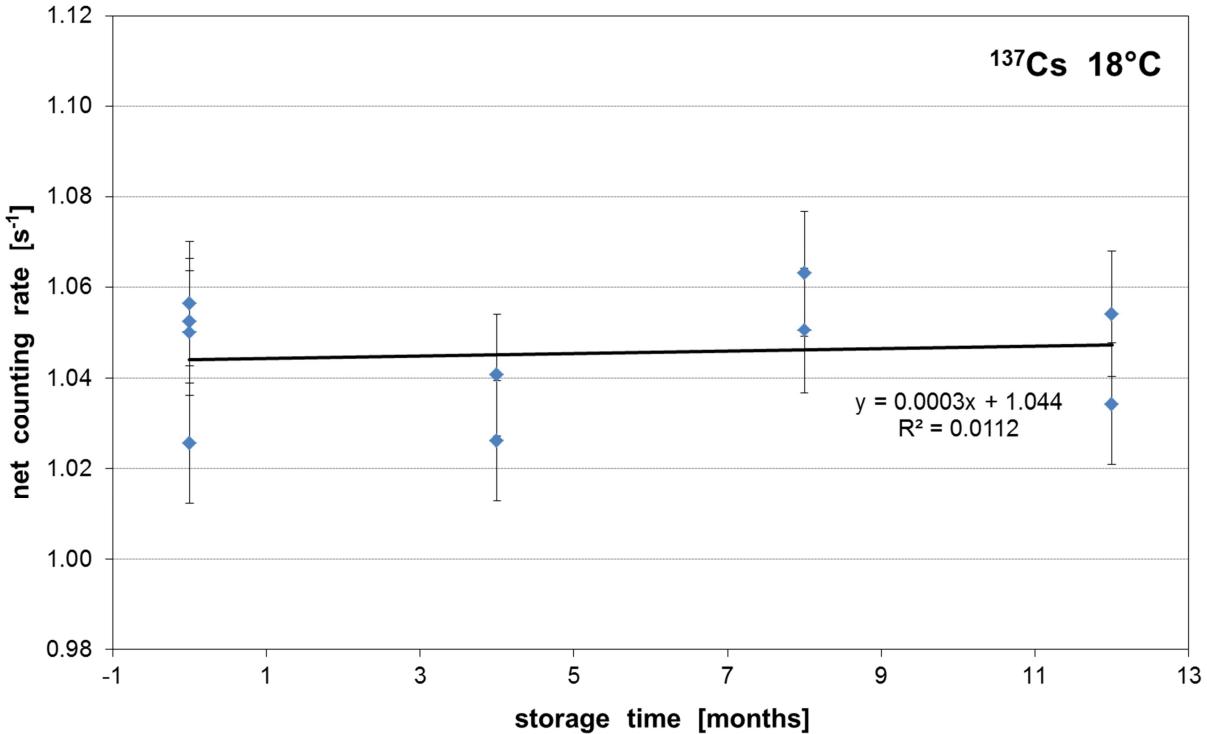


Fig. 12: ¹³⁷Cs results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 18 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

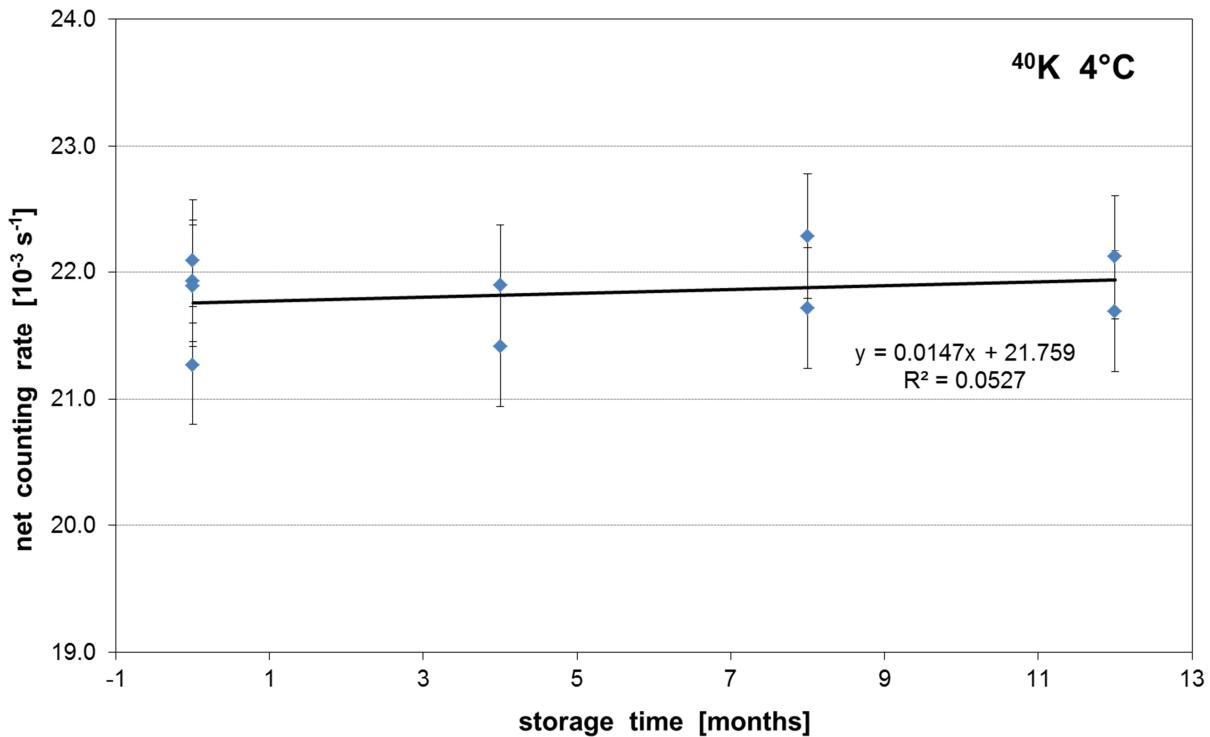


Fig. 13: ^{40}K results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 4°C . Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

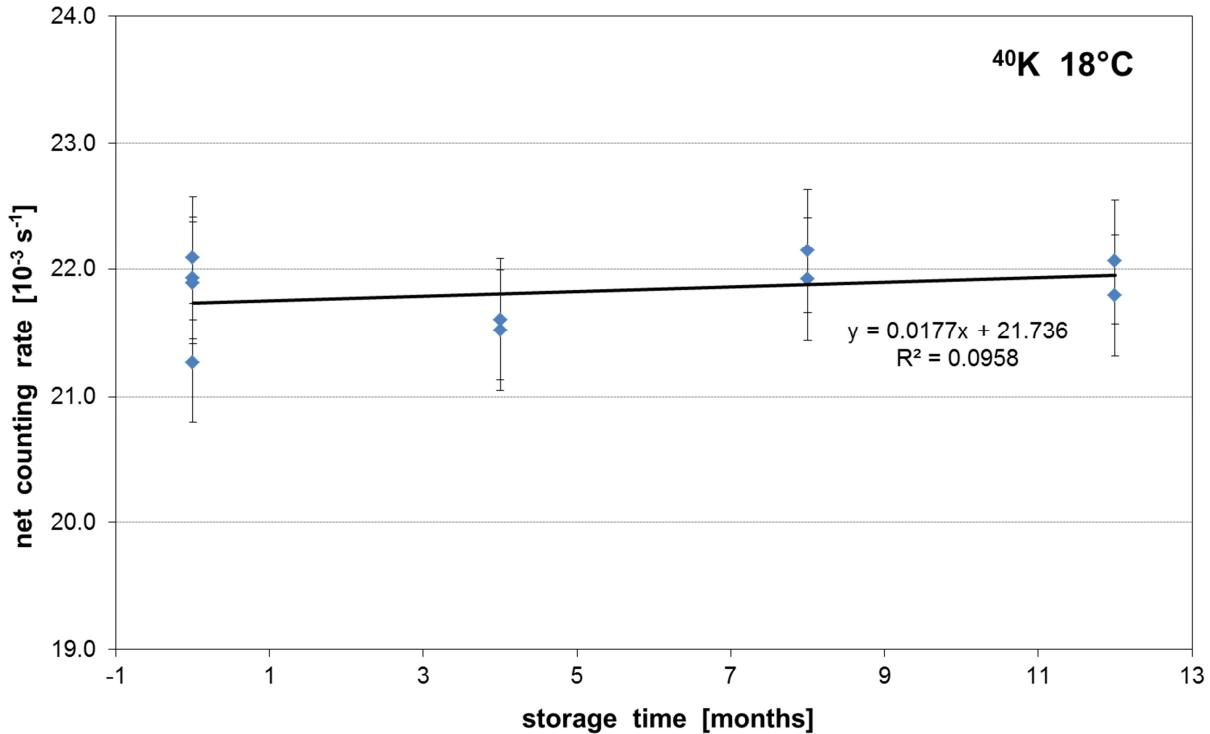


Fig. 14: ^{40}K results displayed as corrected and normalised net counting rate / together with regression line for samples stored at 18°C . Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

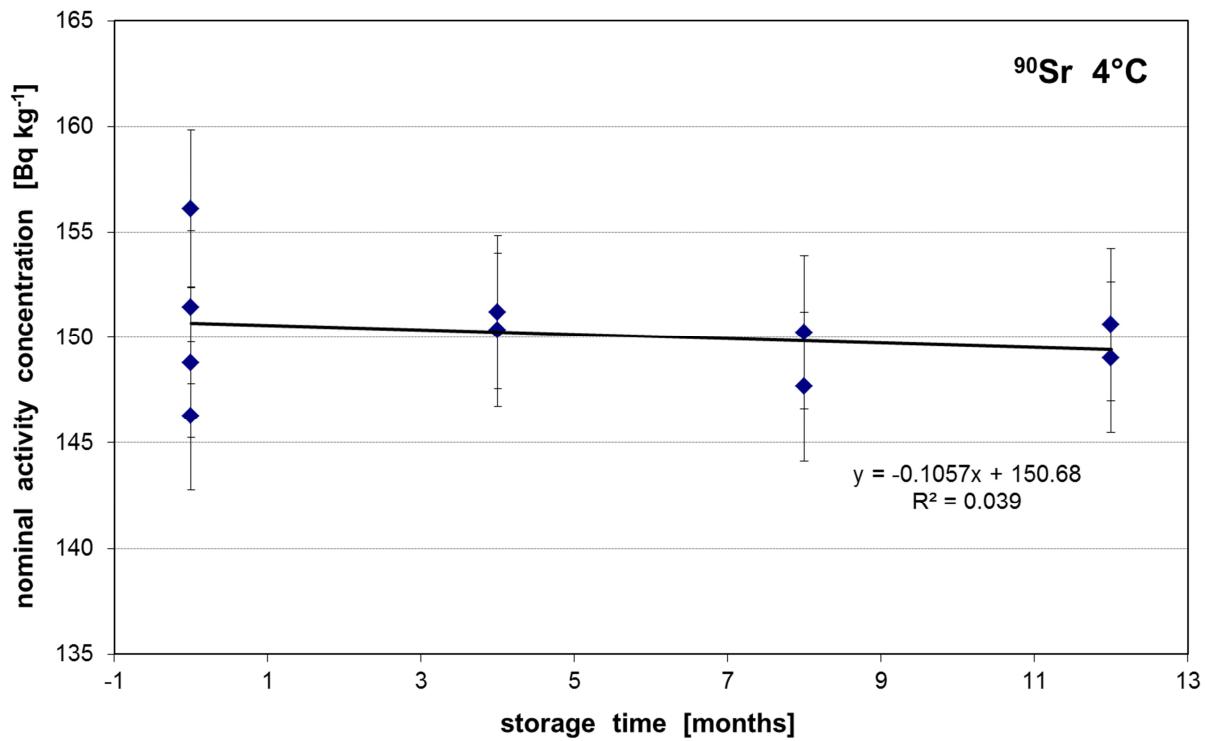


Fig. 15: ^{90}Sr results displayed as nominal activity concentrations A_m and regression line for samples stored at 4 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

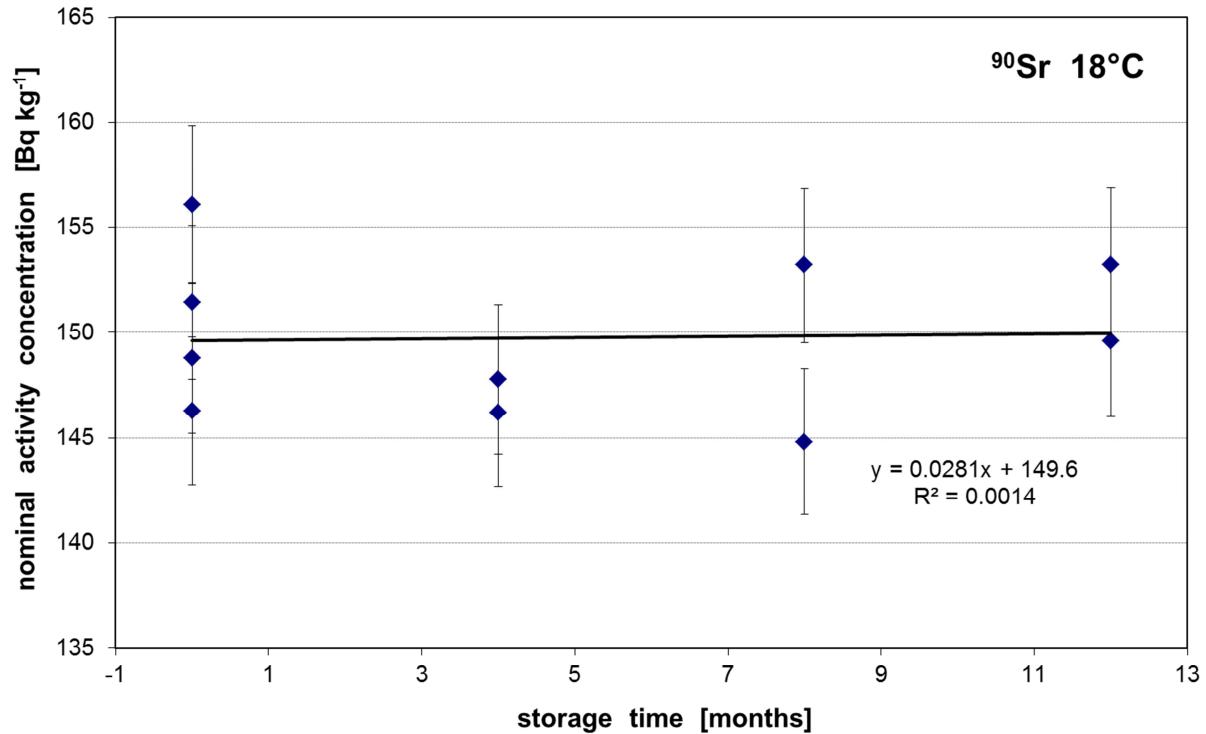


Fig. 16: ^{90}Sr results displayed as nominal activity concentrations A_m and regression line for samples stored at 18 °C. Regression parameters are given in the figure. Error bars indicate combined measurement uncertainty, u_{meas} .

Annex D: Summary of methods used in the characterisation study

Table 16: Overview of the variety of independent methods used for efficiency calibration and efficiency transfer in the gamma-spectrometric determination of ^{137}Cs and ^{40}K (partially reproduced from [Error! Bookmark not defined.]).

Laboratory code	Method for efficiency calibration and transfer	Radionuclides used for calibration	Traceability	Corrections applied	Codes used for applied corrections
L01	point sources and multiple-nuclide standard solution in same geometry; for ^{40}K : KCl solution; efficiency transfer for geometry and/or density	^{54}Mn , ^{60}Co , ^{65}Zn , ^{137}Cs , ^{241}Am natural ^{40}K	primary standardisation of solutions in house; calculated natural ^{40}K content of the KCl solution	- true coincidence summing (^{60}Co) - geometry difference - density difference	GEOLEP, GEANT, EFFTRAN ¹
L02	efficiency tracing with standard addition of ^{137}Cs and ^{152}Eu ; spiked sample dried and homogenised; $\epsilon(^{40}\text{K})$ by extrapolation from ^{152}Eu 1408 keV line	^{137}Cs , ^{152}Eu	primary standardisation of solutions in house (LSC C/N ^{137}Cs) and at MKEH (^{40}K)	true coincidence summing (^{152}Eu)	
L03	efficiency tracing with standard addition of four radionuclides to one sample; $\epsilon(^{40}\text{K})$ by extrapolation to 2 MeV with $P_\gamma(^{214}\text{Bi})$	^{137}Cs , ^{133}Ba , ^{59}Fe , ^{60}Co ^{214}Bi	primary standardisation of solutions in house		
L04	standard solutions; efficiency transfer for geometry and density	^{57}Co , ^{109}Cd , ^{210}Pb , ^{241}Am , ^{7}Be , ^{51}Cr , ^{54}Mn , ^{65}Zn , ^{137}Cs , ^{139}Ce , ^{133}Ba , ^{134}Cs	primary standardisation of solutions in house	- true coincidence summing (^{133}Ba , ^{134}Cs) - geometry difference - density difference	GESPECOR ²
L05	multiple-nuclide standard solution in same geometry; efficiency transfer for density	^{210}Pb , ^{241}Am , ^{109}Cd , ^{57}Co , ^{139}Ce , ^{51}Cr , ^{113}Sn , ^{85}Sr , ^{137}Cs , ^{54}Mn , ^{88}Y , ^{65}Zn , ^{60}Co , ^{22}Na , ^{40}K	primary or secondary standardisation of solutions in house	- density difference with experimental linear attenuation coefficients	

L06	^{137}Cs	efficiency tracing with standard addition of ^{137}Cs to one sample	^{137}Cs	CRM of ^{137}Cs standardised in ionisation chamber, calibrated in house with primary standard solution		
	^{40}K	standard source of natural ^{40}K in KAP, same geometry as samples, tapped to similar density	natural ^{40}K	calculated natural ^{40}K content		
L07		standard sources in similar matrix (zeolite), same geometry as samples	^{137}Cs , ^{60}Co , ^{152}Eu	primary standardisation of solutions in house	true coincidence summing (^{60}Co , ^{152}Eu)	GESPECOR ²
L08	Multiple-nuclide standard solution in same geometry		^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{137}Cs , ^{113}Sn , ^{88}Y , ^{54}Mn , ^{65}Zn	primary standardisation of solutions at NIST	- density difference with experimental linear attenuation coefficients	algorithm from Debertin and Helmer ³
L09	standard sources in similar matrix (silicone resin), same sample container; efficiency transfer for density and sample height $\epsilon(^{137}\text{Cs})$ direct; $\epsilon(^{40}\text{K})$ by interpolation		^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{60}Co , ^{137}Cs , ^{113}Sn , ^{85}Sr , ^{88}Y , ^{203}Hg , ^{54}Mn , ^{65}Zn	primary standardisation of solutions at CMI	- true coincidence summing (^{60}Co , ^{88}Y) - density difference - sample height difference	LABSOCS, confirmed by ETNA ⁴ and EFFTRAN ¹

¹ T. Vidmar, Nucl. Instrum. Methods in Phys. Res. A550 (2005) 603-608.

² O. Sima, Appl. Radiat. Isot. 68 (2010) 1403-1406.

³ K. Debertin, R.G. Helmer, Gamma- and X-ray spectrometry with semiconductor detectors, North-Holland, 1988.

⁴ F. Piton et al., Appl. Radiat. Isot. 52 (2000) 791-795.

Table 17: Radiochemical methods and counting techniques used in the determination of ^{90}Sr (partially reproduced from [14]).

Laboratory	Preconcentration	Sample dissolution	Purification, separation	Tracer used	Source preparation	Counting method
L01	ashing in 11 steps up to 650 °C, 36 h at 650 °C in muffle furnace	predigestion ($\text{HNO}_3 + \text{H}_2\text{O}_2$) over night; Sr carrier added; microwave digestion	Sr-Ca precipitation with fuming HNO_3 ; extraction chromatography (Eichrom® Sr resin)	10 mg stable Sr carrier, gravimetical; nat. Sr of sample with ICP-MS	oxalate precipitate, filtered, dissolved in HNO_3 ; Insta-Gel Plus® added	LSC-C/N ^3H efficiency tracing, $^{90}\text{Sr}/^{90}\text{Y}$ in equilibrium
L02	tracer added; ashing at 400 °C, 16 h	dissolution using mineral acids	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)	^{85}Sr , added before ashing, gamma-ray spectrometry; calibrated by point standard sources from MKEH	strip of Sr from the resin; transferred to glass scintillation vial	4π Cherenkov counting of ingrowing ^{90}Y in LS counter; ϵ of Cherenkov counting by $^{90}\text{Sr}/^{90}\text{Y}$ ref. sources (LSC C/N)
L06	ashing at 600 °C, 16 h in muffle furnace; Sr carrier added	dissolution in HNO_3 ; MnO_2 dissolved in H_2O_2	primary separation with Eichrom Sr resin; scavenge precipitation (for Ra, Pb) as BaCrO_4 ; Cr(III), Fe(III) hydroxide scavenges	18 mg stable Sr carrier, gravimetical; nat. Sr of sample estimated with literature values	carbonate precipitate, filtered, dried <i>in vacuo</i>	gross beta counting, $^{90}\text{Sr}/^{90}\text{Y}$ in equilibrium, end-window, gas-flow proportional counter
L08	ashing in 5 steps up to 600 °C, 16 h in microwave furnace	dissolution in boiling HCl; Y carrier added	HDEHP extraction of yttrium, back extraction of Y into HNO_3	stable Y carrier, titrated; recovery of Sr from matrix also determined with ^{90}Sr spikes	yttrium hydroxide precipitate, dissolved in HNO_3 ; transferred to PE scintillation vial	4π Cherenkov counting of ^{90}Y in LS counter
L09	ashing at 600 °C; Sr carrier added	sequential dissolutions in HNO_3 , H_2O_2 , HCl	co-precipitation with CaC_2O_4 ; extraction chromatography with Eichrom Sr resin	10 mg stable Sr carrier, gravimetical; nat. Sr of sample with ET-AAS	precipitate of $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, filtered, dissolved in HNO_3 ; Insta-Gel Plus added	LSC, $^{90}\text{Sr}/^{90}\text{Y}$ in secular equilibrium; calibration sources of same Sr carrier and ^{90}Sr standard

Annex E: Dry mass correction

Oven-drying procedure for wild berries 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 for a limited time (NOT to constant mass) at a temperature of 90 °C or 60 °C at atmospheric pressure can be used. See details given below (point 4).**

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 (90 ± 2) °C or (60 ± 2) °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 1 g to 3 g spread out evenly in the drying/weighing container 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. **Drying for a limited time following one of the temperature-time parameter sets:**
 - a. **First alternative: dry at 90 °C for 40 minutes.**
 - b. **Second alternative: dry at 60 °C for 12 hours.**
5. Remove the sample from the drying device and cool to room temperature in a desiccator. 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:

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

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.

Annex F: Results of the characterisation measurements

The tables below present the individual results, mean values and their expanded uncertainties as reported by the laboratories. The graphs are showing the mean value of each laboratory with its expanded uncertainty and the certified values and their expanded uncertainties. All values are stated on dry mass basis. Laboratories L03, L04 and L05 did not participate in the determination of ^{90}Sr .

^{137}Cs

Laboratory code	replicate 1 [Bq kg $^{-1}$]	replicate 2 [Bq kg $^{-1}$]	replicate 3 [Bq kg $^{-1}$]	replicate 4 [Bq kg $^{-1}$]	replicate 5 [Bq kg $^{-1}$]	replicate 6 [Bq kg $^{-1}$]	mean [Bq kg $^{-1}$]	Expanded uncertainty [Bq kg $^{-1}$]
L01	809	814	822	821	809	818	816	43
L02	732	747	758	760	728	761	749	38
L03	760	763	766	764	769	759	763	36
L04	817	823	814	810	817	814	816	22
L05	775	770	774	778	791	780	778	94
L06	758	770	776	779	787	773	774	67
L07	750	775	751	767	760	760	760	43
L08	777	771	808	772	782	773	781	(6) 33*
<i>Results not used for certification</i>								
L09	715.2	719.2	714.5	714.2	709	719.5	715.2	18.6

* corrected value (see text, section 6.5.2)

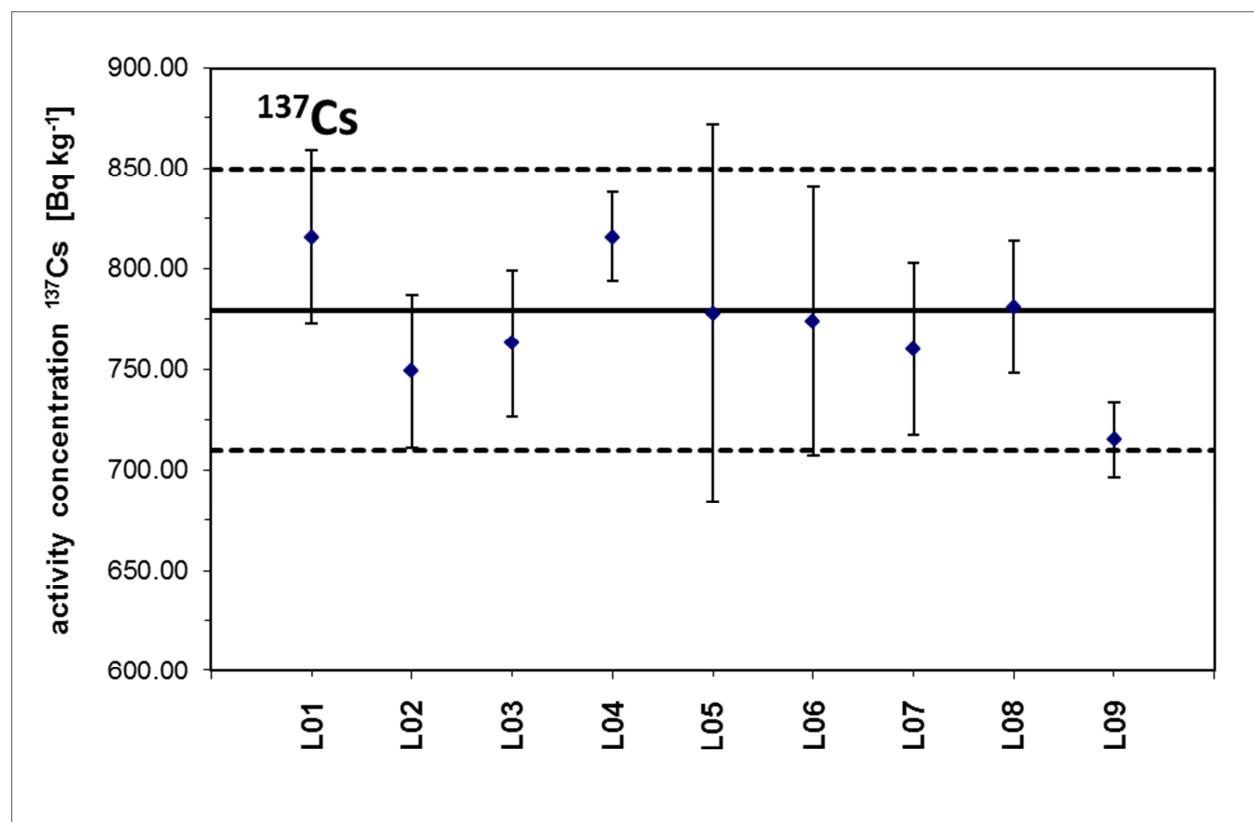


Fig. 17: Laboratory mean values for ^{137}Cs with expanded uncertainty (uncertainty bars) together with the certified value (solid line) and its expanded uncertainty (dashed lines).

^{90}Sr

Laboratory code	replicate 1 [Bq kg $^{-1}$]	replicate 2 [Bq kg $^{-1}$]	replicate 3 [Bq kg $^{-1}$]	replicate 4 [Bq kg $^{-1}$]	replicate 5 [Bq kg $^{-1}$]	replicate 6 [Bq kg $^{-1}$]	mean [Bq kg $^{-1}$]	Expanded uncertainty [Bq kg $^{-1}$]
L01	152	151	142	152	154	153	151	8
L02	150	146	140	149	141	142	145	22
L06	161.78	165.87	166.39	165.92	164.78	166.99	165.3	11.0
L08	152	160	139	156	144	164	153	8
L09	149.6	144.2	158.6	---	---	---	150.8	10.5

Laboratories L03, L04 and L05 did not participate in the determination of ^{90}Sr . The results of laboratory L07 were not taken into evaluation, see discussion in section 6.5.1 and Table 7.

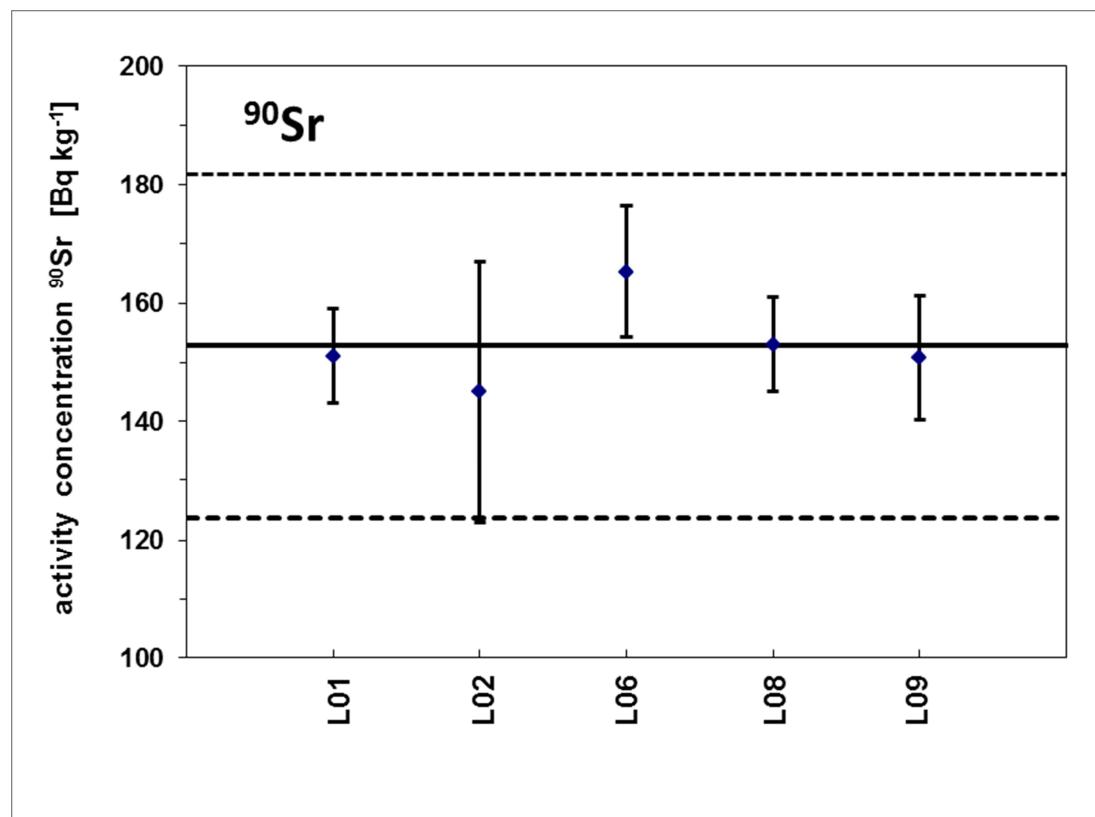


Fig. 18: Laboratory mean values for ^{90}Sr with expanded uncertainty (uncertainty bars) together with the certified value (solid line) and its expanded uncertainty (dashed lines).

^{40}K

Laboratory code	replicate 1 [Bq kg $^{-1}$]	replicate 2 [Bq kg $^{-1}$]	replicate 3 [Bq kg $^{-1}$]	replicate 4 [Bq kg $^{-1}$]	replicate 5 [Bq kg $^{-1}$]	replicate 6 [Bq kg $^{-1}$]	mean [Bq kg $^{-1}$]	Expanded uncertainty [Bq kg $^{-1}$]
L01	258	259	263	263	260	254	259	16
L02	236	235	242	242	235	238	238.3	16.9
L03	290	280	262	282	294	289	283	43
L04	251	254	249	250	252	249	251	10
L05	258	254	255	250	254	236	251	60
L06	233.3	232.7	235.7	240.0	236.0	242.9	237	21
L07	252	256	247	252	250	242	250	32
L08	255	250	267	250	259	252	256	(6) 15*
<i>Results not used for certification</i>								
L09	227.2	225.7	225.1	226.5	216.8	225.8	224.5	9.0

* corrected value (see text, section 6.5.2)

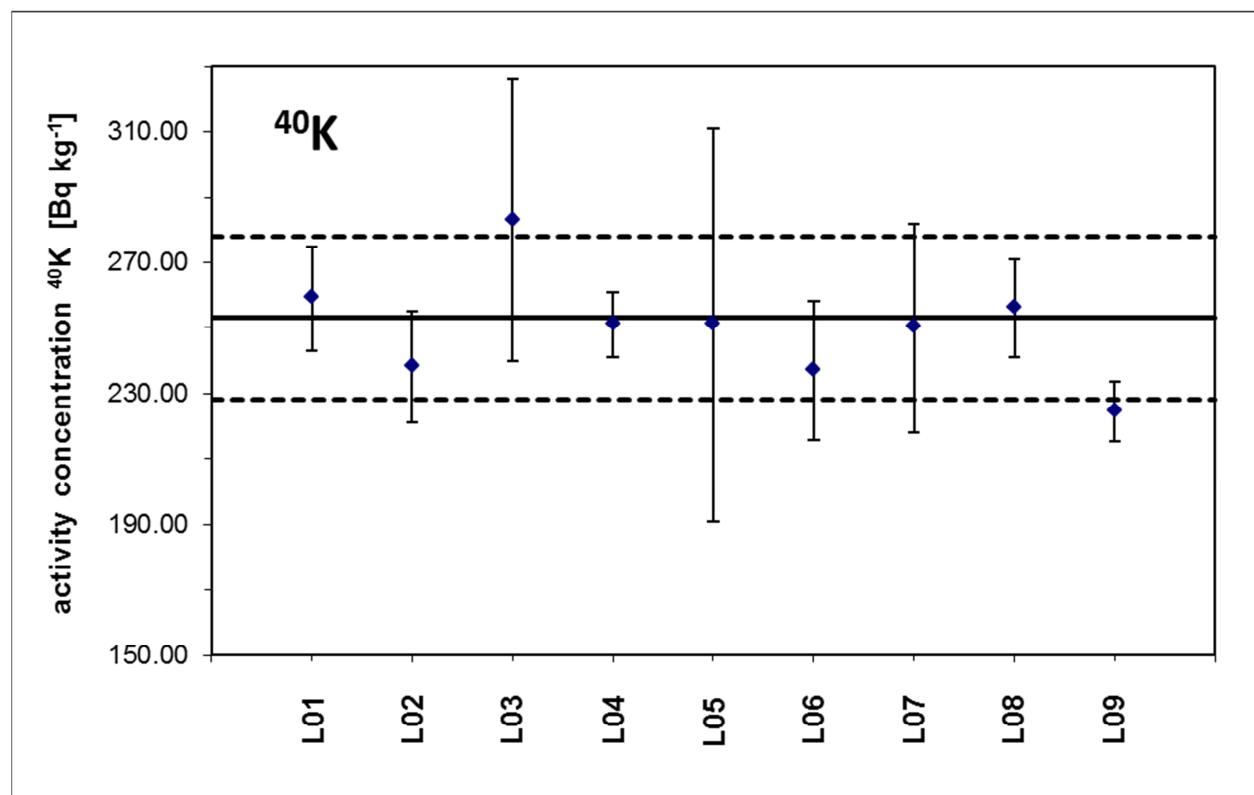


Fig. 19: Laboratory mean values for ^{40}K with expanded uncertainty (uncertainty bars) together with the certified value (solid line) and its expanded uncertainty (dashed lines).

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