NAEL/RM/001

Internal report NAEL/RM/001

Certification of massic activities of ^{89}Sr, ^{90}Sr, ^{134}Cs and ^{137}Cs in CRM IAEA-473 (milk powder) sample

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FOREWORD

To assure reliable evaluation of the potential radiological hazard and proper decision making related to radiation protection measures, the IAEA works through its Environment Laboratories of the Department of Nuclear Sciences and Applications to support its Member States' laboratories to maintain their readiness and improve the quality of the analytical results. It does so by producing reference materials, by developing standardized methods for sample collection and analysis, and by conducting interlaboratory comparisons and proficiency tests as tools for external quality control of analytical results.

Shortly after Fukushima I Nuclear Power Plant was hit by a tsunami triggered by a magnitude 9.0 earthquake on 11 March 2011, a meltdown of three of the plant's six nuclear reactors occurred. The plant began releasing substantial amounts of radioactive material, and in several surrounding prefectures considerable contamination of the food chain resulted. Food control became one of the most important routine tasks of the radioanalytical laboratories, which increased the need for harmonization of the applied methods.

Within this context and to fulfil a part of this demand, the IAEA's Terrestrial Environment Laboratory (NAEL-TEL) has prepared a new certified reference material (CRM), identified as IAEA-473, certified for the massic activity of ^{89}Sr, ^{90}Sr, ^{134}Cs and ^{137}Cs. This report presents the methodologies used for the production and certification of IAEA-473.

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CONTENT

1. INTRODUCTION

To meet the IAEA Member States' needs for a certified reference material of short-lived radionuclides in milk powder following the Fukushima Daiichi nuclear accident, the Terrestrial Environment Laboratory (TEL) prepared IAEA-473 CRM.

Its matrix is a full fat milk powder from which milk with a fat content of 3.5% can be retrieved. This CRM contains two radio-strontium isotopes, ^{89}Sr and ^{90}Sr. Strontium-89 has a relatively short half-life of 50.57 days [1], and the presence of this isotope interferes with the determination of ^{90}Sr. For the exact determination of the ^{90}Sr isotope in presence of ^{89}Sr, a special combined radioanalytical method should be used; this new reference material is intended to provide an opportunity to test such a method. To simulate real accident circumstances, both radio-caesium ^{134}Cs and ^{137}Cs are also added to the material.

This report presents the sample preparation methodology, materials, and assignment of property values and their associated uncertainty for ^{89}Sr, ^{90}Sr, ^{134}Cs and ^{137}Cs.

The new IAEA-473 CRM can be used for the verification of performance indicators (precision, repeatability, reproducibility) of the simultaneous measurement of ^{89}Sr and ^{90}Sr in the presence of radio-caesium isotopes. The quick decaying rate of the ^{89}Sr isotope gives an opportunity to study the behavior of the radioanalytical method at different ^{89}Sr/^{90}Sr ratios.

2. METHODOLOGY

2.1. PREPARATION OF THE MATERIAL

High quality fresh milk powder with 26% fat content was used as raw material. It was produced in the Czech Republic and purchased from a commercial supplier. The raw milk powder was tested both for radio-caesium and radio-strontium isotopes.

For gamma emitting radionuclides, a 30% relative efficiency N-type HPGe detector was used, in 10 cm multi-layer shielding made of lead, cadmium and high purity electrolyte copper. The conditions of the gamma-ray spectrum analysis are summarized in Table 1.

TABLE 1. CONDITIONS OF THE GAMMA-RAY SPECTRUM ANALYSIS OF THE RAW MATERIAL

Detector	N-type coaxial HPGe in BIG-MAC cryostat
Energy range	20-2000 keV
Resolution at 122 keV	1.0 keV
Resolution at 1332.5 keV	2.3 keV
Size of the spectrum	8192 channel
Shielding	CANBERRA 747
Sample geometry	450 cm^3 Marinelli-beaker
Sample mass	300.0 grams
Counting time	80000 s
Spectrum evaluation	Genie 2000
Efficiency calibration	LABSOCS (using detector characterization)
Calculation of the detection limit	According to relevant standard [2]

The result was below the detection limits for both radio-caesium isotopes of 0.8 Bq kg^{-1} for ^{137}Cs and 0.6 Bq kg^{-1} for ^{134}Cs, respectively.

The radio-strontium (^{90}Sr) content of the raw material was determined according to the IAEA combined radioanalytical procedure [3] and was found to be below the detection limit as well.

2.1.1. Spiking

The material was prepared by a spiking technique, using first and second dilutions of high precision radioactive reference solutions from commercial providers.

The main steps of the applied techniques are listed below:

- Planning the composition of the master spike solution.
- The diluted stock solutions which were to be used were tested by point source preparation and comparative gamma-ray spectrometry for radio-caesium isotopes and LSC measurement for ^{89}Sr and ^{90}Sr isotopes.
- The required aliquots of the diluted solutions were added to the master spike solution using a special plastic ampoule (pycnometer) technique.
- The isotope mixture was diluted with analytical purity 2-propanol (iso-propanol) up to 50 cm^3 volume.
- This master spike solution was dispersed quantitatively on 450 grams of raw milk powder and dried on open air.

2.1.2. Homogenization

The homogenization was carried out in two steps:

- At first, 1000 g solid concentrate (450 g of spiked and 550 g raw milk powder) was homogenized in a TURBULA 10T power blender (see *FIG. 1.*); to force the homogenization and to destroy potential conglomerates, 15 ceramic balls were added.
- In a second step, the milk powder concentrate was diluted to 20 kg and homogenized in the TURBULA 51 power blender for 60 hours.

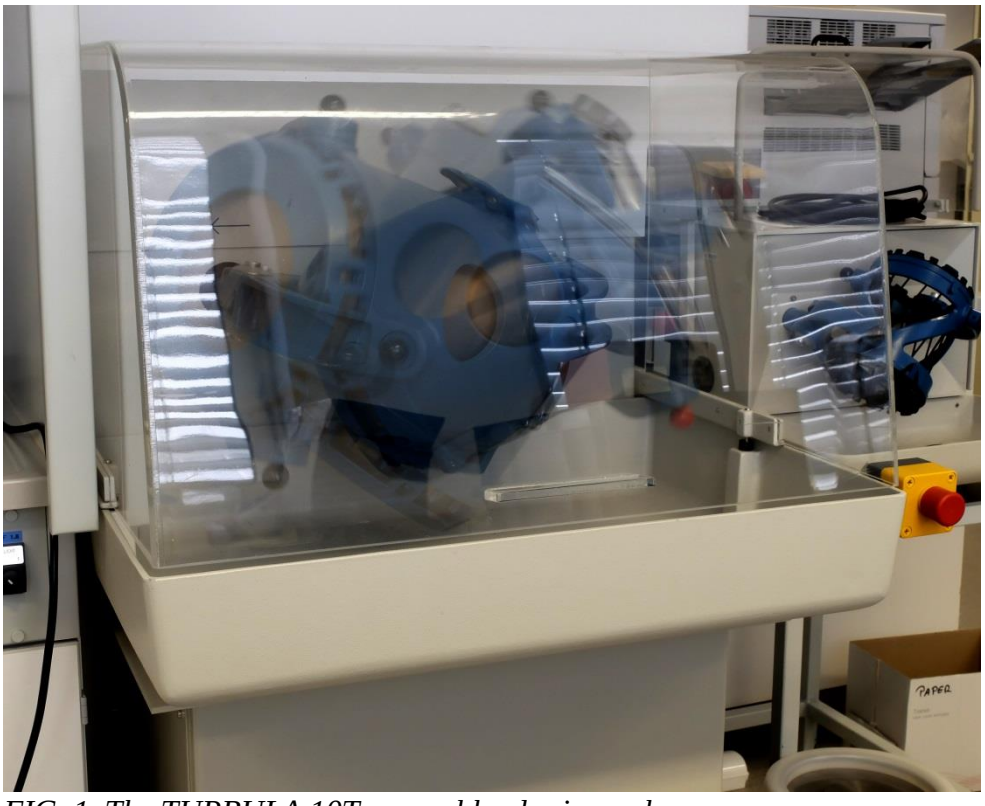

FIG. 1. The TURBULA 10T power blender in work

2.1.3. Bulk homogeneity test

The bulk homogeneity of the material was tested by gross beta measurement using a liquid scintillation counter (Quantulus 1220). For this purpose seven samples were taken (20 g each) and three subsamples (1 g each) were analyzed at the different phases of the homogenization process. When the control measurements were finished the homogenization process was stopped and the remaining part of the subsample material was added back to the bulk material. After 60 hours of blending, the control measurements showed sufficient homogeneity. The conditions of the bulk homogeneity test are summarized in Table 2.

TABLE 2. THE CONDITIONS OF THE BULK HOMOGENEITY TEST

Counting technique	Liquid scintillation
Equipment	Quantulus 1220
Counting mode	High energy beta
Scintillator	Insta-Gel Plus
Type of the vial	Low diffusion, plastic
LSC Sample	
Sample	1 g milk powder[1]
High purity water	5 cm^3
Scintillator	15 cm^3
Counting time	1200 s
Number of Cycle	3
Number of samples to be analyzed	21 (3 subsamples from 7 samples)

[1] After a short shaking period the milk powder dissolved into the water-scintillator system and remained transparent for the period of the counting time, including three cycles.

The applied preparation procedure consists of clearly physical processes, thus there was no reason for the separation of the spiked isotopes and the determination of the gross-beta activity of the samples was enough to demonstrate the homogeneity of the material.

The statistical evaluation of the measurement results is shown in Table 3. The measurements took 42 hours and during this time 2.37% of the ^{89}Sr decayed due to its short half-life (50.57 (3) days) [1]. For the statistical evaluation the radioactive decay of the ^{89}Sr was considered accordingly to the elapsed time from the sampling up to the beginning of the measurement of each subsample.

TABLE 3. RESULTS OF THE STATISTICAL EVALUATION OF THE BULK HOMOGENEITY TEST

Parameter	Results/Value
Number of samples	21
Number of considered measurements	63
Sample mass	1.00 g
Average count number (decay corrected)	16881 (during 1200 s)
SD	219
RSD	1.3%
Median	16895
Minimum	16467 (-2.4%)
Maximum	17401 (2.9%)
Uncertainty due to the radioactive decay[1]	0.77%
Average method repeatability from the repeated measurement cycles[2]	0.93%
Combined uncertainty	1.21%
Likely contribution due to the heterogeneity	0.48%
F (crit, α=0.05)	2.85
F (from ANOVA)	2.21
r(within sample)	1.11%
r(between sample)	1.65%

[1] Theoretical limit (from the square-root of the detected count numbers)
[2] Calculated from the average variances of the repeated measurements

The distribution of the measurement result is shown in *FIG.2*. The range of the vertical scale is ± 10% of the arithmetical mean value. The minimum and maximum values (within the three measurement cycles) are marked with red lines.

FIG. 2. The measurement results of the bulk homogeneity test

2.1.4. Particle size distribution

The particle size distribution was determined by a laser scattering particle size analyzer (Horiba LA 950) using dry conditions. The results of three independent measurements are shown in *FIG. 3.*

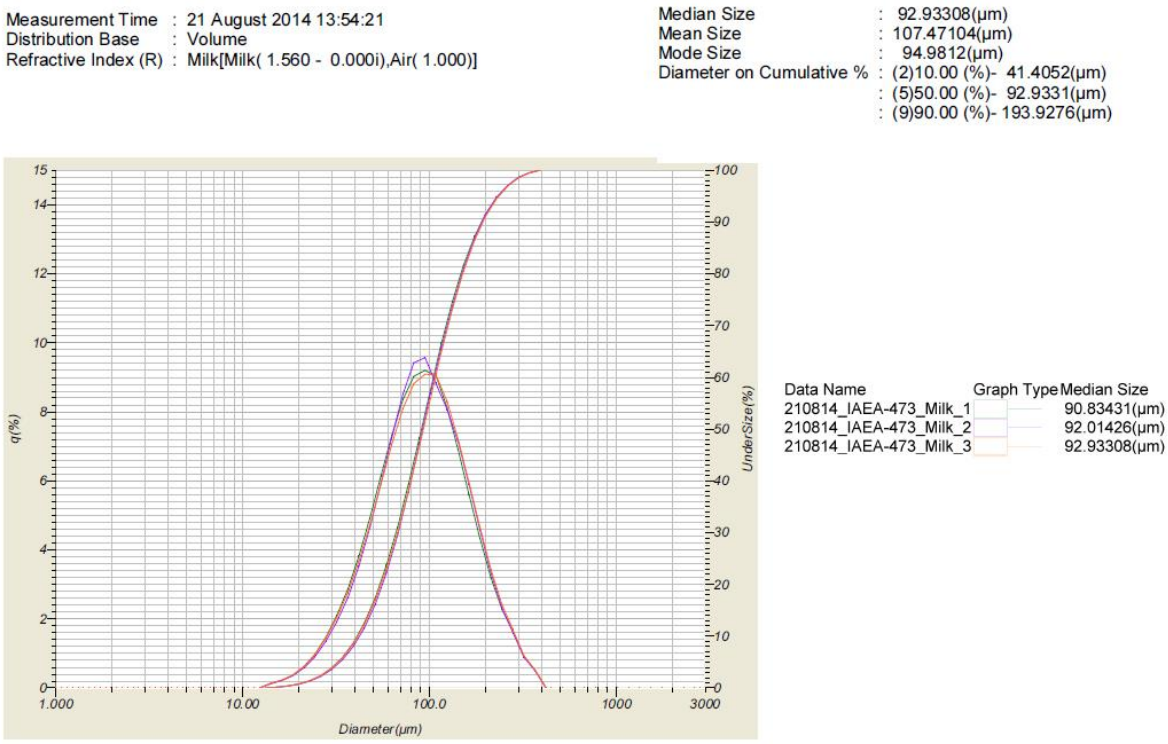

FIG. 3. The result of the particle size analysis

2.1.5. Bottling

The IAEA-473 CRM was bottled under normal laboratory conditions; 197 bottles were filled in one day. The bottles were labeled with pre-printed labels bearing a serial number according to the production order, arranged into plastic boxes and sterilized using gamma ray irradiation with a total dose of 25 kGy using a ^{60}Co source.

The unit size was determined to be 100 g; the exact weight of the material in each bottle was recorded and used for establishing the technological material balance of the entire production process.

Each bottle is provided with a wide neck secure-sealed cover to preserve the integrity of the reference material in the bottle.
The average moisture content of the material after bottling was determined by drying 2 g overnight at 90°C. The moisture content of the material was 3.8% at the bottling period.

2.2. FINAL HOMOGENEITY STUDY

Right after the bottling, 10 out of the 197 bottles were selected randomly for the final homogeneity study. During the planning phase of the measurements

- the method repeatability,
- the reasonably low sample volume,
- the realistic counting time

were taken into consideration.
The measurements were carried out by gamma-ray spectrometry on 5 gram pellets prepared using 16 tons pressure.
Three subsamples (5 g) were taken from each bottle (without shaking) and pellets were prepared using high pressure pelletizer (see *FIG.4.*). The exact weight of the pellets was determined and considered during the evaluation of the results. The thickness of the pellets was controlled by precision digital caliper for the uniformity of the sample geometry.

FIG. 4. Pellets from milk powder produced by high pressure equipment

One pellet was prepared from a special milk powder calibrant spiked with mixed gamma solution (the brown one on the right side of the picture).
The conditions of the sample preparation and gamma-ray spectrum analysis are summarized in Table 4.

TABLE 4. CONDITIONS OF THE HOMOGENEITY STUDY

Sampling and Sample Preparation	
Number of subsamples from each bottle	3
Sample mass	5.0 g
Pelletizer	SPEX 3635
Applied pressure	16 tons
Dwell time	2 min
Release time	1.5 min
Diameter of the pellet	24 mm
Thickness of the pellet	5.30 ± 0.05 mm
Measurement by gamma spectrometer equipped with automatic sample changer	
Detector	P-type HPGe
Relative efficiency	60%
Resolution	1.1 keV (at 122 keV) 2.4 keV (at 1332.5 keV)
Cryostat	Low background
Energy range	60-2000 keV
Spectrum size	8196 channels

Shielding	10 cm lead and 1 mm copper
Counting time (live time)	30000 s
Software	Genie 2K with control of the automatic sample changer

The measurement repeatability was determined by a series of measurements of a selected sample at the activity level of the individual pellet, including the sample replacement procedure using the automatic sample changer system.

FIG.5. Automatic sample changer

The spectra were evaluated for net peak areas (counts detected during the measurement) of the 604.72 keV energy peak of the ^{134}Cs and 661.67 keV energy peak of the ^{137}Cs. The results for both isotopes are summarized in Table 5.

TABLE 5. STATISTICAL EVALUATION OF THE FINAL HOMOGENEITY STUDY

Parameter	^{134}Cs	^{137}Cs
Number of samples	30	
Number of considered measurements	30	
Sample mass	4.97-5.05 g	
Average count number (decay corrected)	2197	1430
SD	70	43
RSD	3.18%	2.99%
Median	2219	1431 (0.07%)
Minimum	2096	1374 (-4.53%)
Maximum	2349	1538 (6.87%)
Uncertainty due to the radioactive decay[1]	2.1%	2.66%
Average method repeatability from the three measurement cycles[2]	3.93%	3.67%
Likely contribution due to the heterogeneity	n.a.	n.a.
F (crit, α=0.05)	2.40	2.40
F (from ANOVA)	1.98	2.06

s^2_{wb}(within bottle)	3736	1398
s^2_{bb}(between bottle)	1221	493

[1] The square-root of the detected count numbers
[2] Calculated from the average variances of the repeated measurements

The measurement results are shown in *FIG. 6.* below.

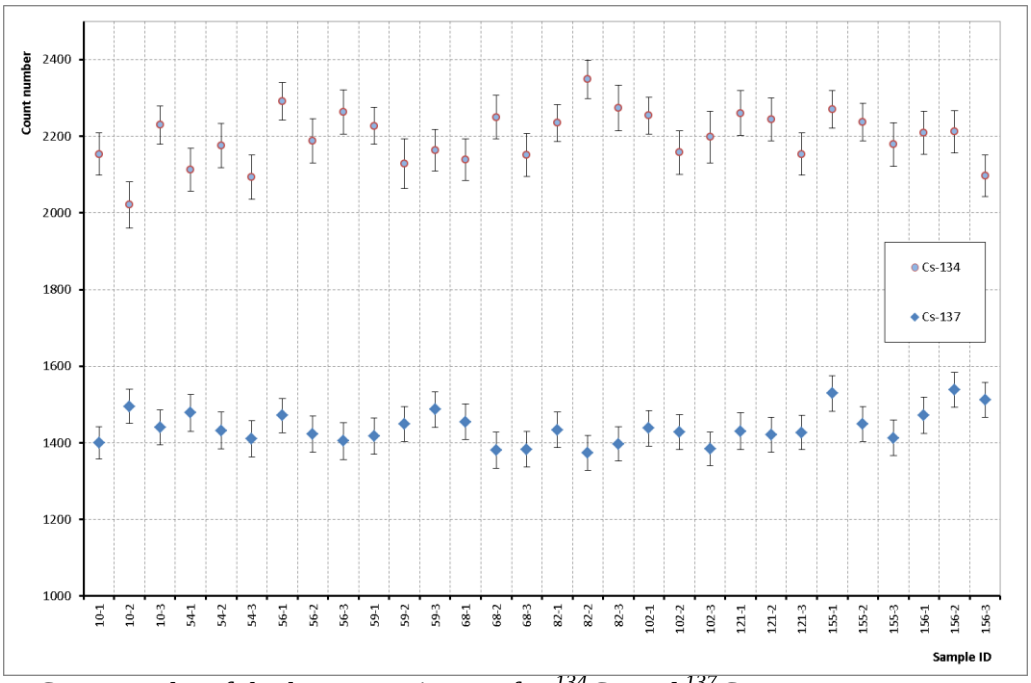

FIG. 6. Results of the homogeneity test for ^{134}Cs and ^{137}Cs.

A comprehensive homogeneity study was carried out on this CRM to estimate the uncertainty associated with its heterogeneity. Between-bottle heterogeneity was tested by the determination of the net counts by the measurement of three uniform subsamples from the each randomly selected 10 bottles of IAEA-473. The measurements have been carried out by gamma-ray spectrometer system equipped with 60% relative efficiency HPGe detector and automatic sample changer. The analysis for the homogeneity study was performed under repeatability conditions. The repeatability parameters were determined at the same activity level using identical geometry conditions.

The collected set of data was evaluated by ANOVA. From regular ANOVA parameters the within and between bottle homogeneity was determined using the recommended formula from ISO Guide 35[3]:

$$s^2_{wb} = MS_{within} \tag{1}$$

$$s^2_{bb} = \frac{MS_{among} - MS_{within}}{n_0} \tag{2}$$

$$u_{bb} = \sqrt{\frac{s_{wb}^2}{nbot \cdot n} + \frac{s_{bb}^2}{n_{bot}}} \quad (3)$$

Where:

MS_{among}	Mean square (ANOVA) between bottles
MS_{within}	Mean square (ANOVA) within bottles
n	Number of observations
n_{bot}	Number of bottles
n_0	(Effective) number of (sub) group members
s_{bb}^2	Variance between bottles
s_{wb}^2	Variance within bottles
u_{bb}	Uncertainty associated with the between-bottle heterogeneity

There was no missing data from the ANOVA pattern, thus the $n_0 = n$ (number of observations) is used for the estimation of the s_{bb} value [3].

For the uncertainty calculation the following uncertainty budget was applied:

- Uncertainty of the standard radioactive solutions (from the certificates)
- Uncertainty of the dilution steps (gravimetric)
- Losses of the spike solution (0.1%)
- Uncertainty of the milk powder mass determination (0.01%)
- Uncertainty of the dry content determination (0.2%)
- Losses of the milk powder at different steps of the preparation (0.1%)
- Between and within bottle heterogeneity: 1.5% and 1.11% respectively.

During the homogeneity test the nuclide specific measurement did not identify any heterogeneity, thus the results of the last bulk homogeneity test were used for the uncertainty calculation as conservative approach. The uncertainty components by isotopes of the master spike solution are summarized in Table 7 below.

TABLE 7. UNCERTAINTIES BY RADIONUCLIDES IN % (at *k*=1)

Radionuclide	Spike solution	From preparation	From heterogeneity*	Combined standard
Sr-89	2.81	0.25	1.65	3.2
Sr-90	1.7	0.25	1.65	2.4
Cs-134	1.1	0.25	1.65	2.0
Cs-137	1.4	0.25	1.65	2.2

*From the most conservative estimation

The uncertainty components are shown in *FIG. 7.*

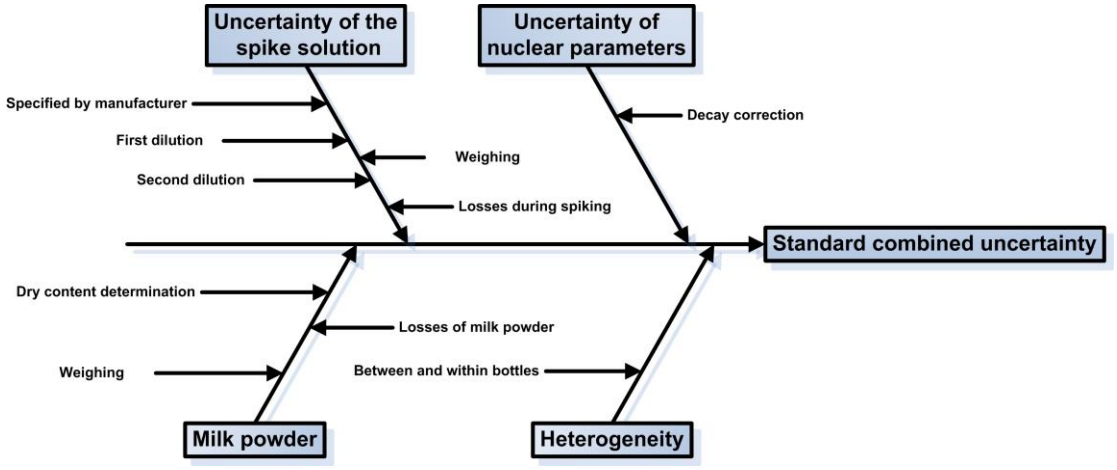

FIG. 7. Uncertainty components

The standard uncertainty associated with the material heterogeneity was calculated using the formulae stated in ISO Guide 35 [3]. One-way ANOVA results were used to apply formulae 1 to 3. Table 1 shows the results of the homogeneity study results. The outcome of the homogeneity study demonstrated that the uncertainty due to between-bottle heterogeneity u_{bb} is generally very small and the material can be considered sufficiently homogeneous for the spiked analytes at the level of 5 gram sample intake.

2.3. ASSIGNMENT OF PROPERTY VALUES AND ASSOCIATED UNCERTAINTIES

The characterization of the material was carried out by "formulation" based on the specified massic activity values on the certificates of the reference solutions and the applied dilution factors.

2.3.1. Calculation of certified property values

The raw milk powder does not contain any detectable radio-caesium and radio-strontium isotopes. Therefore, the absolute massic activities of the master spike solution and the identified losses during the preparation steps were used for calculation of the property values.

The losses of the radioactive isotopes were determined by measurement of the remaining activity on the surface of the applied tools by gamma-ray spectrometry.
To minimize losses due to contact with the spike solution and the spiked material, it was planned to use as few tools as reasonably possible in the spiking process. The losses of the milk powder were determined by technological materials balance [4].

Each step of the preparation was controlled by mass determination and the discrepancy of the material input and output was also considered. According to its definition, the material balance is a calculation to inventory material inputs versus outputs in a process system.

(Note: The materials balance (also called mass balance) is an application of the most obvious conservation law: the conservation of mass. The reference material preparation is considered a technology which consists of a series of physical and/or chemical steps, and the control calculation of the inventory is called "technological materials balance".)

The deep understanding of the technological process, identification of all uncertainty sources and well established metrological traceability chain allow all the assigned property values to be considered as certified as presented in Table 6.

The property values were verified by high precision control measurement by gamma-ray spectrometry. Both radio-caesium isotopes were within the specified uncertainty range at 95% probability level.

TABLE 6. CERTIFIED VALUES FOR MASSIC ACTIVITIES
(based on dry mass)

Radionuclide	**Certified value** [Bq kg^{-1}]	**Uncertainty*** [Bq kg^{-1}]	**Half-life** [1]
Sr-89	2405	77	50.57 (3) days
Sr-90	209	5	28.80 (7) years
Cs-134	357	7	2.0644 (14) years
Cs-137	224	5	30.05 (8) years

*The uncertainty is expressed as a combined standard uncertainty with a coverage factor $k = 1$ estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [5].

TABLE 7. RESULTS OF THE CONFIRMATION MEASUREMENTS
(based on dry mass)

Radionuclide	**Measured value** [Bq kg^{-1}]	**Uncertainty*** [Bq kg^{-1}]
Cs-134	323.2	16.8
Cs-137	218.8	5.3

*The uncertainty is expressed as a combined standard uncertainty with a coverage factor $k = 1$ estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [5].

2.4. MOISTURE CONTENT DETERMINATION

The reference value for the calculations was 3.8% at 90°C determined from several test portions by overnight drying in laboratory drying oven without air circulation.

Proposed dry content determination for general use: the dry content of the material should be determined in laboratory drying oven without air circulation using the conditions are listed below:

- Mass of the test portion min. 2 grams (recommended value is between 2-5 grams),
- Temperature 90^{o}C,
- Drying period: overnight.

2.5. METROLOGICAL TRACEABILITY

All dilution steps and the technological material balance of the entire preparation process were tracked by weight measurement. According to this three metrological traceability chains are considered. For massic activity, the information on metrological traceability was taken from the certificates of the radioactive solutions used for the preparation. For all weighing processes the traceability was established by using calibrated balances, and balance performance checked with certified control weights. These checks were performed for all respective mass ranges. The certified values are reported on a dry mass basis, whereby the temperatures applied during drying were controlled by calibrated thermometer. The mentioned certificates are presented in Table 8.

TABLE 8. CERTIFICATES FOR THE TRACEABILITY

Item	Serial number of the certificate	Certificate issued by
Sr-89 solution	SR89ELSB45 79241/1	LEA
Sr-90 solution	NIST SRM 4234 A	NIST
Cs-134 solution	Cs134ELSR50	CERCA
Cs-137 solution	CDZ64/S4/14/70	Amersham
Control weight (analytical series)	G7-291 D-K-19408-01-00	KERN and Sohn GmbH
Control weight, (1 kg)	Z13 07840 ZX13A	ZWIEBEL
Thermometer*	552696	INNOCAL

For the preparation of the spike solution the Mettler XP205 No. 11106024 analytical balance was used. The weight determination of bulk material the Ohaus Adventurer ARC-120 SNR: 1120173131 tare balances was applied. Both balances are maintained regularly by the authorized service company.

2.6. INTENDED USE

This certified reference material is intended to be used for verification of performance indicators (precision, repeatability, reproducibility) of the simultaneous measurement of Sr-89 and Sr-90 in presence of radio-caesium isotopes. These radio-caesium isotopes are simulating the case of the real nuclear emergency situation. The relatively low uncertainty of the property values minimize the contribution of the CRM to the combined standard uncertainty derived from the measurement.

The quick decaying of the Sr-89 isotope gives an opportunity to study the behavior of the radioanalytical method at different Sr-89/Sr-90 ratios.

The CRM is not intended for any calibration purpose.

2.7. INSTRUCTIONS FOR USE

The IAEA-473 certified reference material is supplied in 100 g units. The material homogeneity is guaranteed if a minimum test portion of 10 g is used.

The particle size distribution of the material is in a narrow range of 41 – 194 microns (at 10% and 90% cumulative percentage respectively), which minimizes any chance for segregation. However, to overcome segregation effects due to storage or transportation, the material should be mixed before opening the bottle. All necessary precautions should be taken when opening the bottle to prevent any spread of the powder in the laboratory.

Since the moisture content can vary with ambient humidity and temperature, it is recommended to check it prior to analysis and to calculate all results on a dry mass basis.

The original unopened bottle should be stored securely at ambient temperature in a dark and dry place. It is recommended to avoid direct exposure to sunlight or to a source of heat.

The material is for laboratory purpose only, e. g., internal QC, method validation or verification.

Retrieving 3.5% fat content milk: mix 33.5 g of milk powder in 500 cm^3 warm water (60^oC) for 10 minutes or until the conglomerates dissolve completely.

2.8. MATERIAL SAFETY

The radioactive content of the material is below the exemption level, thus it does not require special handling and storage [6]. It is strongly recommended that it be used only by experienced persons in the laboratory.

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