European Commission

European Reference Materials

CERTIFICATION REPORT

The certification of the mass fractions of elements in skimmed milk powders: ERM®-BD150 and ERM®-BD151

Certified Reference Material ERM®-BD150
Certified Reference Material ERM®-BD151

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The certification of the mass fractions of elements in skimmed milk powders: ERM®-BD150 and ERM®-BD151

Certified Reference Material ERM®-BD150
Certified Reference Material ERM®-BD151

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Summary

This report describes the production of ERM BD150 and ERM BD151, skimmed milk powder materials certified for the mass fractions of elements. The material was produced following ISO Guide 34:2009 [1].

The starting material was 1000 L of fresh raw milk. The milk was skimmed and pasteurised, and divided in two batches of about 500 L. Spike solutions of Cd, Cu, Fe, Hg and Pb were added to each batch. The batches were again pasteurised, concentrated by evaporation, and spray dried to produce fine powders.

Between unit-homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006 [2]. Within-unit homogeneity was quantified to determine the minimum sample intake.

The material was characterised by an inter-comparison 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) [3] and include uncertainties related to possible inhomogeneity, instability and characterisation.

The materials are intended for quality control and assessment of method performance. As any reference material, they can be used for control charts or validation studies. The CRMs are available in glass bottles containing 20 g of dried powder. The minimum amount of sample to be used is 500 mg for Fe and 200 mg for all other elements.

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

The following values were assigned:

ERM-BD150	Mass Fraction	
	Certified value [1,2) [g/kg]	Uncertainty [2,3) [g/kg]
Ca	13.9	0.8
Cl	9.7	2.0
K	17.0	0.7
Mg	1.26	0.10
Na	4.18	0.19
P	11.0	0.6
	Certified value [1,2) [mg/kg]	Uncertainty [2,3) [mg/kg]
Cd	0.0114	0.0029
Cu	1.08	0.06
Fe	4.6	0.5
Hg	0.060	0.007
I	1.73	0.14
Mn	0.289	0.018
Pb	0.0193	0.004
Se	0.188	0.014
Zn	44.8	2.0

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of Units (SI).

2) Certified mass fractions are corrected for the water content of the material (and expressed as dry mass), determined as described in the section "Instructions for use".

3) The uncertainty is expanded with a coverage factor k = 2 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.

ERM-BD151	Mass Fraction	
	Certified value [1,2)] [g/kg]	Uncertainty [2,3)] [g/kg]
Ca	13.9	0.7
Cl	9.8	1.2
K	17.0	0.8
Mg	1.26	0.07
Na	4.19	0.23
P	11.0	0.6
	Certified value [1,2)] [mg/kg]	Uncertainty [2,3)] [mg/kg]
Cd	0.106	0.013
Cu	5.00	0.23
Fe	53	4
Hg	0.52	0.04
I	1.78	0.17
Mn	0.29	0.03
Pb	0.207	0.014
Se	0.19	0.04
Zn	44.9	2.3

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of Units (SI).

2) Certified mass fractions are corrected for the water content of the material (and expressed as dry mass), determined as described in the section "Instructions for use".

3) The uncertainty is expanded with a coverage factor k = 2 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.

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Glossary

AAS	Atomic absorption spectrometry
AFS	Atomic fluorescence spectrometry
ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
c	Mass concentration $c = m / V$ (mass / volume)
CC	Collision cell
CCT	Collision cell technology
CEN	European Committee for Standardization
CI	confidence interval
CIPM	CIPM Comité International des Poids et Mesures (International Committee of Weights and Measures)
CRM	Certified reference material
CV-A-AFS	Cold vapour atomic fluorescence spectrometry with gold amalgamation
CV-AAS	Cold vapour atomic absorption spectrometry
CV-AFS	Cold vapour atomic fluorescence spectrometry
DMA	Direct mercury analyser
DRC	Dynamic reaction cell
EC	European Commission
ERM®	Trademark of European Reference Materials
EU	European Union
ET-AAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
GUM	Guide to the Expression of Uncertainty in Measurements [3]
HG-AFS	Hydride generation-atomic fluorescence spectrometry
HPLC	High performance liquid chromatography
IC	Ion chromatography
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-QMS	ICP-Quadrupole mass spectrometry
ICP-SFMS	ICP-Sector field mass spectrometry
ID	Isotope dilution
IDMS	isotope dilution mass spectrometry

(I)NAA	(Instrumental) neutron activation analysis
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JCGM	Joint Committee for Guides on Metrology
JRC	Joint Research Centre of the European Commission
k	Coverage factor
k_0-NAA	k_0-Neutron activation analysis
KFT	Karl Fischer titration
LC-MS	Liquid chromatography-mass spectrometry
LGC	LGC Ltd. (formerly: Laboratory of the Government Chemist)
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass spectrometry
$MS_{between}$	Mean of squares between-unit from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
n.d.	Not detectable
NIST	National Institute of Standards and Technology (USA)
OES	Optical emission spectrometry
PSA	Particle size analysis
QA	Quality assurance
QC	Quality control
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
RNAA	Radiochemical neutron activation analysis
RSD	Relative standard deviation
RSE	Relative standard error (=RSD/$\sqrt{n}$)
r^2	Coefficient of determination of the linear regression
s	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
SDS	Safety data sheet

se	Standard error
SF-MS	Sector field mass spectrometry
SI	International System of Units
s_{meas}	Standard deviation of measurement data; an additional index "rel" is added as appropriate
s_{ns}	Standard deviation of results of normal stock samples
SSAAS	Solid sampling atomic absorption spectrometry
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
T	Temperature
t	Time
t_i	Time point for each replicate
$t_{\alpha,\,df}$	Critical *t*-value for a *t*-test, with a level of confidence of 1-α and df degrees of freedom
t_{sl}	Proposed shelf life
t_{tt}	Chosen transport time
u	standard uncertainty
U	expanded uncertainty
u^{*}_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate
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_{cal}	Standard uncertainty of calibration
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_{lts}	Standard uncertainty of the long-term stability; an additional index "rel" is added as appropriate
u_{meas}	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate

u_t	Standard uncertainty of trueness
UV	Ultraviolet
V	Volume
VIM	Vocabulaire International de Métrologie – Concepts Fondamentaux et Généraux et Termes Associés (International Vocabulary of Metrology – Basic and General Concepts and Associated Terms) *[ISO/IEC Guide 99:2007]*
$\overline{x}$	Arithmetic mean
$\overline{x}_{ns}$	Arithmetic mean of all results of normal stock samples
$\overline{x}_{ref}$	Arithmetic mean of results of reference samples
$\overline{y}$	Arithmetic mean of replicate measurements
α	significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{s,meas}$	Degrees of freedom for the determination of the standard deviation s_{meas}
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

This report describes the production of two certified skimmed milk powder reference materials intended to replace BCR-150 and BCR-151 (skimmed milk powders). The project aimed to certify the mass fractions of trace elements with target contents at natural levels for the elements Ca, Cl, Co, I, K, Mg, Mn, Na, P, Se, and Zn and for Cd, Cu, Fe, Hg and Pb, which were spiked at two levels. The amount of spike added was intended to produce one material (ERM-BD150) with mass fractions of about one tenth of the regulatory limit for food contaminants in milk and other foodstuffs (EC466/2001 and amendment 1881/2006; Pb < 0.020 mg/kg in milk), and one material with mass fractions around the regulatory limit. An unspiked material was not produced, as CRMs for elements at natural levels in skimmed milk powder are available from other producers. Compared to previous BCR CRMs for skimmed milk powder, a larger range of trace elements was studied; Ca, Cd, Cl, Co, Cu, Fe, Hg, I, K, Mg, Mn, Na, P, Pb, Se and Zn. The expanded list of elements for which values are provided aims to provide a material useful for a wider variety of laboratory studies.

The reference materials described in this report are intended to provide quality control for trace element measurements, like the materials they replace. In particular, the materials may be of use for measurements made in support of upholding EC Directives such as those concerning food safety.

1.2 Choice of the material

Skimmed milk powder provides a matrix representative of many dairy products, with the only manipulation being that it is heated and dehydrated. The milk spray-drying process creates a fine powder, expected to be homogenous at the sample intake range of common element analysis techniques. The powder is also expected to be stable at room temperature over the envisaged 10-year sales period of the reference materials.

Spiking was necessary to ensure that the levels of elements regarded as contaminants were high enough to be measured reliably, and thereby provide reference values with sufficiently low uncertainty for the control of quantitative measurement methods. The milk used as starting material for the reference material production contained these elements at mass fractions close to the LOD of common analytical techniques. To ensure that the candidate CRMs were as similar as possible to milk powder naturally contaminated with the spiked elements, the spiking took place before concentration and drying of the milk, which was the earliest opportunity within the production process.

1.3 Design of the project

The stability and homogeneity of the material was evaluated through studies involving measurement of all certified elements. The certified mass fractions were established by an inter-comparison of different laboratories with different measurement methods and techniques.

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)

NIZO Food Research B.V., Ede, NL

2.3 Homogeneity 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)

The Food and Environment Research Agency, York, UK
(Measurements performed under ISO/IEC 17025 accreditation; UKAS 1642)

2.4 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)

ALS Scandinavia AB, Luleå (SE)
(Measurements performed under ISO/IEC 17025 accreditation; SWEDAC 1087)

The Food and Environment Research Agency, York, UK
(Measurements performed under ISO/IEC 17025 accreditation; UKAS 1642)

2.5 Characterisation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
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(Measurements performed under ISO/IEC 17025 accreditation, BELAC No. 268-TEST)

Australian Nuclear Science and Technology Organisation, Kirawee (AU)

ALS Scandinavia AB, Luleå (SE)
(Measurements performed under ISO/IEC 17025 accreditation; SWEDAC 1087)

Ceinal, S.A. (Silliker), Área Análisis Físico-Químicos, Barcelona (ES)
(Measurements performed under ISO/IEC 17025 accreditation; ENAC 257/LE413)

The Food and Environment Research Agency, York (UK)
(Measurements performed under ISO/IEC 17025 accreditation; UKAS 1642)

Helmholtz Zentrum München - Deutsches Forschungszentrum für Gesundheit und Umwelt GmbH, München (DE)

Institut "Jozef Stefan", Ljubljana, (SI)
(Measurements performed under ISO/IEC 17025 accreditation; Slovenska Akreditacija LP-090)

Laboratoire national de métrologie et d'Essais, Paris (FR)
(Measurements performed under ISO/IEC 17025 accreditation; COFRAC 22)

LGC Ltd., Teddington (UK)
(Measurements performed under ISO/IEC 17025 accreditation; UKAS 0003)

muva kempten, Kempten (DE)
(Measurements performed under ISO/IEC 17025 accreditation; DAkkS D-PL-14429-01)

SCK-CEN, Mol (BE)
(Measurements performed under ISO/IEC 17025 accreditation; BELAC 015-TEST)

Umweltbundesamt GmbH, Wien (AT)
(Measurements performed under ISO/IEC 17025 accreditation; Wirtschaftsministerium 92714/499-IV/9/01)

3 Material processing and process control

3.1 Origin of the starting material

The starting material was 1000 L of raw milk supplied by Friesland Foods, NL.

3.2 Processing

The processing of the raw milk to a dry powder was performed by NIZO, Ede, NL, and the spike solutions were prepared at IRMM. Spike solutions were prepared from standards with certified mass fractions of about 10 g/kg for Cu and Fe, and 1 g/kg for Cd, Hg, and Pb all in 5 % nitric acid (Certipur grade, Merck, DE). The spike solutions were mixed by weighing aliquots into 100 mL polypropylene bottles, which were weighed and closed for transport to NIZO. The raw milk was skimmed, pasteurised at 72.5 ºC for 15 s, and checked for microbial quality and composition. Results showed that significant microbial contamination was absent and that the fat content was below 0.1 % (m/m). The material was therefore suitable for further processing. The milk was separated into 2 stainless steel vats with stirrers, each containing about 500 L, and was kept at 4 ºC for 48 h. Spike solutions were added to each of the vats, which were continually stirred during and after spiking. The two batches of milk were pasteurised again at 72.5 ºC for 15 s, and passed through an evaporator for concentration to about 50 % (m/m) dry matter content. The batches were then passed into a spray-dryer (NIRO 25), and the powder was collected in polypropylene bags containing about 20 kg. The powder was stored at 4 ºC, and the particle size distribution and moisture content were measured. Results showed that 90 % of particles were < 98 µm and that the size was evenly distributed, and that the moisture content was below 4 %. The material was therefore considered suitable for further processing at IRMM and was transported to IRMM by refrigerated courier.

The emptied bottles of spike solution were re-weighed to calculate the amounts of added spikes.

After arrival at IRMM the bags were emptied in acid-washed plastic drums of 200 l that were then placed in a Dynamix CM-200 mixer (WAB, Basel, CH) for mixing during 60 minutes. A automatic filling machine, fitted with a Teflon funnel and screw, (All Fill, Sandy, United Kingdom) was used to transfer the milk powder into 60 mL amber glass bottles. The filling machine was placed in a clean area under a flow of HEPA-filtered air. Each bottle was filled with slightly more than 20.0 g. Once the bottles were filled, PE-inserts were pressed into the bottle necks. All bottles and inserts had been acid washed with 2 % HNO_3 (m/m) and rinsed with Milli-Q water before drying in a drying cabinet. Screw-caps were fitted and shrink-film was wrapped around bottle necks using automated systems (Bausch & Ströbel and BBK, respectively, Germany). White shrink-film was fitted to bottles of BD150, and red film to BD151. Bottles were then labelled according to the order of filling. In total, 1970 bottles of BD150 were produced, and 2022 bottles of BD151.

3.3 Process control

After processing, 5 bottles were selected at random and 2 replicate micrographs, water measurements and particle size counts were made on each bottle.

Micrographs showed irregularly shaped particles with no fibres or agglomerations present in any of the images, and no discernable differences in particles of different sizes were detected.

The water content was measured using Karl Fischer titration. The mean result (n = 5) was 2.92 % water (m/m) with s = 0.03 %, for BD150 and 3.99 % water (m/m) with s = 0.19 % for BD151. The results indicate that the materials were homogeneously dried.

The particle size analysis was made using the Low Angle Laser Light Scattering technique with a Sympatec Helos instrument (Clausthal Zellerfeld, Germany). Five different samples of both candidate CRMs were measured in duplicate. Results showed that the 90 % of particles of BD150 were below a mean of 82.3 µm, with measurement RSD of 1.6 %, and for BD151; 89.6 µm with a RSD of 1.4 %. This shows that the target particle size for both materials (< 250 µm) was achieved and that the materials are homogeneous and uniform over the batches with respect to particle size distribution.

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. It is not relevant if the 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.

Although the within-unit homogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, it does determine the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit homogeneity is therefore necessary to determine the minimum sample intake.

'Unit' is defined as an individual glass bottle of ERM-BD150 or BD151.

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 corresponds to approximately the cubic root of the total number of the produced units. The 13 units were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the batch was divided into 13 groups (with a similar number of units) and one unit was selected randomly from each group. Six independent samples of about 200 mg were taken from each selected unit, and analysed by ICP-MS after wet-digestion. 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 water content, which was determined once in each unit (Section 6.5). The results are shown as graphs in Annex 1.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence were visible at the 99 % confidence level for either material. Significant (99 % confidence level) trends in the analytical sequence were visible for most elements measured, in both materials, pointing to a signal drift of the ICP-MS. The correction of biases, even if they are statistically not significant, was found to combine the smallest uncertainty with the highest probability to cover the true value [4]. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit inhomogeneities. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

$$corrected\ result = measured\ \ result - b \cdot i \qquad \textbf{Equation 1}$$

b = slope of the linear regression

i = position of the result in the analytical sequence

The trend-corrected datasets were tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. Some outlying individual results and outlying unit means were detected. Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Quantification of between-unit homogeneity was accomplished by analysis of variance (ANOVA), which can separate the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole unit.

Evaluation by ANOVA requires unit means which follow at least a unimodal distribution and results for each unit that follow unimodal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Too few data are available for the unit means to make a clear statement of the distribution. Therefore, it was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Table 1.

Table 1: Results of the statistical evaluation of the homogeneity studies at the 99 % confidence level

mass fraction ERM-BD150	Trends (before correction)		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
Ca	yes	no	none	none	unimodal	unimodal
Cd	yes	no	none	none	unimodal	unimodal
Cl	yes	no	none	none	unimodal	unimodal
Co	no	no	1	none	unimodal	unimodal
Cu	yes	no	none	none	unimodal	unimodal
Fe*	no	no	1	none	unimodal	unimodal
Hg	yes	no	none	none	unimodal	unimodal
I	no	no	none	none	unimodal	unimodal
K	yes	no	none	none	unimodal	unimodal
Mg	yes	no	none	none	unimodal	unimodal
Mn	yes	no	1	none	unimodal	unimodal
Na	yes	no	none	none	unimodal	unimodal
P	no	no	none	none	unimodal	unimodal
Pb	no	no	1	none	unimodal	unimodal
Se	no	no	1	none	unimodal	unimodal
Zn	yes	no	none	none	unimodal	unimodal

*Results of the dataset taken from the long-term stability study

mass fraction ERM-BD151	Trends (before correction)		Outliers		Distribution	
	Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
Ca	yes	no	none	none	unimodal	unimodal
Cd	no	no	none	none	unimodal	unimodal
Cl	yes	no	none	none	unimodal	unimodal
Co	no	no	1	none	unimodal	unimodal
Cu	yes	no	none	none	unimodal	unimodal
Fe	yes	no	1	none	unimodal	unimodal
Hg	yes	no	none	none	unimodal	unimodal
I	yes	no	none	none	unimodal	unimodal
K	yes	no	none	none	unimodal	unimodal
Mg	yes	no	none	none	unimodal	unimodal
Mn	yes	no	1	none	unimodal	unimodal
Na	yes	no	none	none	unimodal	unimodal
P	yes	no	none	none	unimodal	unimodal
Pb	yes	no	none	none	unimodal	unimodal
Se	yes	no	none	none	unimodal	unimodal
Zn	yes	no	none	none	unimodal	unimodal

One has to bear in mind that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [5]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}}$$ **Equation 2**

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}}$$ **Equation 3**

$$u^{*}_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{v_{MSwithin}}}}{\bar{y}}$$ **Equation 4**

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

$MS_{between}$ mean squares between-unit from an ANOVA

$\bar{y}$ mean of all results of the homogeneity study

n mean number of replicates per unit

$v_{MSwithin}$ degrees of freedom of MS_{within}

Table 2:: Results of the homogeneity studies

mass fraction ERM-BD150	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^{*}_{bb,rel}$ [%]	$u_{bb,rel}$ [%]
Ca	1.54	0.20	0.37	0.37
Cd	7.79	n.c.	1.89	1.89
Cl	2.51	n.c.	0.61	0.61
Co	56.5	n.c.	13.0	13.0
Cu	4.10	n.c.	0.99	0.99
Fe	7.20	n.c.	2.13	2.13
Hg	3.29	n.c.	0.80	0.80
I	1.42	n.c.	0.34	0.34
K	1.63	n.c.	0.39	0.39
Mg	1.51	n.c.	0.37	0.37
Mn	5.27	n.c.	1.26	1.26
Na	1.58	0.36	0.38	0.38
P	2.01	n.c.	0.49	0.49
Pb	10.9	n.c.	2.68	2.68
Se	4.44	n.c.	1.07	1.07
Zn	3.08	n.c.	0.75	0.75

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

mass fraction ERM-BD151	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{bb,rel}$ [%]
Ca	4.12	n.c.	1.00	1.00
Cd	2.54	n.c.	0.61	0.61
Cl	2.53	n.c.	0.61	0.61
Co	45.7	n.c.	10.9	10.9
Cu	2.37	n.c.	0.57	0.57
Fe	12.1	n.c.	2.89	2.89
Hg	1.97	n.c.	0.48	0.48
I	1.37	n.c.	0.33	0.33
K	1.85	n.c.	0.45	0.45
Mg	1.97	n.c.	0.48	0.48
Mn	7.75	n.c.	1.86	1.86
Na	2.09	n.c.	0.51	0.51
P	2.03	n.c.	0.49	0.49
Pb	2.47	n.c.	0.60	0.60
Se	4.84	n.c.	1.18	1.18
Zn	2.46	n.c.	0.59	0.59

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

For Fe, a single outlying replicate about double the mean was found in the homogeneity study for ERM-BD150. This gave rise to an outlying unit mean. No technical reason could be found to explain the outlier, and it was unclear as to whether this represented contamination of the sample. Therefore, the homogeneity was assessed using the results of the long-term stability study, in which 6 replicate measurements were made on each of 8 units. For the homogeneity assessment, the potential influence of the different storage conditions (discussed in the following section) was ignored. The results are presented together with those for the other elements in Table 1

The homogeneity study showed no outlying unit means or trends in the filling sequence. Therefore the between-unit standard deviation can be used as estimate of u_{bb}. As u^*_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^*_{bb} is adopted as uncertainty contribution to account for potential inhomogeneity.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, 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 of the whole unit and thus required for an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within the stated uncertainty.

Homogeneity experiments were performed using a 200 mg sample intake. This sample intake gives acceptable repeatability, demonstrating that the within- unit inhomogeneity no

longer contributes to analytical variation at this sample intake. For ERM-BD150 and BD151, the minimum sample intake specified on the certificates is the mass used for the homogeneity studies; 0.5 g for Fe and 0.2 g for all other elements. To verify the suitability of these minimum sample intakes, the minimum sample intake of the material was also determined using solid sampling Zeeman-AAS [6] for selected elements, in single bottles of ERM-BD150 and BD151. Sample intakes of about 0.01 – 0.55 mg were used. At least 30 replicate measurements were carried out per element.

The data was evaluated according to the following equation [5]:

$$m_{\min} = \left(\frac{k'_2 \cdot s_m}{u_{target}} \right)^2 \cdot \overline{m} \qquad \textbf{Equation 5}$$

with m_{min} minimum sample mass, k'_2 factor for the two-sided 95 % tolerance limits for a normal distribution, s_m relative standard deviation of the inhomogeneity experiment, u_{target} maximum relative uncertainty acceptable for sub sampling and $\overline{m}$ mean mass used during the measurements.

The resulting minimum sample masses are summarised in Table 3.

Table 3: Minimum sample masses for a target uncertainty of 2 % as determined by solid sampling AAS

Material code	measurand	m_{min} [mg]	s_m	$\overline{m}$ [mg]
ERM-BD150	Cd	164	18 %	0.30
	Cu	31	9 %	0.23
	Pb	n/a		
	Zn	38	11 %	0.18
ERM-BD151	Cd	47	15 %	0.13
	Cu	n/a		
	Pb	47	13 %	0.19
	Zn	33	11 %	0.16

A target uncertainty of 2 % (k = 1) was applied, as this is below the u_{CRM} of all elements certified. In BD150, the Pb content was below the SSAAS working range and in BD151, the Cu content was above. For each element measured the estimated m_{min} was lower than the target of the homogeneity study of 200 mg. For The overall minimum sample intake for these materials, valid for all elements investigated, is set to 200 mg. For Fe, the homogeneity was assessed through results of the long-term stability study, for which a mean sample intake of 500 mg was used. Therefore, the minimum sample intake is set to 500 mg for Fe.

5 Stability

Time, temperature and UV radiation were regarded as the most relevant influences on stability of the materials. The influence of ultraviolet or visible radiation was minimised by the choice of brown glass bottles for containment, which eliminates most of the incoming light. In addition, materials are stored and dispatched in the dark, thus eliminating the possibility of degradation by light. Therefore, only the influences of time and temperature were 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

warm weather, 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 [7]. 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.

5.1 Short-term stability study

For the short-term stability study, samples of both ERM-BD150 and BD151 were stored at 18 °C and 60 °C for 0, 1, 2 and 4 weeks (at each temperature). The reference temperature was set to -20 °C. Two units per storage time were selected using a random stratified sampling scheme. From each unit, three samples were measured by ICP-MS. 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 water content determined once in each unit.

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 for Pb (Table 4). 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 mass fraction versus time were calculated. The slopes of the regression line were tested for statistical significance (loss/increase due to shipping conditions). For all elements, the slopes of the regression lines were not significantly different from zero (on 99 % confidence level) at both 18 °C and 60 °C.

The results of the measurements are shown in Annex C. The results of the statistical evaluation of the short-term stability are summarised in

Table 4: Results of the short-term stability tests

mass fraction ERM-BD150	Number of individual outlying results		Significance of the trend on a 99% confidence level	
	18 ºC	60 ºC	18 ºC	60 ºC
Ca	none	none	no	no
Cd	none	none	no	no
Cl	none	none	no	no
Co	none	none	no	no
Cu	none	none	no	no
Fe	none	none	no	no
Hg	none	none	no	no
I	none	none	no	no
K	none	none	no	no
Mg	none	none	no	no
Mn	none	none	no	no
Na	none	none	no	no
P	none	none	no	no
Pb	none	1	no	no
Se	none	none	no	no
Zn	none	none	no	no

mass fraction ERM-BD151	Number of individual outlying results		Significance of the trend on a 99% confidence level	
	18 ºC	60 ºC	18 ºC	60 ºC
Ca	none	none	no	no
Cd	none	none	no	no
Cl	none	none	no	no
Co	none	none	no	no
Cu	none	none	no	no
Fe	none	none	no	no
Hg	none	none	no	no
I	none	none	no	no
K	none	none	no	no
Mg	none	none	no	no
Mn	none	none	no	no
Na	none	none	no	no
P	none	none	no	no
Pb	none	1	no	no
Se	none	none	no	no
Zn	none	none	no	no

Two statistical outliers were detected for Pb, which were retained for the estimation of u_{STS}. None of the trends was statistically significant on a 99 % confidence level for any of the temperatures.

The material can therefore be dispatched without further precautions under ambient conditions.

5.2 Long-term stability study

For the long-term stability study, samples of both ERM-BD150 and BD151 were stored at 18 °C for 0, 4, 8 and 12 months. The reference temperature was set to -20 °C. Two samples per storage time were selected using a random stratified sampling scheme. From each unit, six samples were measured by ICP-MS. 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 water content determined once in each unit.

The obtained data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test. Some outlying individual results were found (Table 5). As no technical reason for the outliers could be found all data were retained for statistical analysis.

Furthermore, the data were plotted against storage time and linear regression lines of mass fraction versus time were calculated. The slope of the regression lines was tested for statistical significance (loss/increase due to storage conditions). For all elements except Se in ERM-BD151, the slopes of the regression lines were not significantly different from zero (on 99 % confidence level).

The results of the long term stability measurements are shown in Annex C. The results of the statistical evaluation of the long-term stability study are summarised in Table 5.

Table 5: Results of the long-term stability tests

mass fraction ERM-BD150	Number of individual outlying results	Significance of the trend on a 99% confidence level
	18 ºC	18 ºC
Ca	none	no
Cd	none	no
Cl	none	no
Co	none	no
Cu	none	no
Fe	1	no
Hg	none	no
I	none	no
K	none	no
Mg	none	no
Mn	none	no
Na	none	no
P	none	no
Pb	1	no
Se	none	no
Zn	none	no

mass fraction ERM-BD151	Number of individual outlying results	Significance of the trend on a 99% confidence level
	18 ºC	18 ºC
Ca	1	no
Cd	none	no
Cl	none	no
Co	none	no
Cu	none	no
Fe	none	no
Hg	none	no
I	none	no
K	none	no
Mg	none	no
Mn	none	no
Na	none	no
P	none	no
Pb	none	no
Se	none	yes
Zn	1	no

Technically unexplained outliers were observed in 4 of the studies and these were retained for the estimation of u_{LTS}. For Se in ERM-BD151, a negative trend was observed at 18 °C. There is no technical reason why Se should show less stability compared to the other elements measured in this matrix, and no trend was observed for ERM-BD150 which possesses an identical matrix. The observed trend was therefore regarded to be a statistical artefact. However, without additional evidence for the stability of Se in ERM-BD151, the mass fraction is given with combined uncertainty with u_{LTS} including potential degradation of the material. As additional information becomes available as part of the post-certification monitoring programme for this material, it may prove possible to revise the assigned uncertainty. For all other elements in both materials, none of the trends were statistically significant on a 99 % confidence level. The material can therefore be stored at 18 °C.

5.3 Estimation of uncertainties related to stability

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 ± x % per time".

Uncertainties of stability during dispatch and storage were estimated as described in [8] for each element. For this approach, the uncertainty of the linear regression line with a slope of

zero is calculated. The uncertainty contributions u_{sts} and u_{lts} are calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{tt}$$ Equation 6

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl}$$ **Equation 7**

RSD relative standard deviation of all results of the stability study

x_i result at time point *i*

$\bar{x}$ mean results for all time points

t_{tt} chosen transport time (1 week at 60 ºC)

t_{sl} chosen shelf life (24 months at 18 ºC)

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies. The 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 24 months storage at 18 °C.

The results of these evaluations are summarised in

Table 6: Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a temperature of 60 °C and 1 week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and 2 years

mass fraction ERM-BD150	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
Ca	0.28	2.61
Cd	0.32	11.9
Cl	1.24	9.67
Co	2.49	23.8
Cu	0.42	1.77
Fe	0.49	4.12
Hg	0.52	1.82
I	0.45	2.51
K	0.36	1.61
Mg	0.28	3.69
Mn	0.71	1.86
Na	0.26	2.00
P	0.51	2.05
Pb	0.52	6.17
Se	0.41	2.62
Zn	0.40	1.54

mass fraction ERM-BD151	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
Ca	0.35	1.82
Cd	0.40	5.06
Cl	1.44	5.48
Co	1.17	18.1
Cu	0.22	1.73
Fe	0.37	1.74
Hg	0.59	2.21
I	0.76	2.86
K	0.41	2.04
Mg	0.30	2.25
Mn	0.45	3.89
Na	0.32	2.42
P	0.62	1.98
Pb	0.52	2.55
Se	0.53	9.43
Zn	0.41	2.18

No significant degradation during dispatch even at 60 °C was observed. Therefore, the material can be transported at ambient conditions without special precautions.

After the release of the material, it 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 inter-comparison of expert laboratories, i.e. the mass fractions of elements in the materials were determined in different laboratories that applied different measurement procedures to demonstrate the absence of a measurement bias. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Selection of participants

Twelve laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a

quality system and to deliver documented evidence of its laboratory proficiency in the field of element measurements in relevant matrices by submitting results for inter-comparison exercises or method validation reports. 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).

Some participants were able to measure one or more elements by two or more independent techniques. For the study, such measurements were listed under separate lab codes as independent measurement results.

6.2 Study setup

Each laboratory received 2 units of ERM-BD150 and 2 units of ERM-BD151, and was requested to provide 6 independent results for each material, 3 per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparation and measurements had to be spread over at least two days to ensure intermediate precision conditions, with the exception of measurements by NAA. An independent calibration was performed for each result. The water content had to be determined once in each unit and results are reported on dry mass basis.

Each participant received a sample of SRM-1549 Skimmed milk powder (NIST, USA) as a blinded quality control (QC) sample. The results for this sample were used to support the evaluation of the characterisation results.

Laboratories were also requested to give estimations of the expanded uncertainties 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

A variety of digestion methods (acid or alkaline digestion with or without microwave assistance) with different quantification steps (AAS, ICP-OES and ICP-MS, amongst others) as well as methods without sample preparation (NAA, pyrolysis AAS) were used to characterise the material. The combination of results from methods based on different principles mitigates undetected method bias.

All methods used during the characterisation study 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. The lab-method code consists of a number assigned to each laboratory (e.g. L01) and abbreviation of the measurement method used, (e.g. ICP-MS).

6.4 Evaluation of results

The characterisation campaign resulted in between 6 and 15 laboratory means per element. All individual results of the participants, grouped per element are displayed in tabular and graphical form in Annex E.

6.4.1 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 two days, and the analytical sequence and water content determination.
- absence of values given as below limit of detection or below limit of quantification
- method performance demonstrated by agreement of the measurement results with the assigned value of the QC sample according to ERM Application Note 1 [10] (only for the elements Ca, Cl, Cu, Fe, I, K, Mg, Mn, Na, P, Pb, Se and Zn, for which mass fractions were certified in the QC sample at similar levels to the samples. The certified mass fractions of Cd and Hg were too low to be relevant.)

Based on the above criteria, 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

mass fraction ERM-BD150	Lab- code	Description of problem	Action taken
Cl	5, 20	Measurements of QC sample did not agree with assigned values	not used for evaluation
Co	20	Measurements of QC sample did not agree with assigned values	not used for evaluation
Cu	5, 6, 7, 20	Measurements of QC sample did not agree with assigned values	not used for evaluation
Fe	3, 20	Measurements of QC sample did not agree with assigned values	not used for evaluation
I	15	Measurements of QC sample did not agree with assigned values	not used for evaluation
Pb	6, 7, 20, 22	Measurements of QC sample did not agree with assigned values	not used for evaluation
Se	17	Measurements on 3 replicates were below the method LOQ	not used for evaluation

mass fraction ERM-BD151	Lab- code	Description of problem	Action taken
Cl	5, 20	Measurements of QC sample did not agree with assigned values	not used for evaluation
Co	20	Measurements of QC sample did not agree with assigned values	not used for evaluation
I	15	Measurements of QC sample did not agree with assigned values	not used for evaluation
Pb	1, 7, 20, 22	Measurements of QC sample did not agree with assigned values	not used for evaluation

Two laboratories, 10 and 17, only measured the QC sample on one occasion. However, both laboratories applied techniques based on NAA, under reproducibility conditions. The deviation from the protocol was therefore considered not to influence the results, and all were retained for the evaluation.

6.4.2 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. *p*: number of technically valid datasets

mass fraction ERM-BD150	*p*	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
Ca	11	0	1	yes	13902	498	823	368
Cd	8	0	0	yes	0.0114	0.0008	0.0014	0.0007
Cl	7	0	1	yes	9730	412	677	319
Co	7	0	0	yes	0.0049	0.0021	0.0036	0.0008
Cu	11	0	1	yes	1.077	0.056	0.086	0.064
Fe	7	0	1	yes	4.60	0.15	n.c.[1]	0.52
Hg	9	0	0	yes	0.0603	0.0094	0.0160	0.0041
I	8	0	1	yes	1.730	0.140	0.240	0.046
K	11	0	1	yes	17002	638	872	960
Mg	11	0	1	no	1262	46	72	47
Mn	12	0	1	yes	0.289	0.021	0.034	0.019
Na	11	0	1	yes	4181	134	219	107
P	7	0	1	no	10965	423	714	232
Pb	6	0	0	yes	0.0193	0.0027	0.0042	0.0027
Se	13	0	0	yes	0.1885	0.0161	0.0274	0.0070
Zn	15	0	1	yes	44.76	2.38	3.87	2.05

[1)] n.c.: cannot be calculated as $s_{between} < s_{within}$

mass fraction ERM-BD151	*p*	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
Ca	11	0	0	yes	13888	595	1000	353
Cd	9	0	1	yes	0.1055	0.0094	0.0158	0.0057
Cl	7	0	0	yes	9773	418	709	208
Co	7	0	1	yes	0.0054	0.0016	0.0027	0.0010
Cu	15	0	0	yes	4.999	0.270	0.422	0.282
Fe	10	0	0	yes	52.73	2.42	3.82	2.42
Hg	11	0	1	yes	0.5170	0.0508	0.0851	0.0313
I	8	0	0	yes	1.776	0.186	0.319	0.068
K	11	0	1	yes	17009	583	852	765
Mg	11	0	1	yes	1264	47	78	33
Mn	12	0	0	yes	0.292	0.030	0.049	0.024
Na	11	0	0	yes	4195	140	231	104
P	7	0	0	yes	10952	462	789	196
Pb	7	0	1	yes	0.207	0.010	0.010	0.020
Se	14	0	0	yes	0.189	0.015	0.025	0.012
Zn	15	0	2	yes	44.87	2.12	3.39	1.99

For most elements in both materials, the laboratory means follow normal distributions and the data does not contain outlying means or variances. Datasets for these elements are therefore consistent and the mean of laboratory means is a good estimate of the true value. Standard deviations between laboratories are considerably larger than the standard deviation within laboratories, except for Fe in ERM-BD150. This shows that confidence intervals of replicate measurements are generally unsuitable as estimates of measurement uncertainty.

The statistical evaluation flags various laboratories as having outlying variance for some datasets. However, the variance merely reflects the fact that different methods have different intrinsic variability. As all measurement methods were found technically sound, all results were retained.

In addition to the statistical tests, the agreement of individual laboratories' results with the dataset means was tested according to ERM Application Note 1.[10] For Co, Hg, I, Mn, Pb and Zn in ERM-BD150 and Cd, Co, Hg, I and Mn in ERM-BD151, one or more results did not agree with the dataset within the combined U_{CRM} and reported measurement uncertainty, U_m. As approaches to uncertainty estimation differ between laboratories, it is possible that not all sources of uncertainty are included in the budgets. For some of the disagreeing results, only one other result provided using the same technique was available, and it was therefore not possible to make a judgement on the expected U_m per technique. Therefore, for these labs, U_m of 20 % were assigned as this was considered to represent an acceptable level of U_m for inclusion in the dataset.

For Mg and P in ERM-BD150, statistical tests flagged the datasets as not having normal distribution at the 95 % confidence level. However, no outlying results or any multi-modal distribution of results were apparent in either case.

The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means. Uncertainties are listed by element, before rounding, in Table 9.

Table 9: Uncertainty of characterisation

mass fraction ERM-BD150	*p*	Mean [mg/kg]	*s* [mg/kg]	u_{char} [mg/kg]
Ca	11	13902	498	150
Cd	8	0.0114	0.0008	0.0003
Cl	7	9730	412	156
Co	7	0.0049	0.0021	0.0008
Cu	11	1.077	0.056	0.017
Fe	7	4.60	0.15	0.06
Hg	9	0.0603	0.0094	0.0031
I	8	1.730	0.140	0.049
K	11	17002	638	192
Mg	11	1262	46	14
Mn	12	0.289	0.021	0.006
Na	11	4181	134	40
P	7	10965	423	160
Pb	6	0.0193	0.0027	0.0011
Se	13	0.189	0.016	0.005
Zn	15	44.76	2.38	0.62

mass fraction ERM-BD151	*p*	Mean [mg/kg]	*s* [mg/kg]	u_{char} [mg/kg]
Ca	11	13888	595	179
Cd	9	0.1055	0.0094	0.0031
Cl	7	9773	418	158
Co	7	0.0054	0.0016	0.0006
Cu	15	4.999	0.270	0.070
Fe	10	52.73	2.42	0.76
Hg	11	0.5170	0.0508	0.0153
I	8	1.776	0.186	0.066
K	11	17009	583	176
Mg	11	1264	47	14
Mn	12	0.292	0.030	0.009
Na	11	4195	140	42
P	7	10952	462	175
Pb	7	0.207	0.010	0.004
Se	14	0.189	0.015	0.004
Zn	15	44.87	2.12	0.55

6.5 Dry mass determination

For all measurements carried out during certification (homogeneity, stability and characterisation studies) the following protocol for dry mass determination was applied:
Oven drying at 102 ± 1 ºC until constant weight.

The water content determined by the laboratories was in the range of 2.9 – 7.0 g/100 g. The variance in reported contents most likely reflects different environmental conditions and procedures between the laboratories. As laboratories reported dry-mass corrected mass fractions for the characterisation datasets, any variance introduced by dry-mass correction will be reflected in the variance of the characterisation datasets and hence the u_{Char} of the mean value.

7 Value Assignment

Certified values were assigned for all elements investigated except Co. The combined expanded uncertainties on the values, calculated according to equation 8, were greater than 50 % (relative, k = 2) for both materials. As such, the values were not considered be sufficiently reliable.

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. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3] were established.

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 the certified value for each parameter, after rounding.
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). The uncertainty related to degradation during transport was found to be negligible. These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM,\ rel}$) with a coverage factor k as:

$$U_{CRM,rel} = k \quad \sqrt{u^2_{char,rel} + u^2_{bb,rel} + u^2_{lts,rel}} \ . \qquad \textbf{Equation 8}$$

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 4.1.
- 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, a coverage factor k of 2 was applied, to obtain the expanded uncertainties.
The certified values and their uncertainties are summarised in Table 10.

Table 10: Certified values and their uncertainties

mass fraction ERM-BD150	Certified value[1)] [g/kg]	$u_{char,\ rel}$ [%]	$u_{bb,\ rel}$ [%]	$u_{lts,\ rel}$ [%]	$U_{CRM,\ rel}$ [%]	U_{CRM} [g/kg] [2)]
Ca	13.9	1.08	0.37	2.61	5.7	0.8
Cl	9.7	1.60	0.61	9.67	19.6	2.0
K	17.0	1.13	0.39	1.61	4.0	0.7
Mg	1.26	1.10	0.37	3.69	7.7	0.10
Na	4.18	0.96	0.38	2.00	4.5	0.19
P	11.0	1.46	0.49	2.05	5.1	0.6
mass fraction ERM-BD150	Certified value[1)] [mg/kg]	$u_{char,\ rel}$ [%]	$u_{bb,\ rel}$ [%]	$u_{lts,\ rel}$ [%]	$U_{CRM,\ rel}$ [%]	U_{CRM} [mg/kg] [2)]
Cd	0.0114	2.61	1.89	11.9	24.6	0.0029
Cu	1.08	1.57	0.99	1.77	5.1	0.06
Fe	4.6	1.23	2.13	4.12	9.6	0.5
Hg	0.060	5.20	0.80	1.82	11.1	0.007
I	1.73	2.85	0.34	2.51	7.6	0.14
Mn	0.289	2.10	1.26	1.86	6.1	0.018
Pb	0.019	5.63	2.68	6.17	17.5	0.004
Se	0.188	2.37	1.07	2.62	7.4	0.014
Zn	44.8	1.38	0.75	1.54	4.4	2.0

[1)]: reported on dry mass basis (Section 6.5)
[2)] Expanded (k = 2) and rounded uncertainty

mass fraction ERM-BD151	Certified value[1)] [g/kg]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [g/kg] [2)]
Ca	13.9	1.29	1.00	1.82	4.9	0.7
Cl	9.8	1.62	0.61	5.48	11.5	1.2
K	17.0	1.03	0.45	2.04	4.7	0.8
Mg	1.26	1.12	0.48	2.25	5.1	0.07
Na	4.19	1.01	0.51	2.42	5.3	0.23
P	11.0	1.60	0.49	1.98	5.2	0.6
mass fraction ERM-BD151	Certified value[1)] [mg/kg]	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM, rel}$ [%]	U_{CRM} [mg/kg] [2)]
Cd	0.106	2.97	0.61	5.06	11.8	0.013
Cu	5.00	1.39	0.57	1.73	4.6	0.23
Fe	53	1.45	2.89	1.74	7.3	4
Hg	0.52	2.96	0.48	2.21	7.5	0.04
I	1.78	3.71	0.33	2.86	9.4	0.17
Mn	0.29	2.95	1.86	3.89	10.4	0.03
Pb	0.207	1.82	0.60	2.55	6.4	0.014
Se	0.19	2.18	1.18	9.43	19.5	0.04
Zn	44.9	1.22	0.59	2.18	5.1	2.3

[1)]: reported on dry mass basis (Section 6.5)
[2)] Expanded (k = 2) and rounded uncertainty.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

The measurands are clearly defined as total element mass fractions. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias. The measurands are therefore structurally defined and independent of the measurement method.

Quantity value

Only validated methods were used for the determination of the assigned values. 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 select specific (or specific groups of) analytes from the sample for the subsequent steps of the 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 [9] 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.

ERM-BD150 and BD151 were produced from raw milk spiked with 5 elements, and concentrated and spray-dried to a powder by a conventional industrial process. The analytical behaviour will be the same as for a routine sample of milk powder. Nevertheless, one has to bear in mind that the extractability of the 5 spiked elements from these CRMs can be different to the extractability from an unspiked sample tested by the user's laboratory due to the potential that these elements exist in different chemical forms. For samples other than milk powder, the commutability has to be assessed.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The materials shall be stored at 18 °C ± 5 °C in the dark. Care shall be taken to avoid change of the moisture content once the units are open. 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 of the bulk is 500 mg for the Fe mass fraction, and 200 mg for all other mass fractions.

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 at 102 ^{o}C ± 1 ^{o}C until constant mass (separate weighing should not differ by more than 5 mg) is attained. 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 these materials is to assess method performance, i.e. for checking accuracy of analytical results/calibration. As any reference material, they 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 [10].

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}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty ($u_{\Delta,}$) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_{meas} \leq U_{\Delta}$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

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.

10 Acknowledgments

The authors would like to acknowledge the support received from Anne-Marie Braber of NIZO Food Research B.V. (NL), and Jean Charoud-Got and Håkan Emteborg from IRMM related to the processing of this CRM and from Maria Contreras Lopez concerning the set-up of the required isochronous studies.

Furthermore, the authors would like to thank Philippe Corbisier, Marina Ricci and Andrea Held (IRMM) for the reviewing of the certification report, as well as the experts of the Certification Advisory Panel "Elements", Steve Balsley (IAEA, AT), Thomas Prohaska (BOKU, AT) and Peter Vermaecke (SCK-CEN, BE) for their constructive comments.

11 References

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Annexes

Annex A: Results of the homogeneity measurements

Annex B: Results of the short-term stability measurements

Annex C: Results of the long-term stability measurements

Annex D: Summary of methods used in the characterisation study

Annex E: Results of the characterisation measurements

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Annex A: Results of the homogeneity measurements

Graphs present mass fractions of bottle means relative to the grand mean, against bottle number, and individual measurement replicates, against sequence number. Vertical bars are a confidence interval of 95 % derived from s_{wb} of the homogeneity study.

Figure A101: Ca in ERM-BD150

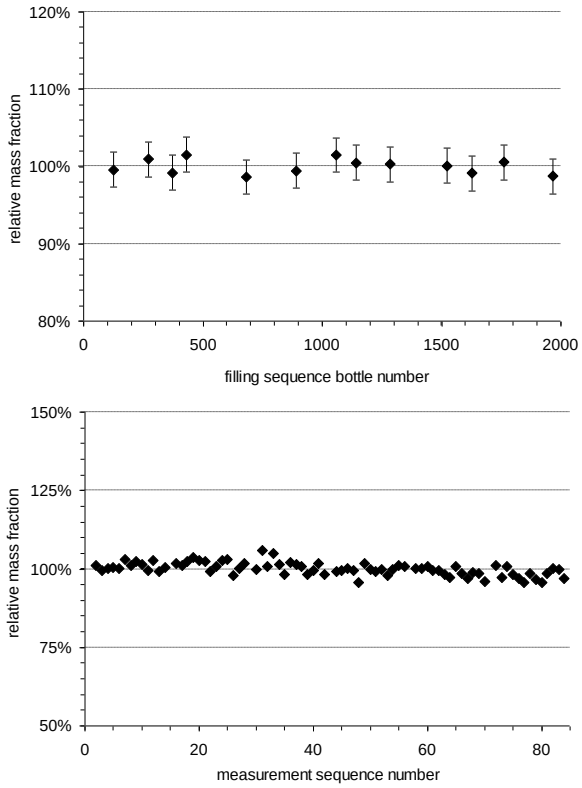


Figure A102: Cd in ERM-BD150

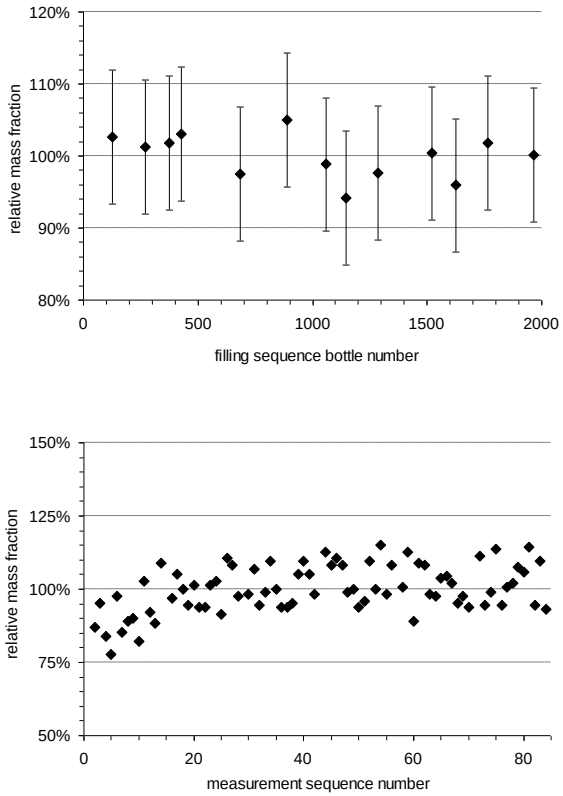


Figure A103: Cl in ERM-BD150

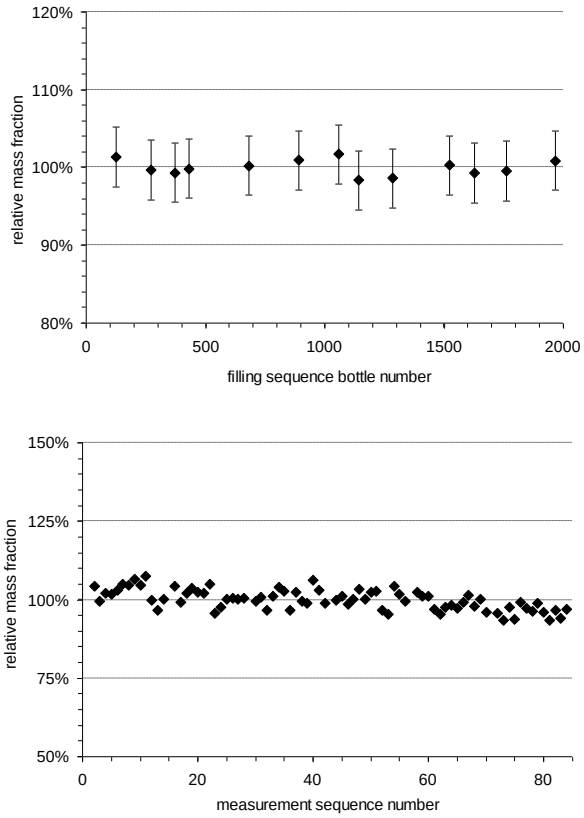


Figure A104: Co in ERM-BD150

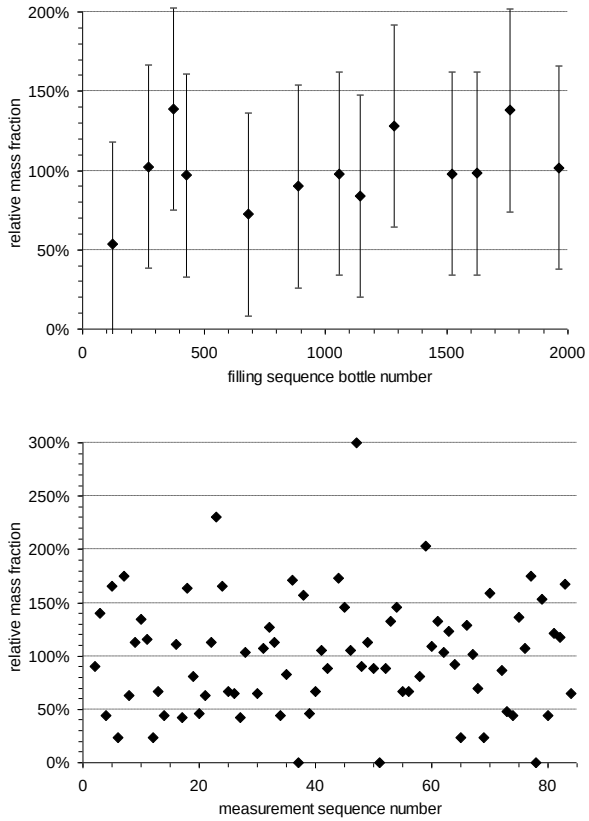


Figure A105: Cu in ERM-BD150

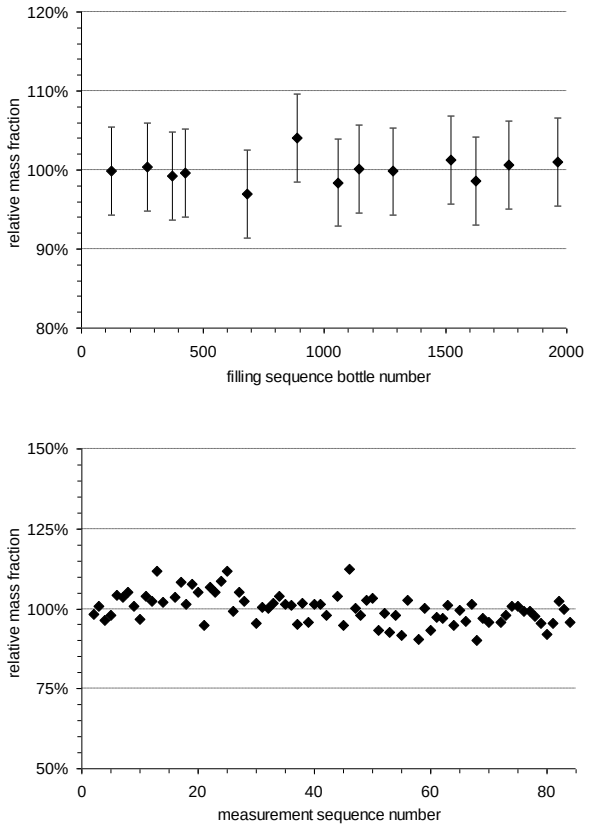


Figure A106: Fe in ERM-BD150

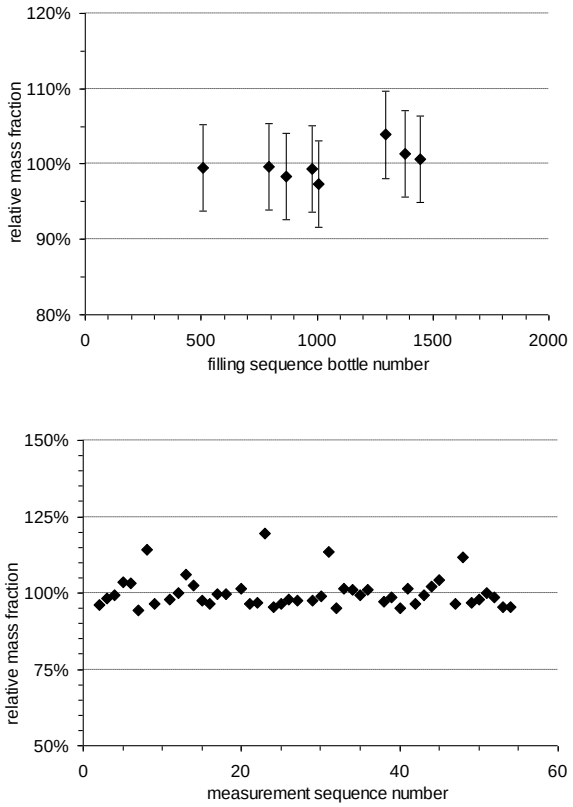


Figure A107: Hg in ERM-BD150

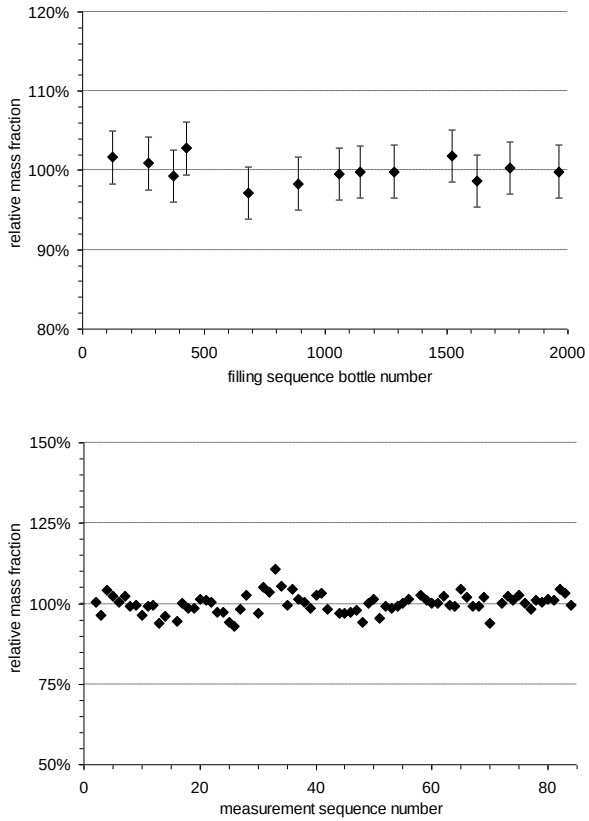


Figure A108: I in ERM-BD150

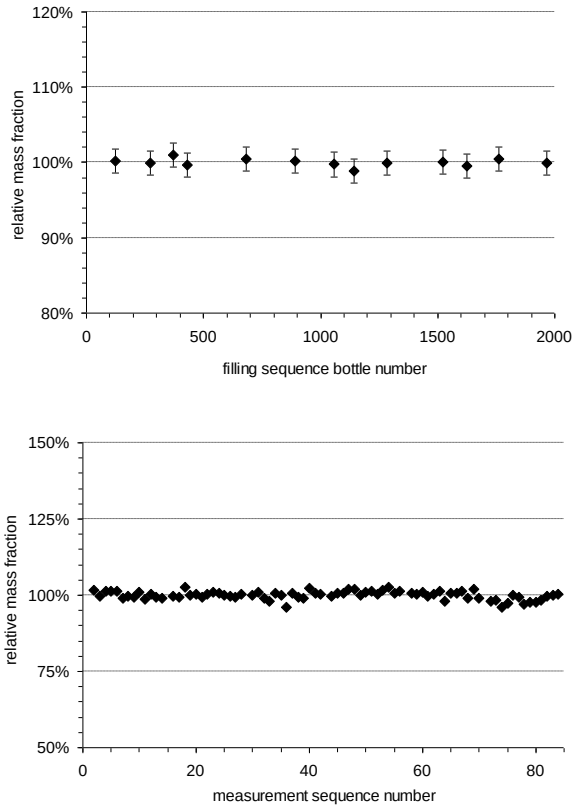


Figure A109: K in ERM-BD150

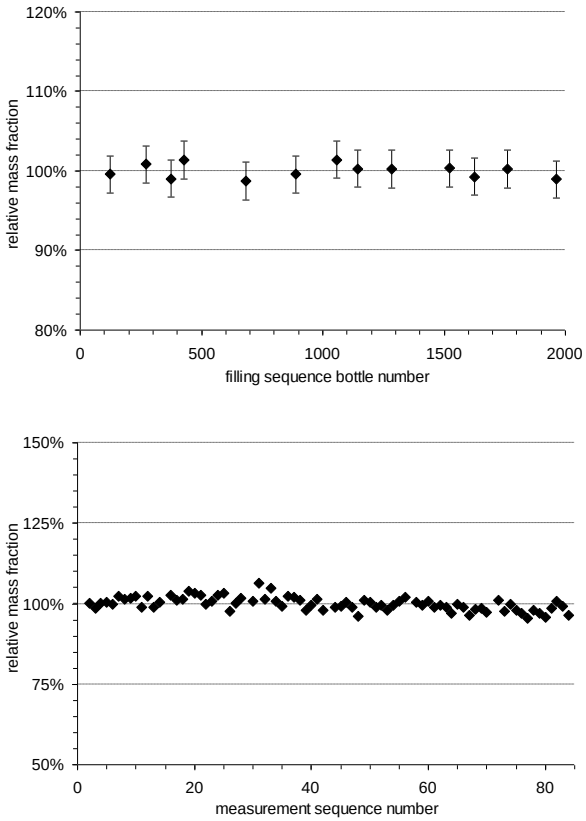


Figure A110: Mg in ERM-BD150

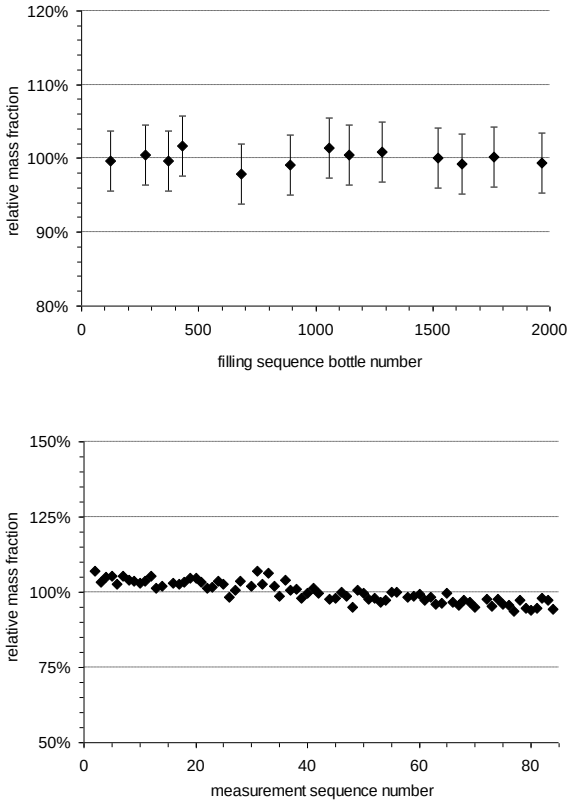


Figure A111: Mn in ERM-BD150

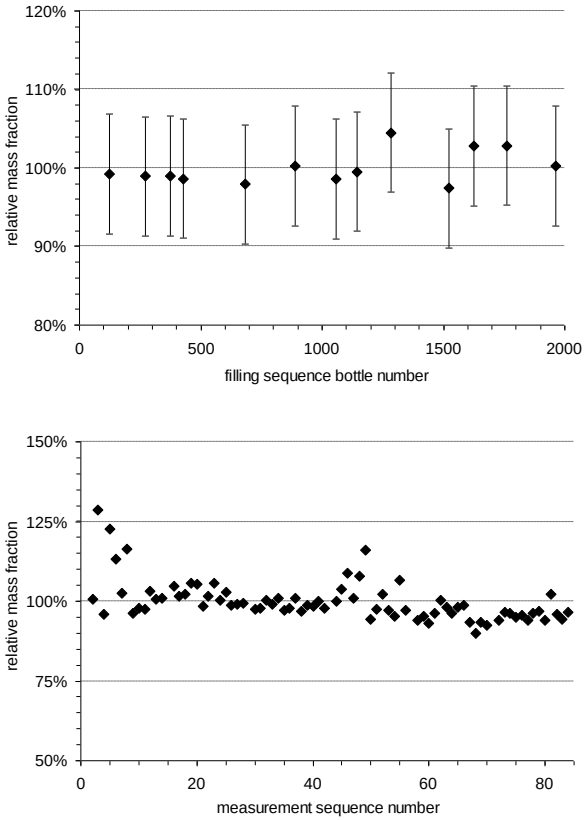


Figure A112: Na in ERM-BD150

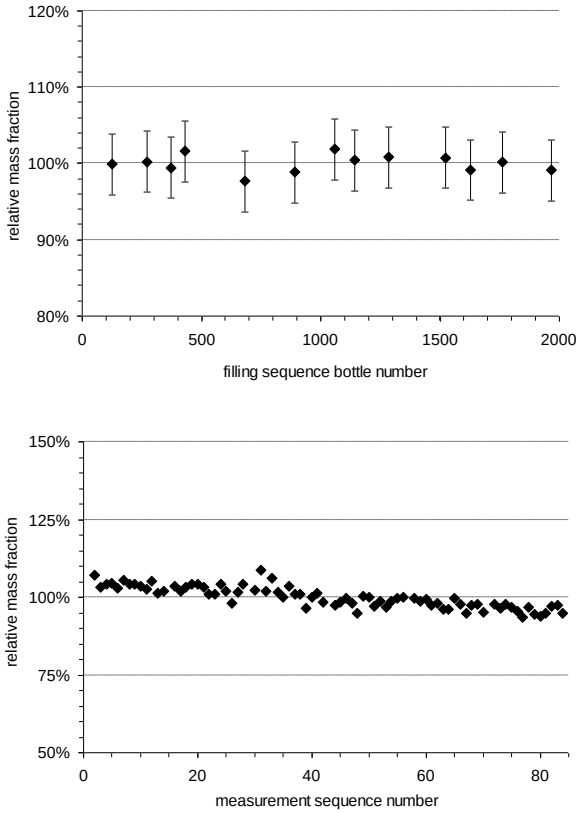


Figure A113: P in ERM-BD150

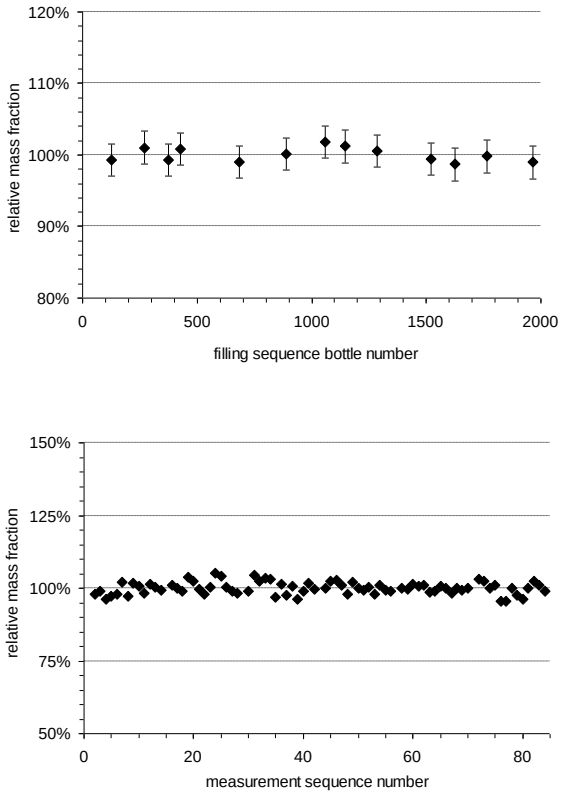


Figure A114: Pb in ERM-BD150

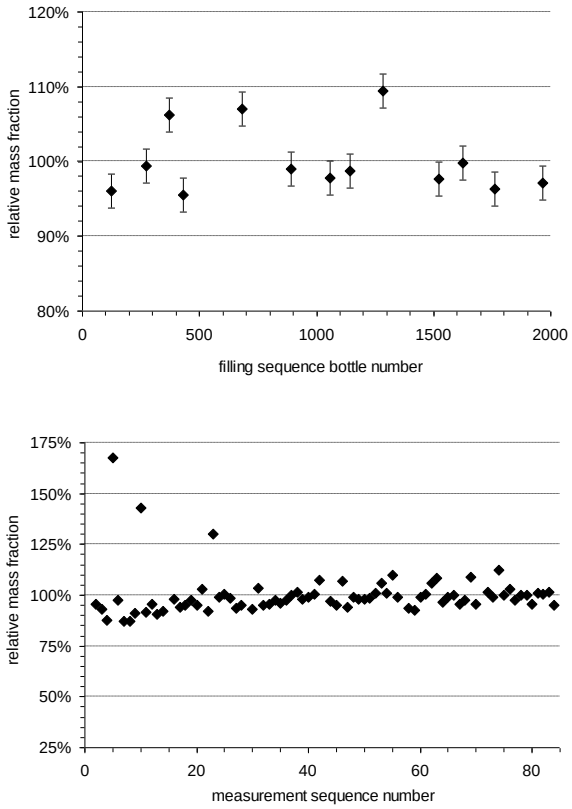


Figure A115: Se in ERM-BD150

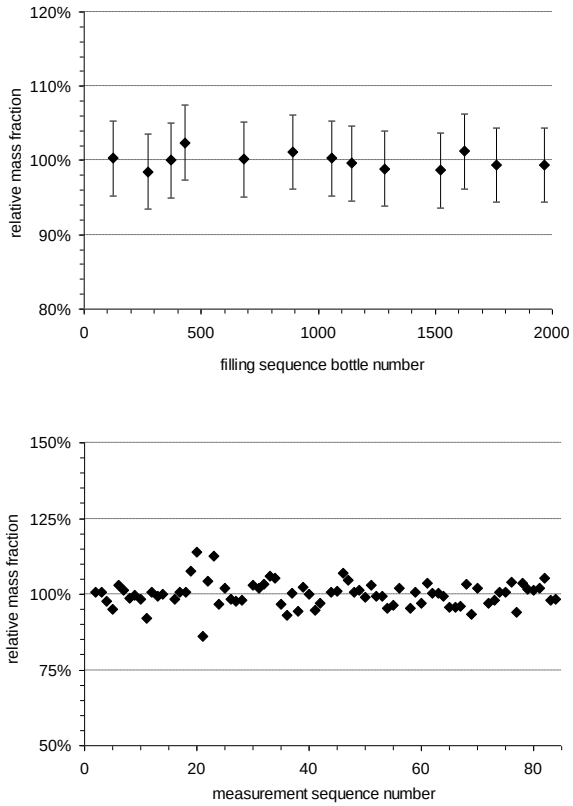


Figure A116: Zn in ERM-BD150

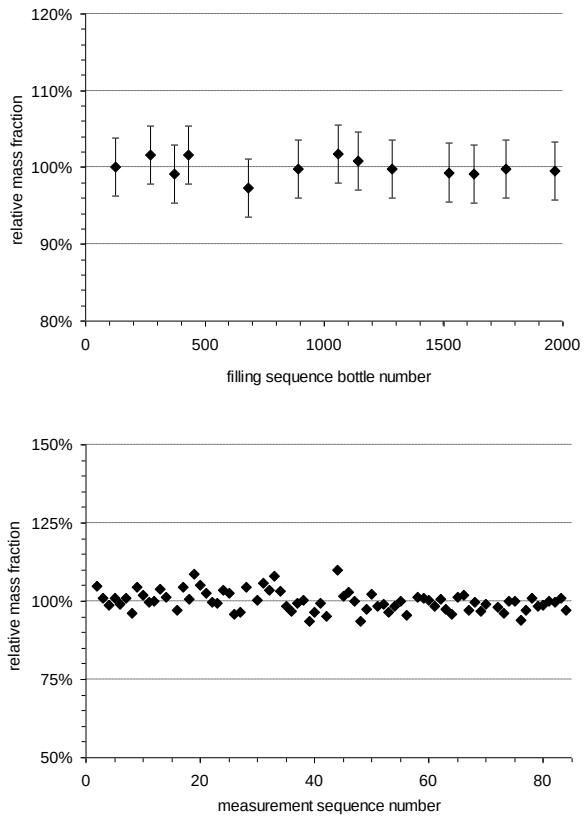


Figure A201: Ca in ERM-BD151

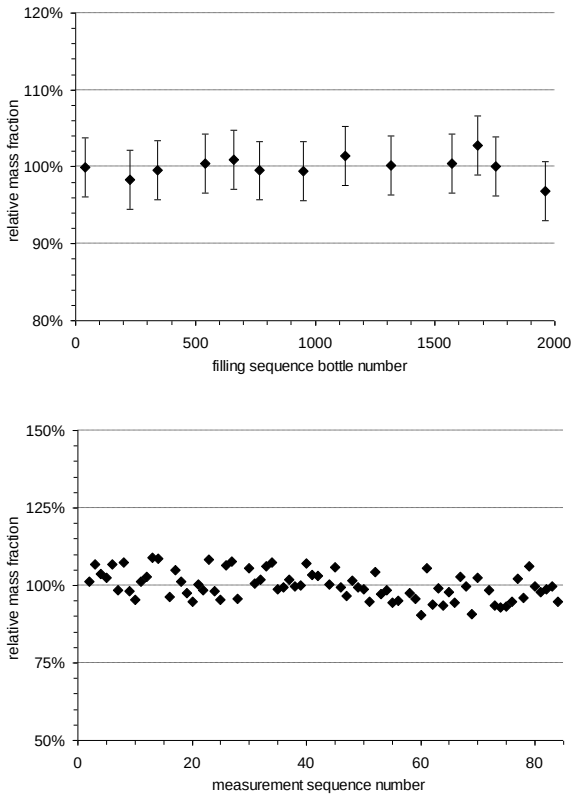


Figure A202: Cd in ERM-BD151

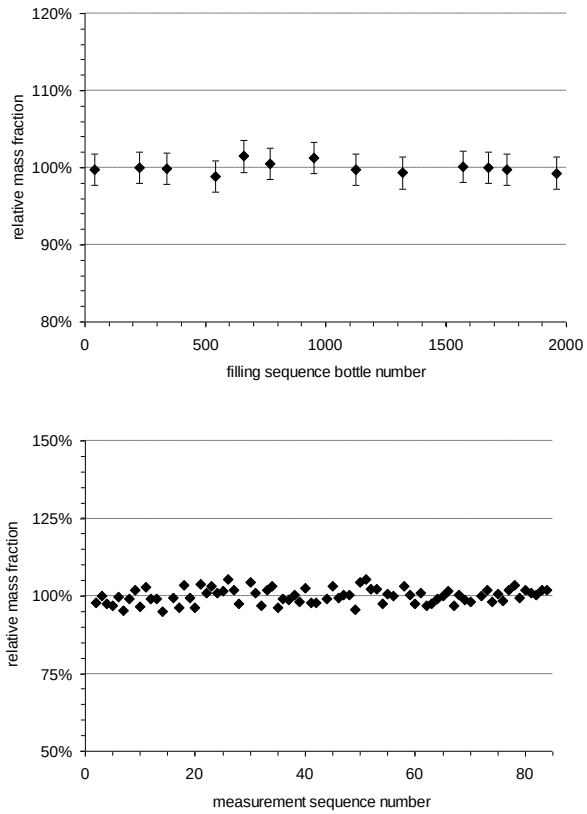


Figure A203: Cl in ERM-BD151

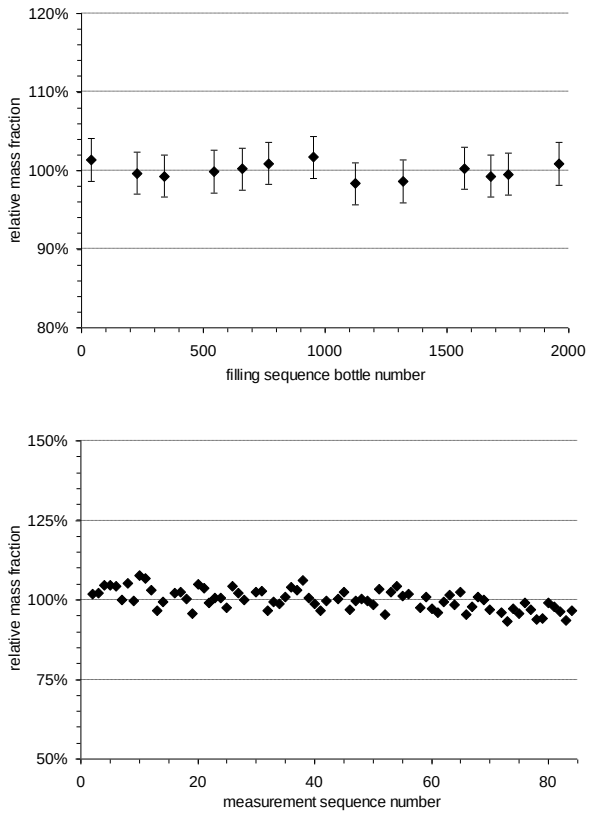


Figure A204: Co in ERM-BD151

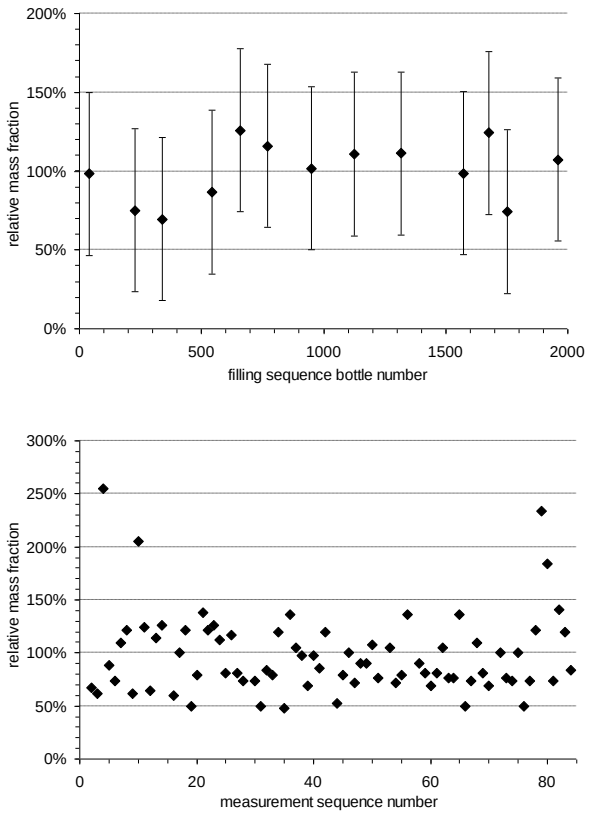


Figure A205: Cu in ERM-BD151

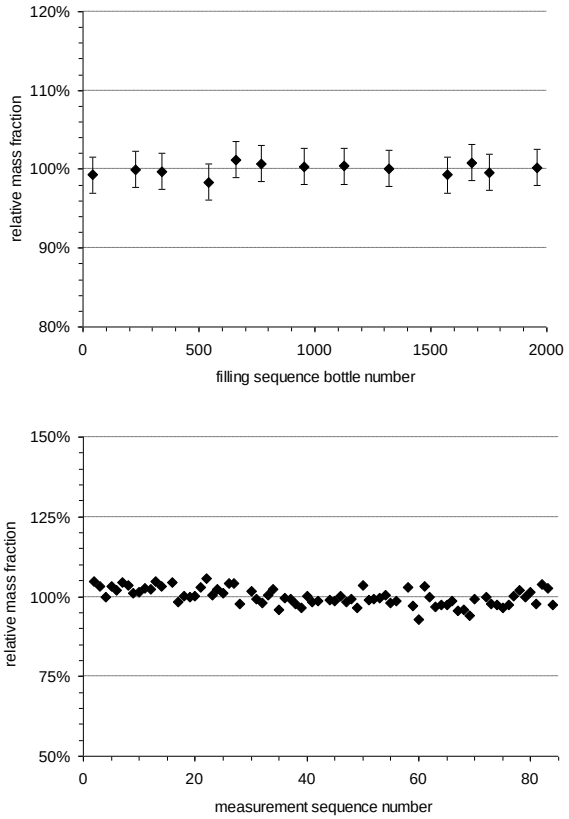


Figure A206: Fe in ERM-BD151

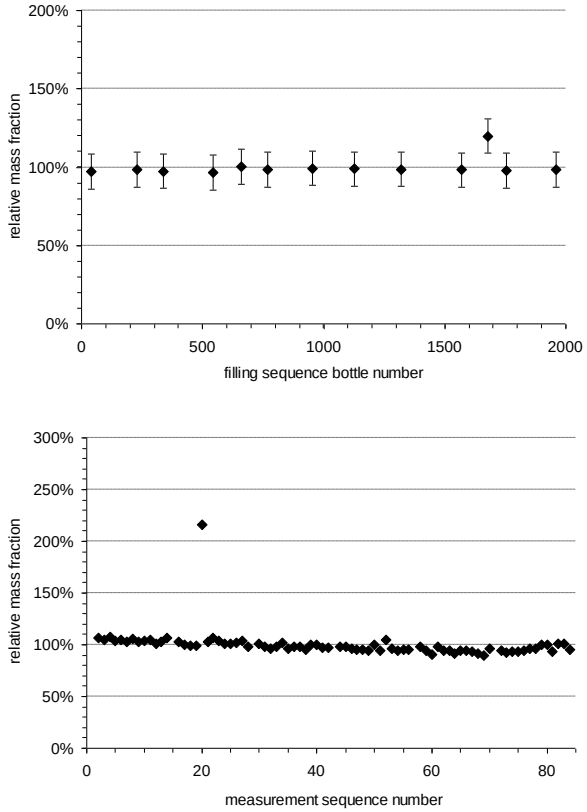


Figure A207: Hg in ERM-BD151

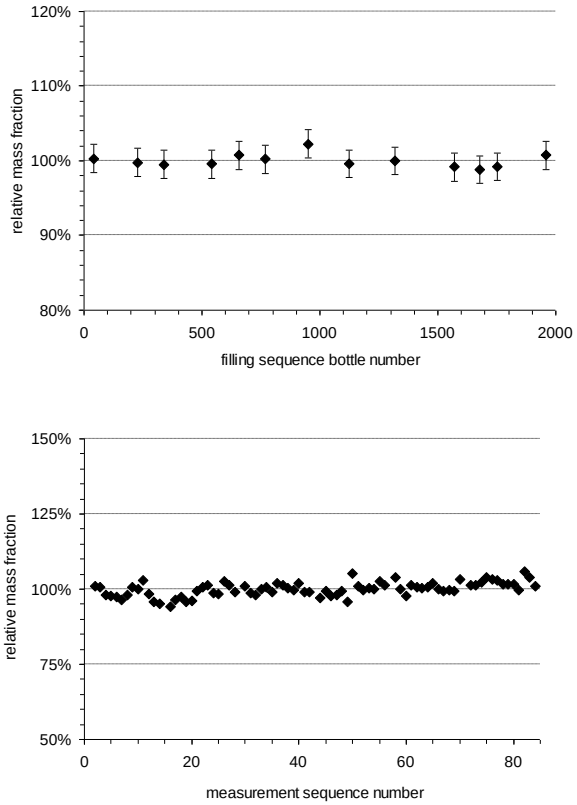


Figure A208: I in ERM-BD151

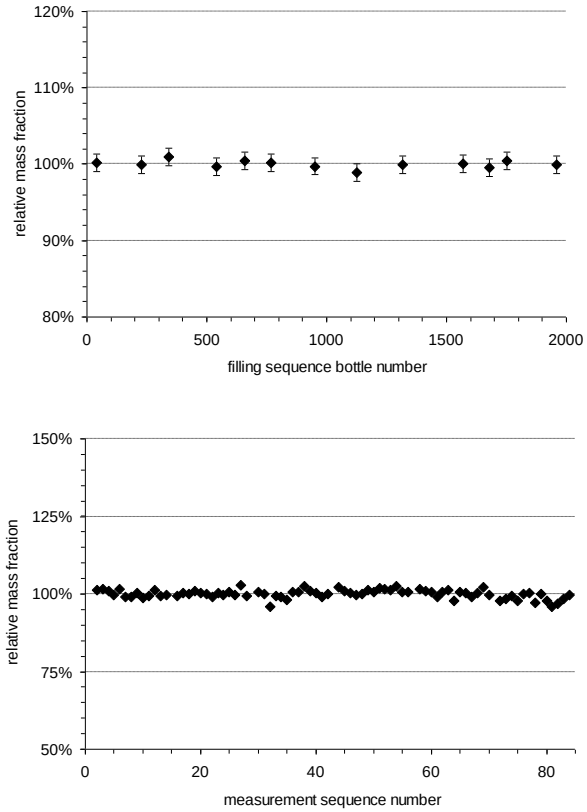


Figure A209: K in ERM-BD151

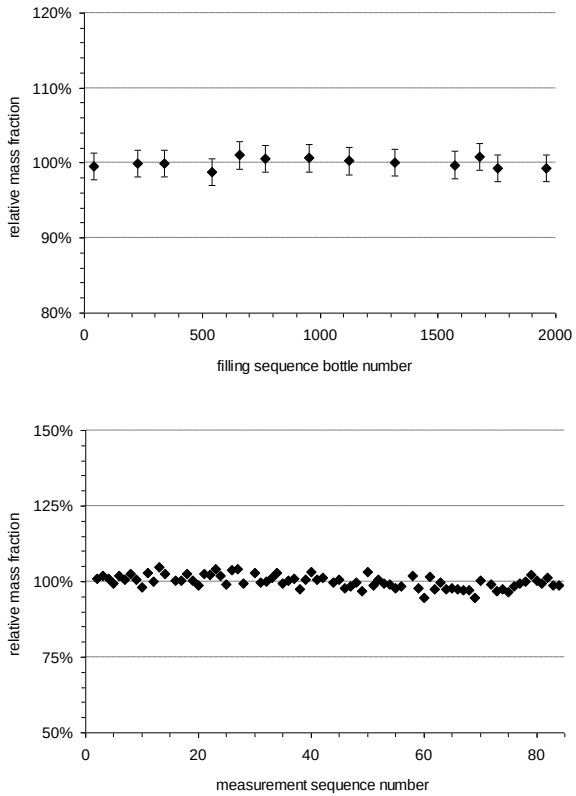


Figure A210: Mg in ERM-BD151

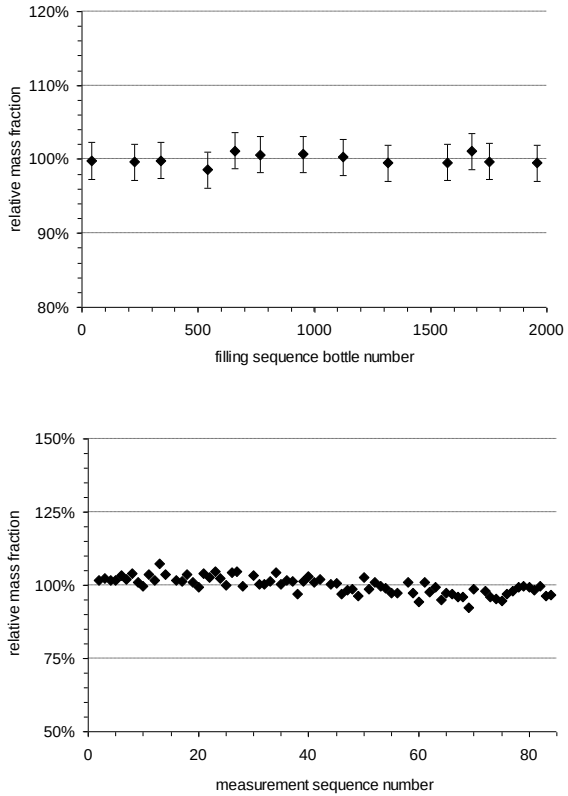


Figure A211: Mn in ERM-BD151

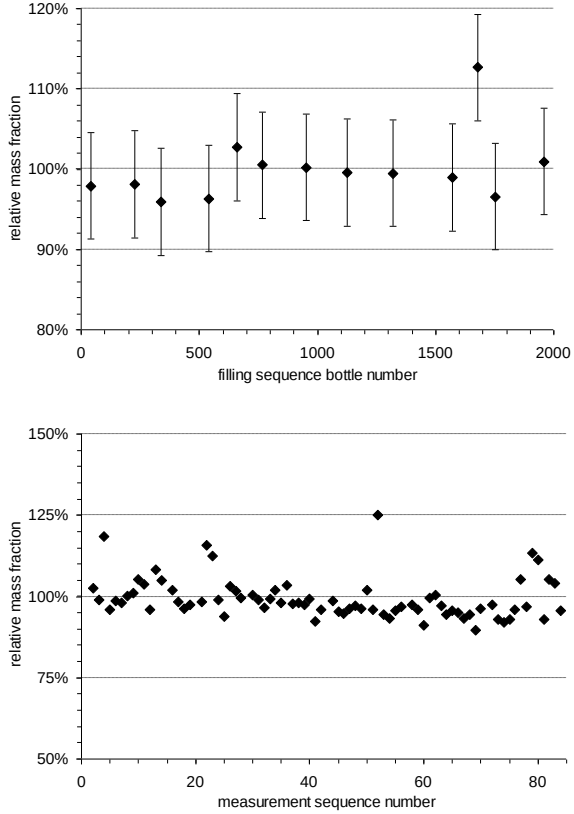


Figure A212: Na in ERM-BD151

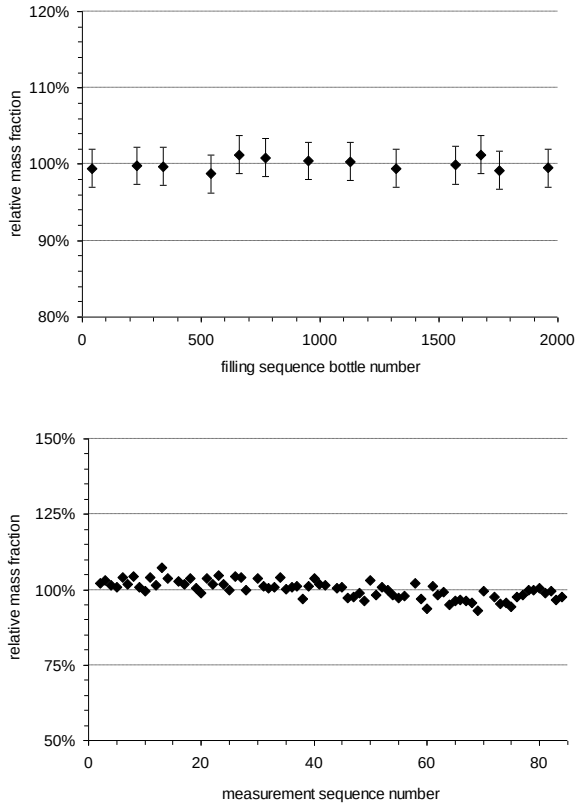


Figure A213: P in ERM-BD151

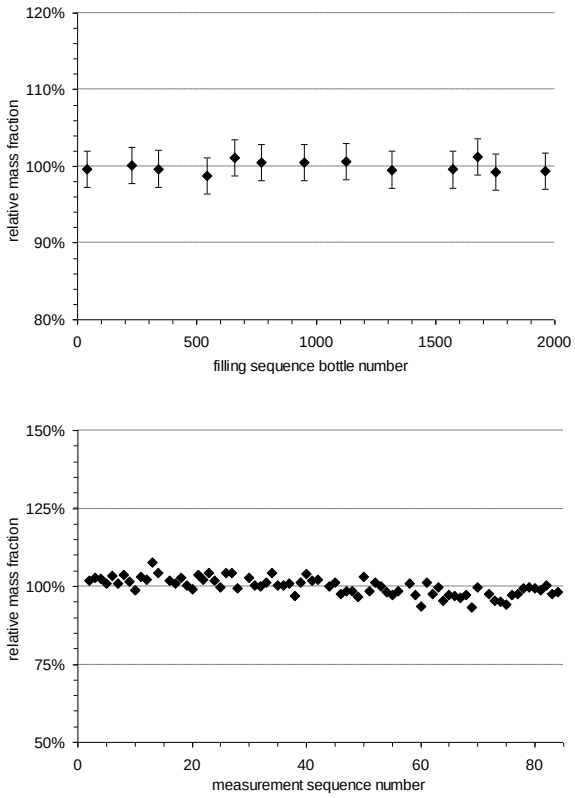


Figure A214: Pb in ERM-BD151

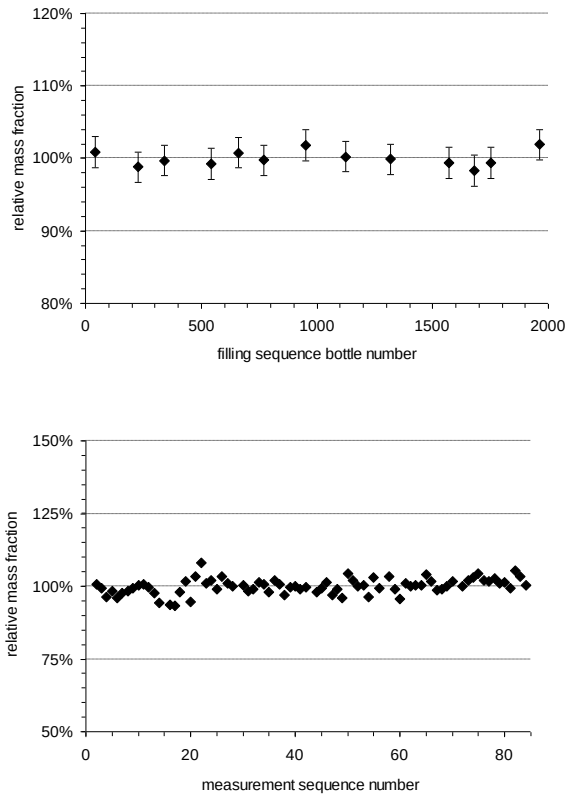


Figure A215: Se in ERM-BD151

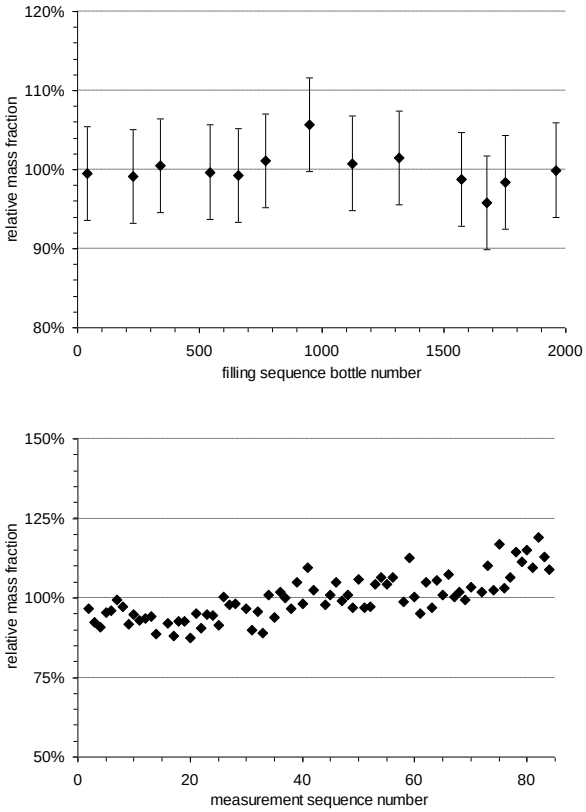
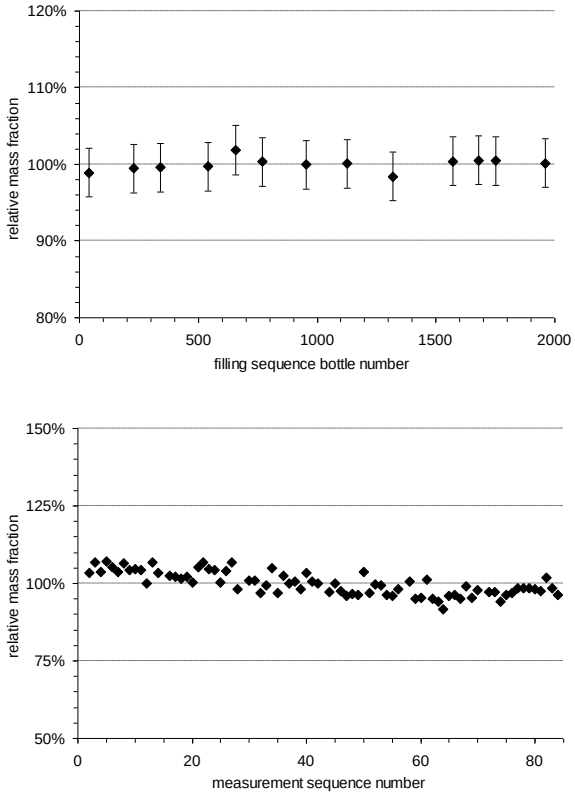


Figure A216: Zn in ERM-BD151



CERTIFICATION REPORT: The certification of the mass fractions of elements in skimmed milk powders: ERM BD150 and ERM BD151

Annex B: Results of the short-term stability measurements

Graphs present the mean mass fractions measured at each time-point relative to the mean at time zero, against the time that the samples were held at 60 ºC. Vertical bars represent the 95 % confidence interval of the measurements, based on the variance of measurements for each time-point calculated by ANOVA.

Figure B101: Ca in ERM-BD150

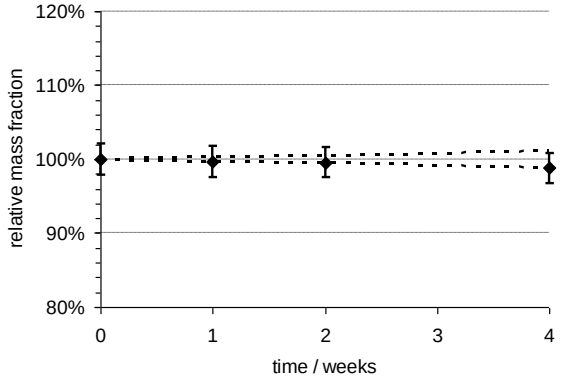


Figure B102: Cd in ERM-BD150

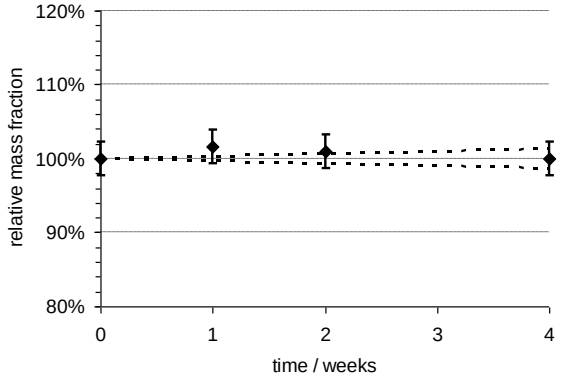


Figure B103: Cl in ERM-BD150

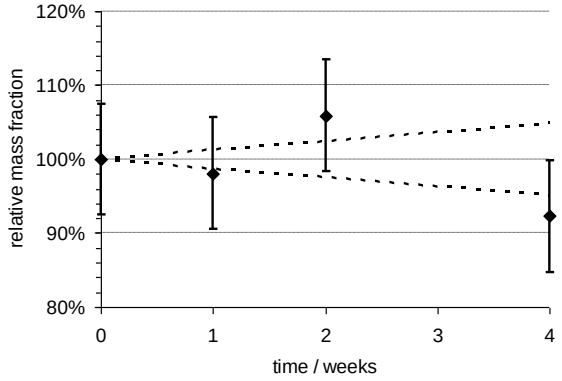


Figure B104: Co in ERM-BD150

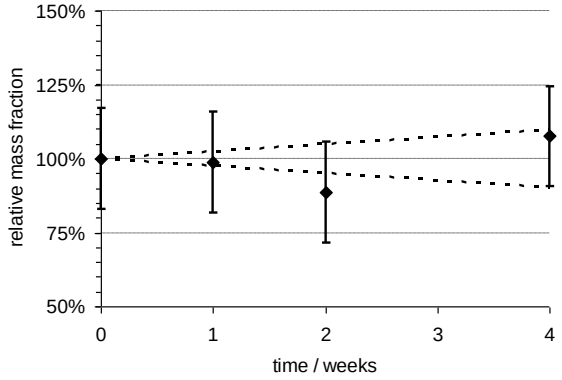


Figure B105: Cu in ERM-BD150

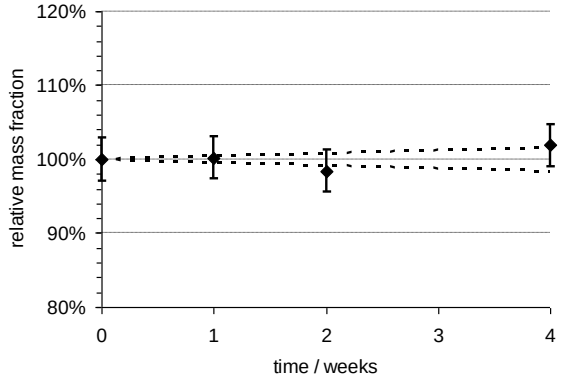


Figure B106: Fe in ERM-BD150

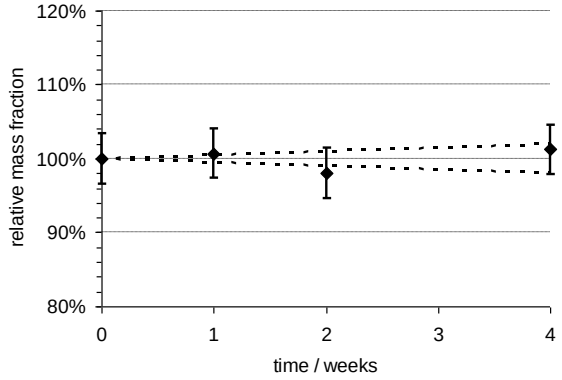


Figure B107: Hg in ERM-BD150

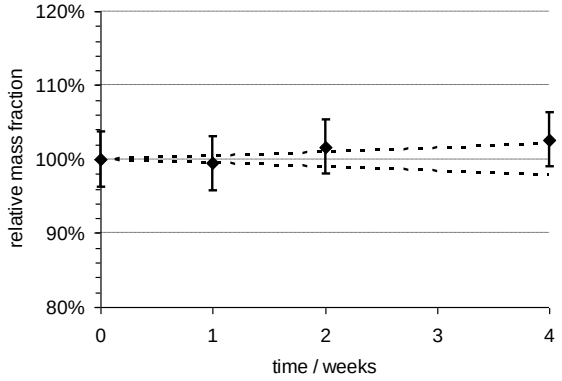


Figure B108: I in ERM-BD150

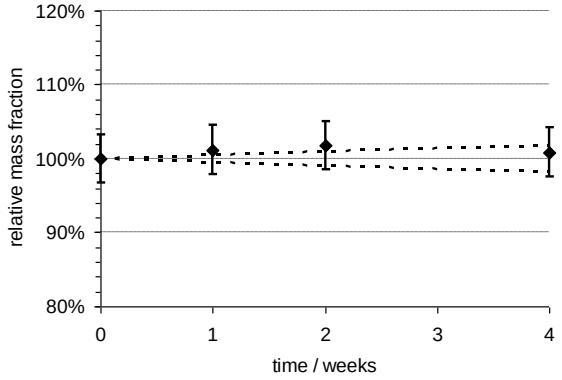


Figure B109: K in ERM-BD150

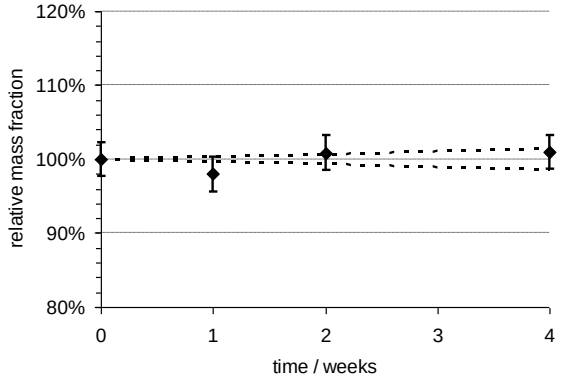


Figure B110: Mg in ERM-BD150

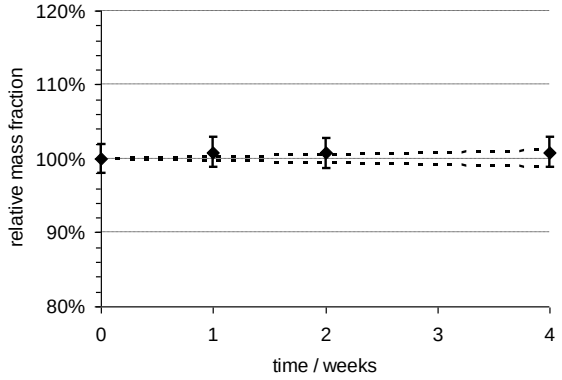


Figure B111: Mn in ERM-BD150

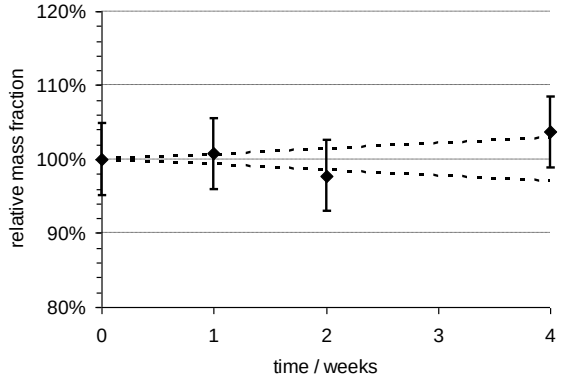


Figure B112: Na in ERM-BD150

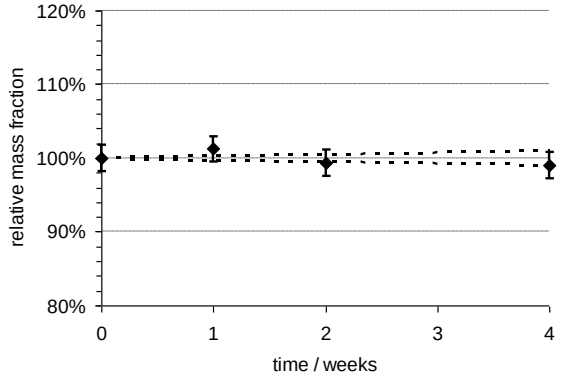


Figure B113: P in ERM-BD150

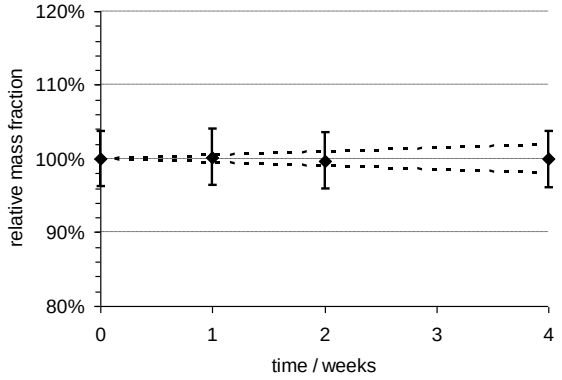


Figure B114: Pb in ERM-BD150

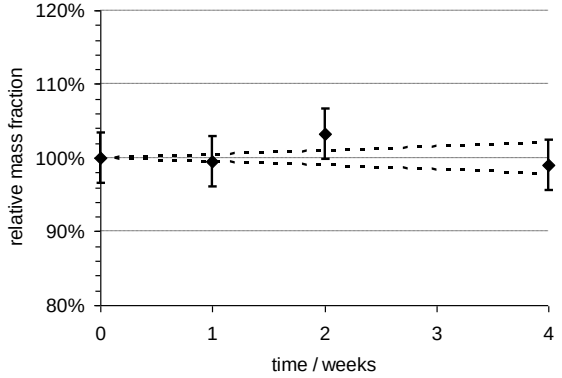


Figure B115: Se in ERM-BD150

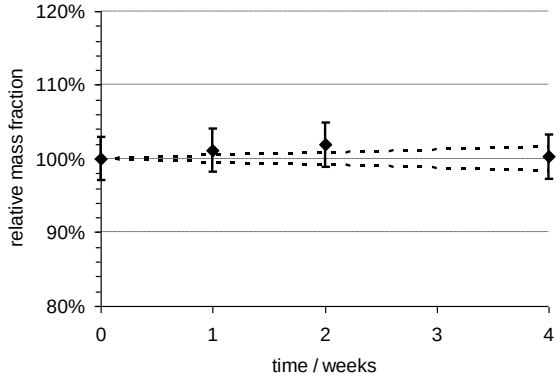


Figure B116: Zn in ERM-BD150

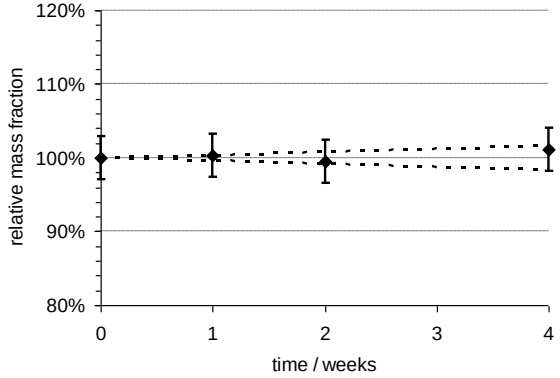


Figure B201: Ca in ERM-BD151

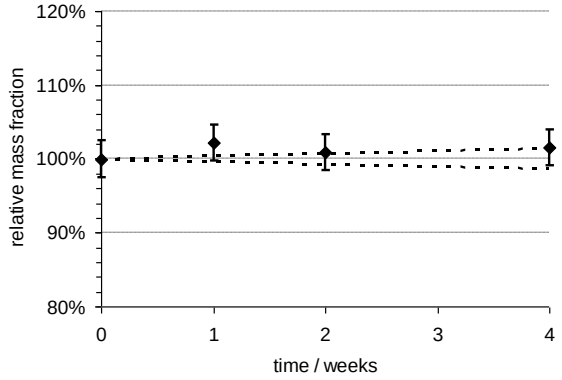


Figure B202: Cd in ERM-BD151

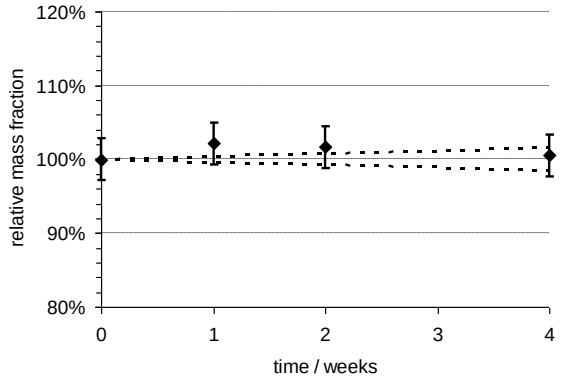


Figure B203: Cl in ERM-BD151

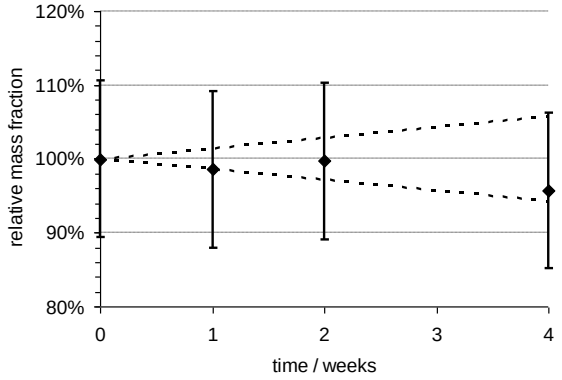


Figure B204: Co in ERM-BD151

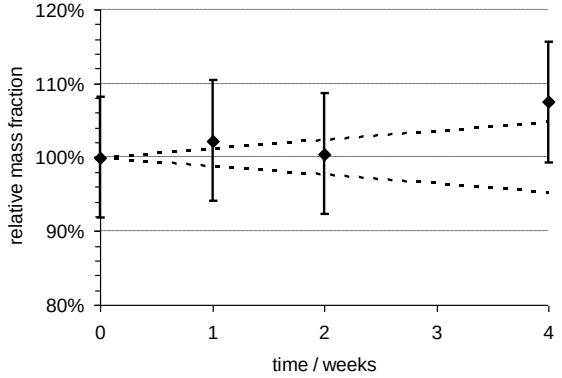


Figure B205: Cu in ERM-BD151

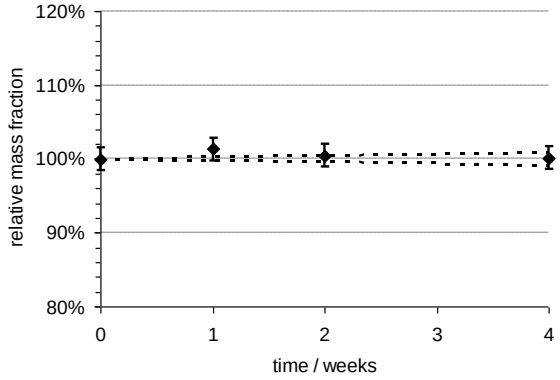


Figure B206: Fe in ERM-BD151

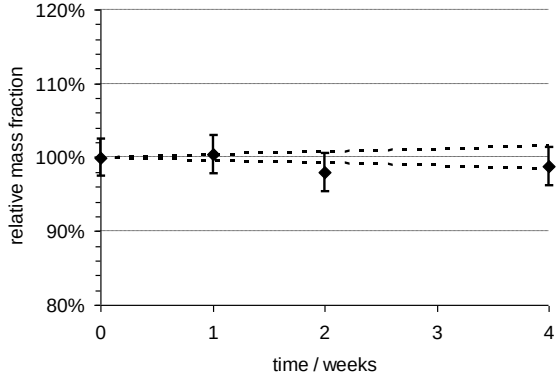


Figure B207: Hg in ERM-BD151

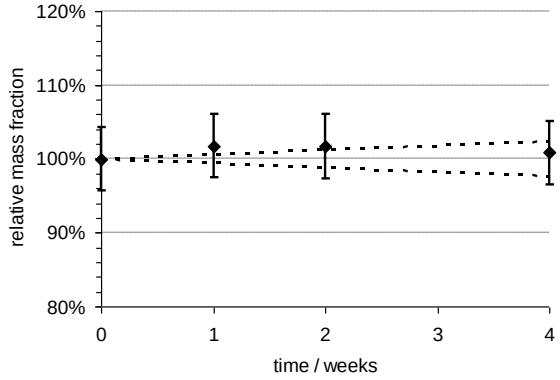


Figure B208: I in ERM-BD151

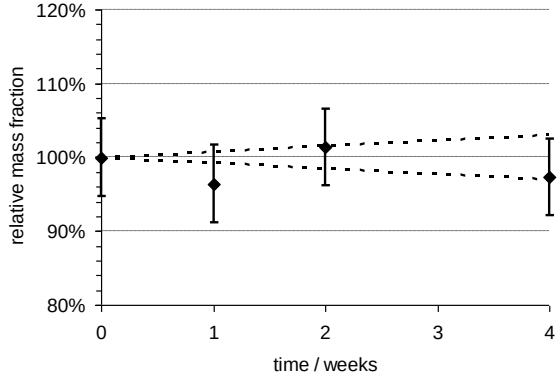


Figure B209: K in ERM-BD151

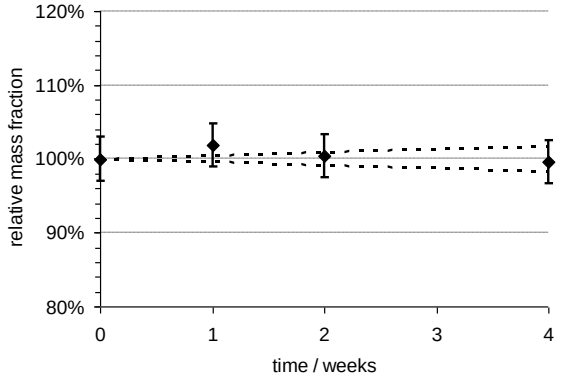


Figure B210: Mg in ERM-BD151

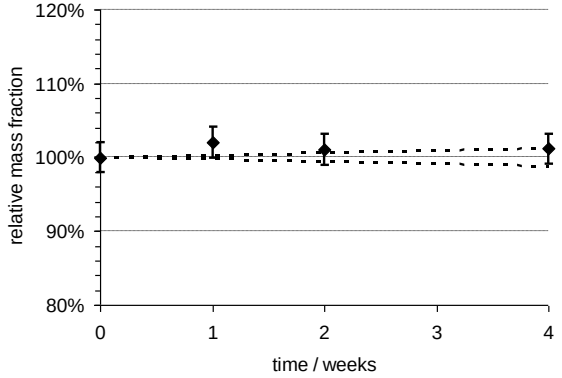


Figure B211: Mn in ERM-BD151

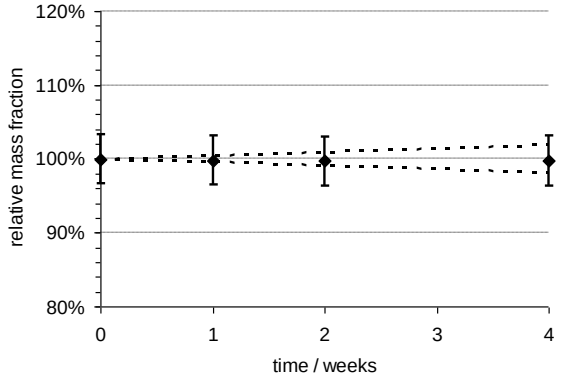


Figure B212: Na in ERM-BD151

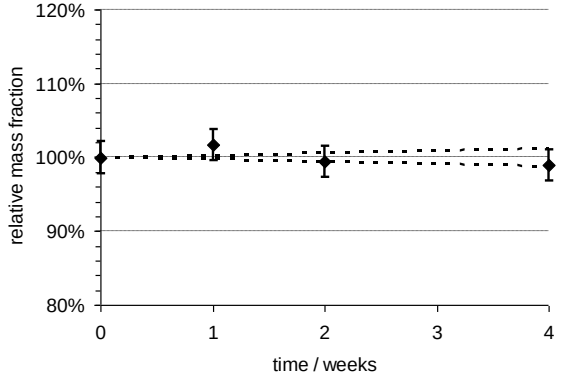


Figure B213: P in ERM-BD151

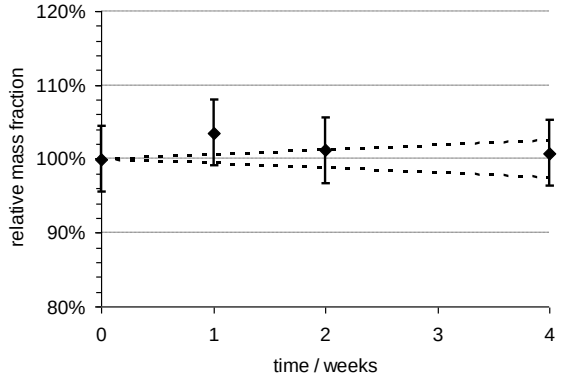


Figure B214: Pb in ERM-BD151

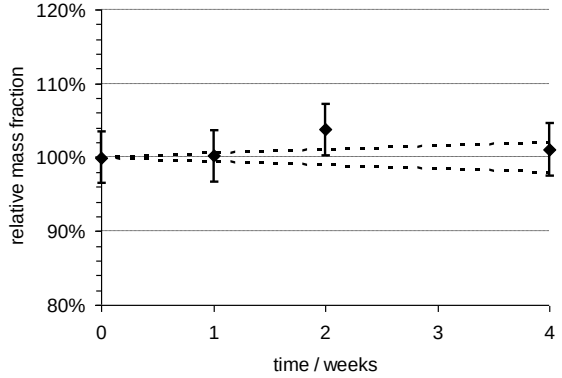


Figure B215: Se in ERM-BD151

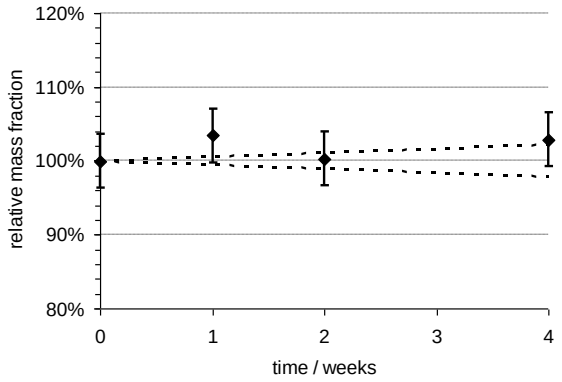
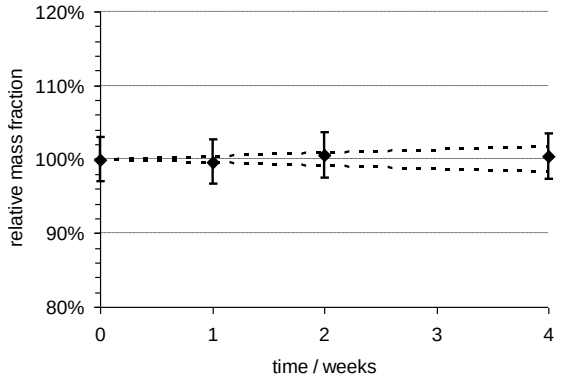


Figure B216: Zn in ERM-BD151



CERTIFICATION REPORT: The certification of the mass fractions of elements in skimmed milk powders: ERM BD150 and ERM BD151

Annex C: Results of the long-term stability measurements

Graphs present the mean mass fractions measured at each time-point relative to the mean at time zero, against the time that the samples were held at 18 ºC. Vertical bars represent the 95 % confidence interval of the measurements, based on the variance of measurements for each time-point calculated by ANOVA.

Figure C101: Ca in ERM-BD150

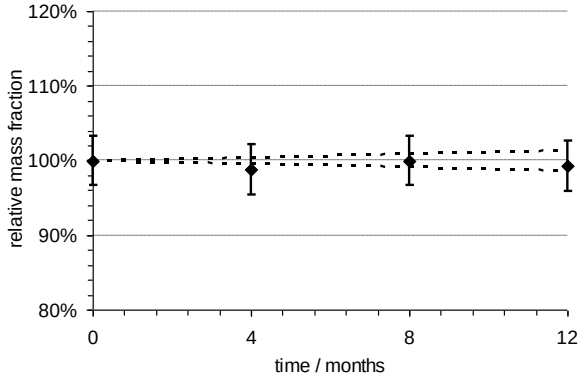


Figure C102: Cd in ERM-BD150

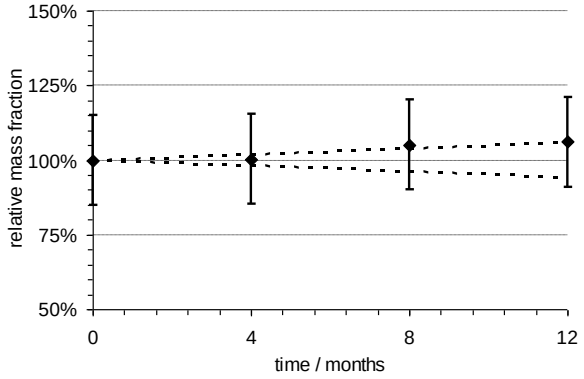


Figure C103: Cl in ERM-BD150

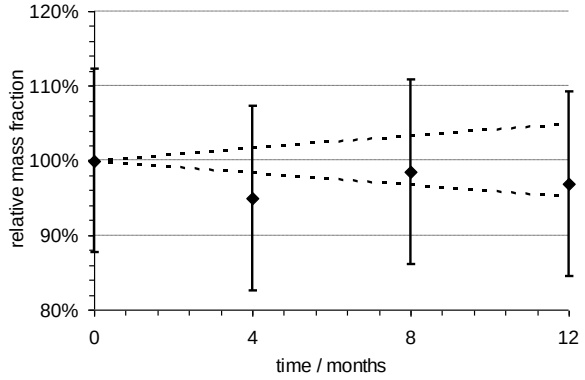


Figure C104: Co in ERM-BD150

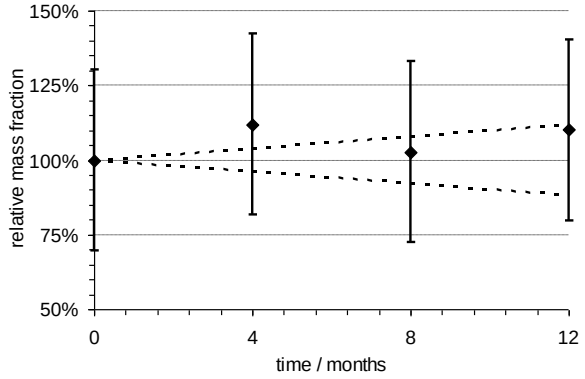


Figure C105: Cu in ERM-BD150

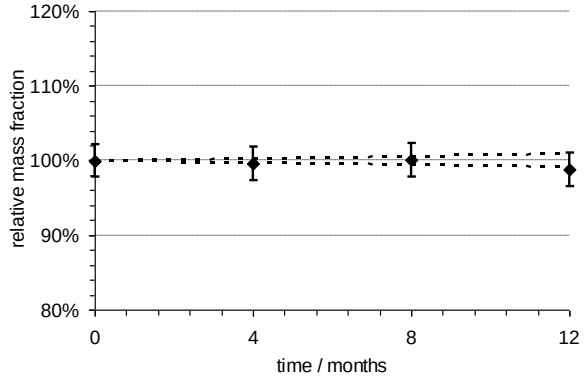


Figure C106: Fe in ERM-BD150

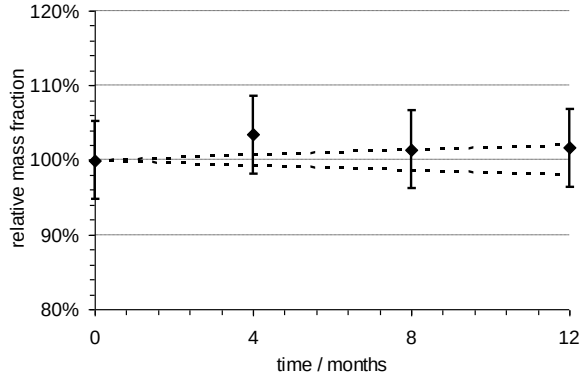


Figure C107: Hg in ERM-BD150

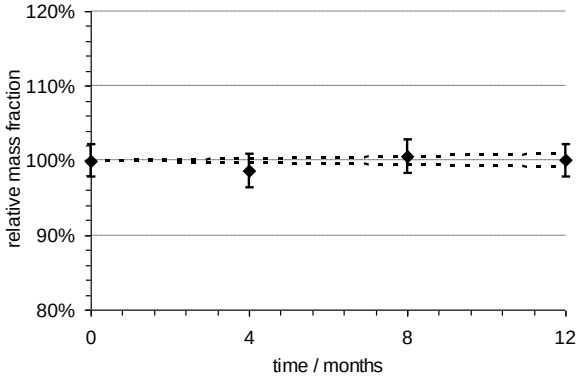


Figure C108: I in ERM-BD150

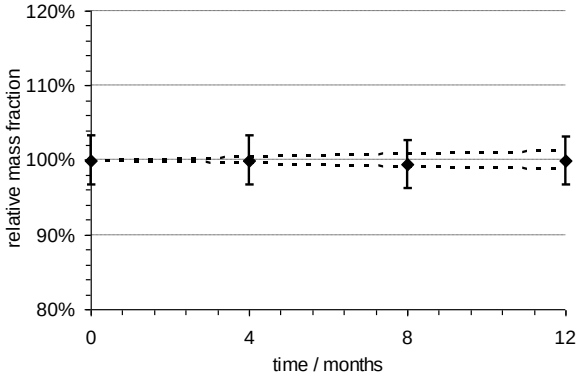


Figure C109: K in ERM-BD150

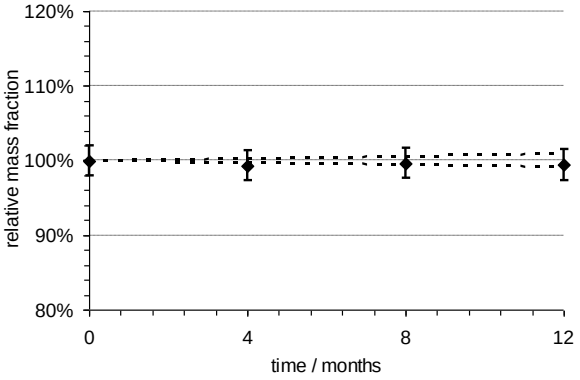


Figure C110: Mg in ERM-BD150

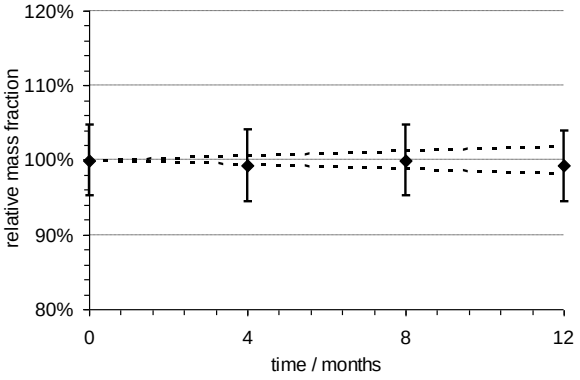


Figure C111: Mn in ERM-BD150

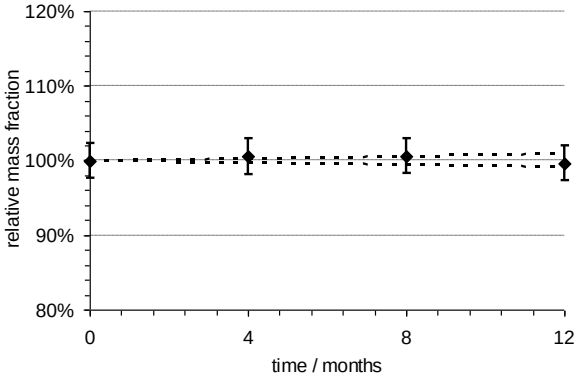


Figure C112: Na in ERM-BD150

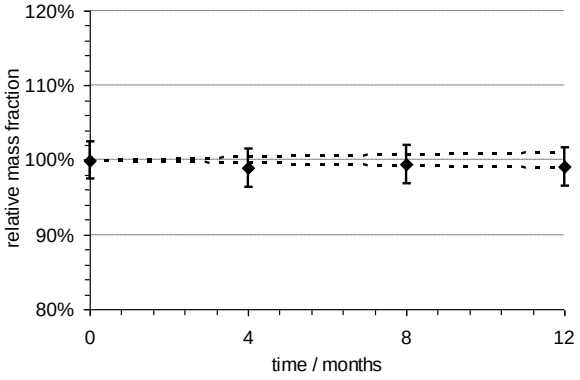


Figure C113: P in ERM-BD150

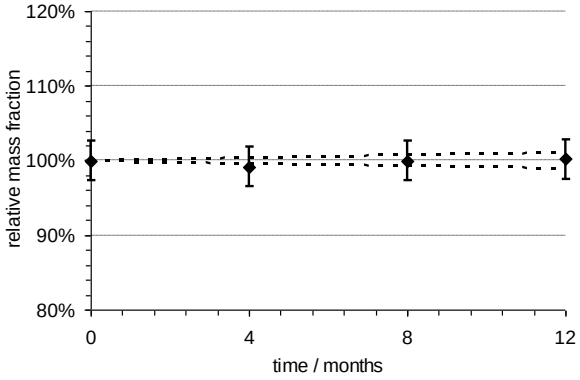


Figure C114: Pb in ERM-BD150

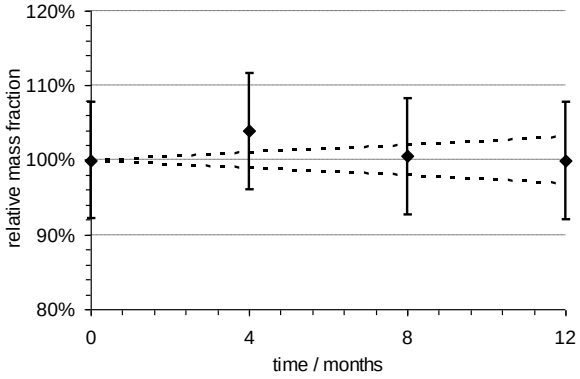


Figure C115: Se in ERM-BD150

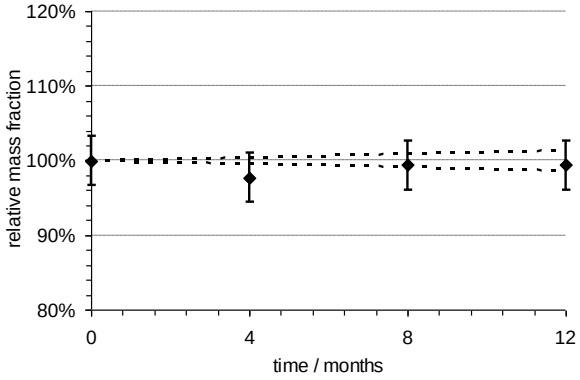


Figure C116: Zn in ERM-BD150

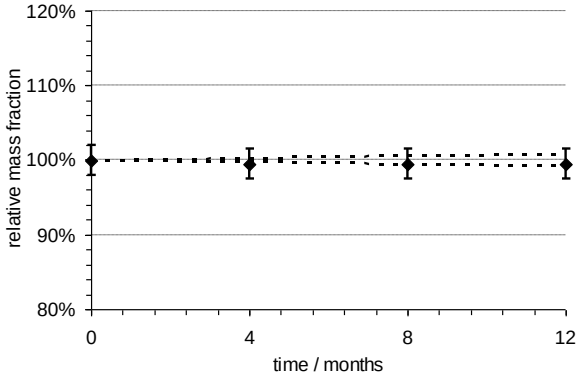


Figure C201: Ca in ERM-BD151

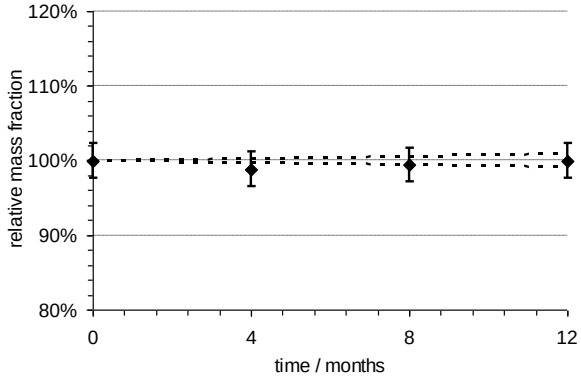


Figure C202: Cd in ERM-BD151

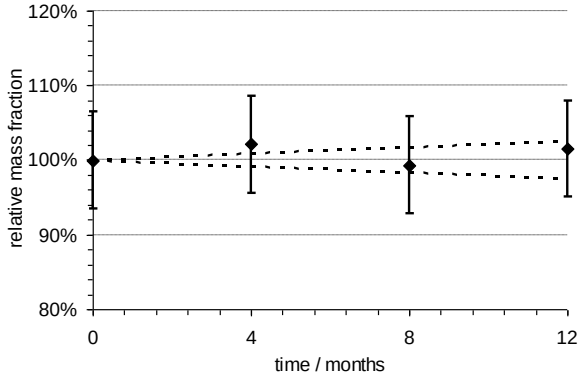


Figure C203: Cl in ERM-BD151

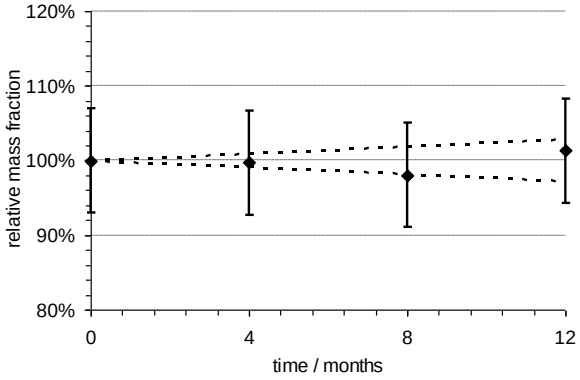


Figure C204: Co in ERM-BD151

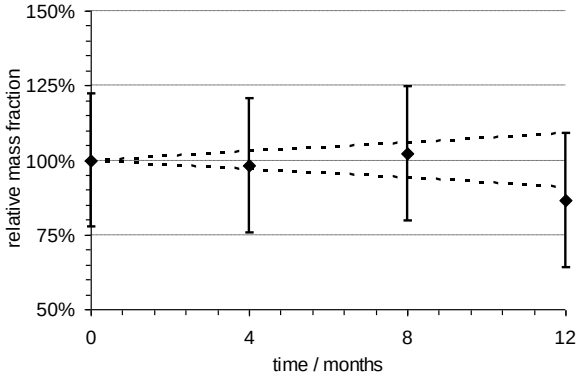


Figure C205: Cu in ERM-BD151

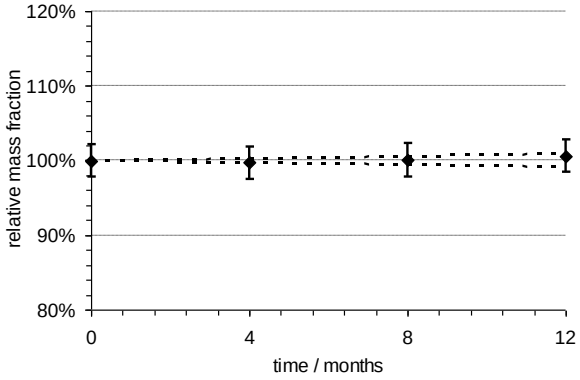


Figure C206: Fe in ERM-BD151

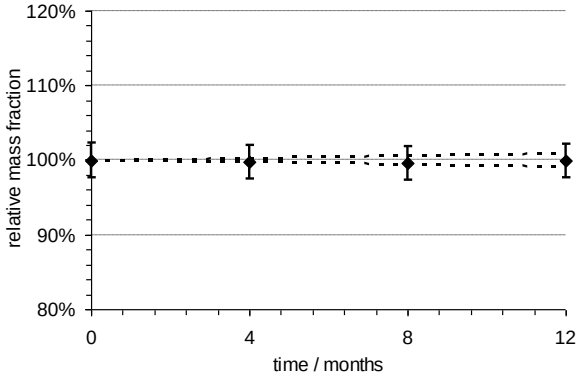


Figure C207: Hg in ERM-BD151

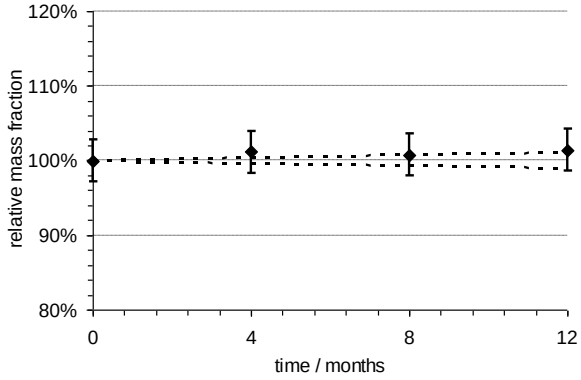


Figure C208: I in ERM-BD151

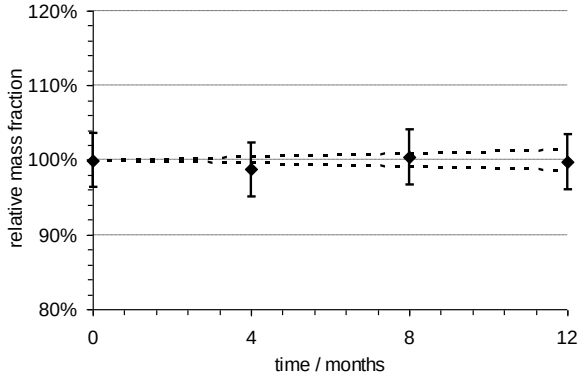


Figure C209: K in ERM-BD151

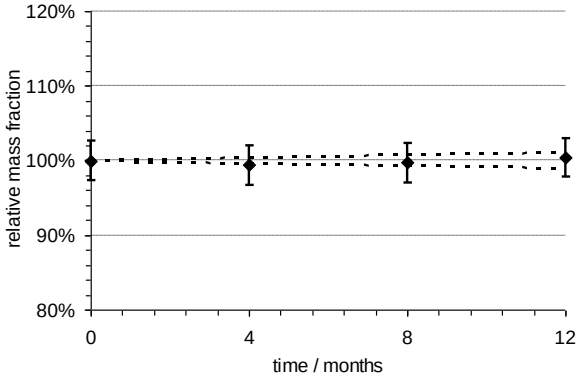


Figure C210: Mg in ERM-BD151

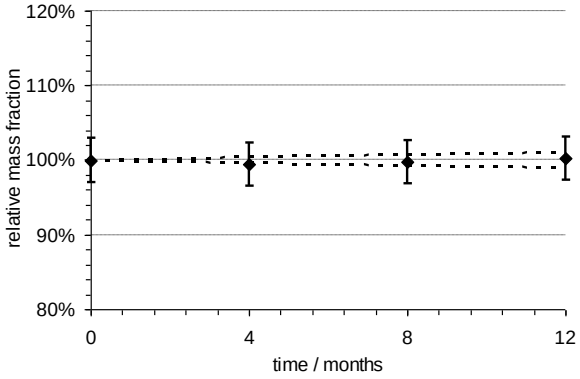


Figure C211: Mn in ERM-BD151

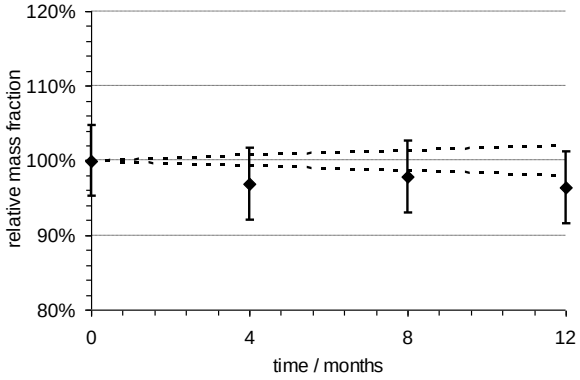


Figure C212: Na in ERM-BD151

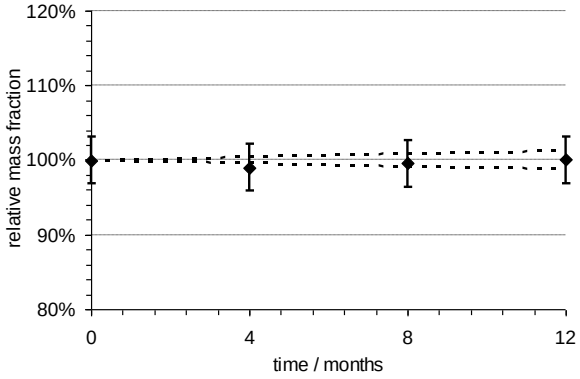


Figure C213: P in ERM-BD151

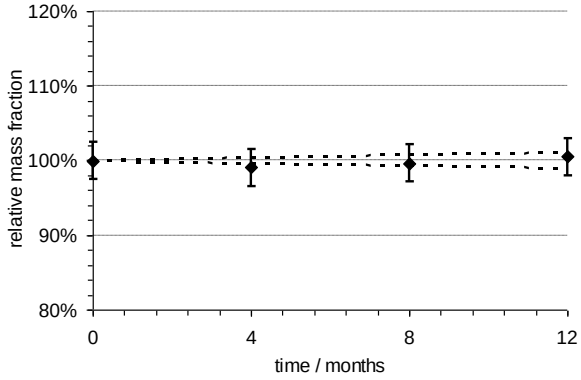


Figure C214: Pb in ERM-BD151

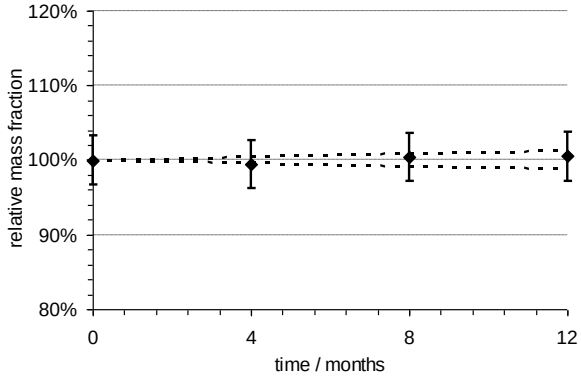


Figure C215: Se in ERM-BD151

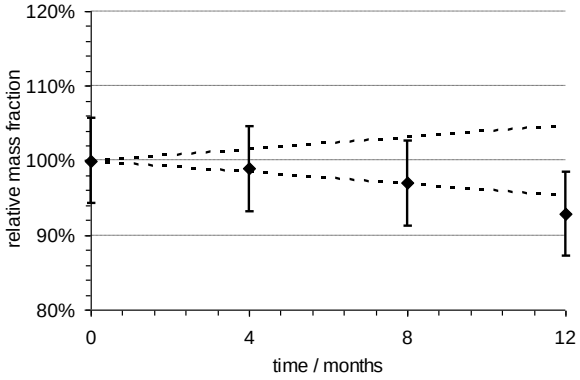
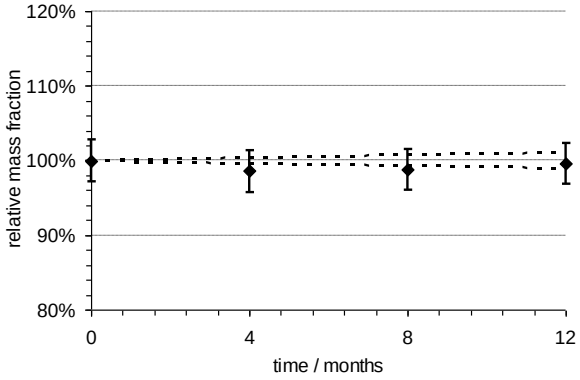


Figure C216: Zn in ERM-BD151



CERTIFICATION REPORT

The certification of the mass fractions of elements in skimmed milk powders: ERM BD150 and ERM BD151

Annex D: Summary of methods used in the characterisation

Each laboratory used the same characterisation method for both ERM-BD150 and BD151.

Note that measurement methods are given as reported by the laboratories, and may not follow the terminology of the Guide to the Expression of Uncertainty in Measurements, [ISO/IEC Guide 98-3:2008], or the International Vocabulary of Metrology – Basic and General Concepts and Associated Terms, [ISO/IEC Guide 99:2007].

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
1	Ca, Cd, Co, Cu, Fe, Hg, K, Mg, Mn, Na, P, Pb, Se, Zn	0.5 g digested in 1 ml HCl + 4 ml HNO_3 using high pressure quartz vessels and microwave heating	Agilent 7500ce ICP-MS [hydrogen mode for Ca, Se, helium mode for Fe, K, Mg, Zn]	External calibration, (seven calibrants spanning three orders of magnitude)	VWR (BDH, Prolabo) standard (Based on NIST SRMs)	Reagent blanks, spiked samples, spiked reagent blank, NIST 1547 (peach leaves), NIST 1567a (wheat flour), NIST 8436 (durum wheat flour)	Estimate based on proficiency test performance
	Cl, I	0.5 g digested in TMAH on a hot block @ 90°C	Axiom ICP-MS, low resolution		Ultra pure HCl and KIO_3, BDH Analar grade	Reagent blanks, spiked samples, spiked reagent blank, BCR 63 (skim milk powder), NIST 1549 (non-fat milk powder), NIST 8435 (whole milk powder)	

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
2	Cu	Microwave acid digestion (HNO_3 and H_2O_2)	Agilent 7500ce ICP-MS	IDMS	NIST SRM 3114 Lot# 011017	Independent Std used as quality check, NIST SRM1548a used as QC for recoveries/matrix effects. Analysis performed following LGCs SOP (UKAS accredited, ISO 17025) for the provision of characterisation values by ID-ICP-MS	The uncertainty of the moisture corrected value was calculated in accordance with ISO Guide to the Expression of Uncertainty in Measurement (GUM) guidelines. Combined uncertainties were calculated following the Kragten spreadsheet method taking into account instrumental performance, IDMS equation, blend to blend variation and uncertainty of moisture determination.
	Fe		HR-ICP-MS Element 2	IDMS	NIST SRM 3126a Lot# 051031		
	Se		HR-ICP-MS Element 2	IDMS	NIST SRM 3149 Lot# 100901		
	Zn		Agilent 7500ce ICP-MS	IDMS	NIST SRM 3168a Lot# 080123		
	I	Alkaline digestion (TMAH)	HR-ICP-MS Element 2	IDMS	KI, Puratronic, +99.99% Alfa Aesar Lot# B703444 and 4318212	Independent Std used as quality check, ERM-BC402a used as QC for recoveries/matrix effects. Analysis performed following LGCs SOP (UKAS accredited, ISO 17025) for the provision of characterisation values by ID-ICP-MS	

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
3	Ca	Sample is digested in microwave (high pressure and temperature), with concentrated nitric acid and hydrogen peroxide. After digestion, sample is diluted to 10 ml with water	Flame atomic absorption. Wavelength: 422,7 nm	external calibration curve with 4 standards (1 to 10 mg/l)	Calcium (1000 mg/l): *Fluka 69349*	- control of digestion with blank (one blank in each digestion batch) - control of the response of the highest standard of the curve - control of correlation coefficient (r^2) and residual analysis - one reference material in each batch	we consider the following contributions: - repeatability - reproducibility - Uncertainty related to exactitude (uncertainty of reference material)
	Cd		Graphite furnace, with 2 matrix modifiers: DHPA (1%l) and Magnesium nitrate (1000 mg/l). Wavelength: 228,8nm	external calibration curve with 4 standards (0,5 to 5 ug/l)	Cadmium (1000 mg/l): *Fluka 20895*		
	Co		ICP - Wavelength: 228,616 nm	external calibration curve with 5 standards (1 a 50 ug/l) (Y as internal standard)	Cobalt (1000 mg/l): *Fluka* 05202 *Ytrium (1000 mg/l): Merck 1.70368.0100*		
	Cu		Graphite furnace, with 2 matrix modifiers: Pd (1000mg/l) and Magnesium nitrate (1000 mg/l). Wavelength: 327,4 nm	external calibration curve with 4 standards (10 to 100 ug/l)	Copper (1000 mg/l): *Fluka 61147*		
	Fe		Graphite furnace, with one matrix modifier: Magnesium nitrate (5000 mg/l). Wavelength: 302,1 nm	external calibration curve with 4 standards (10 to 100 ug/l)	Iron (1000 mg/l): F*luka 44903*		
	Hg		Hydride generation/cold vapour. Wavelength: 253,7 nm	external calibration curve with 4 standards (1 to 10 ug/l)	Mercury (1000 mg/l): *Fluka 16482*		
	K		ICP - Wavelength: 766,490nm	external calibration curve with 5 standards (0,5 to 25 mg/l) (Y as internal standard)	Potassium (1000 mg/l):*Fluka* 96665 *Ytrium (1000 mg/l): Merck 1.70368.0100*		
	Mg		Flame atomic absorption. Wavelength: 285,2 nm	external calibration curve with 4 standards (0,5 to 5 mg/l)	Magnesium (1000 mg/l): *Fluka 42992*		

3	Mn		ICP - Wavelength: 257,610 nm	external calibration curve with 5 standards (1 to 50 ug/l) (Y as internal standard)	Manganese (1000 mg/l): F*luka 63534 Ytrium (1000 mg/l): Merck 1.70368.0100*		
	Na		Flame atomic emission. Wavelength: 589,0 nm	external calibration curve with 4 standards (0,1 to 2,5 mg/l)	Sodium (1000 mg/l): *Fluka 05201*		
	P		ICP - Wavelength: 213,617 nm	external calibration curve with 5 standards (0,5 to 25 mg/l) (Y as internal standard)	Phosphorus (1000 mg/l): Fluka 51474 *Ytrium (1000 mg/l): Merck 1.70368.0100*		
	Pb		Graphite furnace, with 2 matrix modifiers: DHPA (1%l) and Magnesium nitrate (1000 mg/l). Wavelength: 283,3 nm	external calibration curve with 4 standards (1 to 10 ug/l)	Lead (1000 mg/l): F*luka 16595*		
	Se		Hydride generation - Wavelength: 196,0 nm	external calibration curve with 4 standards (1 to 10 ug/l)	Selenium (1000 mg/l): *Fluka 84896*		
	Zn		Flame atomic absorption. Wavelength: 213,9 nm	external calibration curve with 4 standards (0,1 to 2,5 mg/l)	Zinc (1000 mg/l): *Fluka 6457*		
	Cl	sample is diluted in water and acidifed with concentrated nitric acid	Titration	end point is determined with standard. Titration solution is standardized in each batch	Sodium Chloride (>99%): Prolabo 27810.364	- one reference material in each batch - titration factor verified in each batch - repetability verifided in each batch	as above

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
4	Ca, Cd, Co, Cu, Fe, Hg, K, Mg, Mn, Na, P, Pb, Se, Zn	MW-assisted digestion (HNO_3+H_2O_2)	ICP-SFMS	External calibration	Single-element standards, Inorganic Ventures (USA)	QCS, NIST1547	In accordance with T.Ruth 'A model for the evaluation of uncertainty i routine multi-element analysis', Accred Qual Assur (2004) 9:349-354
	Cl, I	ZnO sintering					

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
5	Ca, Cu, Fe, K, Mg, Mn, Na, P, Zn	microwave (Multiwave 3000) digestion in HNO_3 (6 mL), 1000 W, 80 bar, 280 ºC	ICP-OES	external, 6 point	CPI single standard, 1000 mg/L certified	Co-digestion and co-analysis of BCR 63R. Each measurement series started with blanks, calibration standards, blanks, control standards1, followed from sample digests and control standards2 + blanks (every tenth sample), ended from control-calibration standards and blanks. Samples not matching the calibration range were appropriate diluted and measured again. Measurement of certified standards together with samples prepared at sample concentrations determined. Preparation and measurement of blank digestions together with the samples. Preparation and measurement of a control standard at the measured sample concentration allowed fine-correction for instrumental drift.	Uncertainty was estimated as twice the reproducibility standard deviation of BCR-63R. Reproducibility standard deviation was derived from 10 digests performed on 10 different days and analysed on 10 different days.
	Cl	digestion with TMAH (5%), at 30 ºC in US bath			SPEX single standard, 1000 mg/L certified		

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
6	Cd, Co, Cu, Hg, Mn, Pb, Se	microwave (Multiwave 3000) digestion in HNO_3 (6 mL), 1000 W, 80 bar, 280 ºC	ICP-MS	external, 8 point	CPI single standard, 1000 mg/L certified	as lab 5	as lab 5
	I	digestion with TMAH (5%), at 30 ºC in US bath			SPEX single standard, 1000 mg/L certified		

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
7	Cd, Co, Cu, Hg, Mn, Pb, Se	microwave (Multiwave 3000) digestion in HNO_3 (6 mL), 1000 W, 80 bar, 280 ºC	HR-ICP-MS	external, 8 point	CPI single standard, 1000 mg/L certified	as lab 5	as lab 5
	I	digestion with TMAH (5%), at 30 ºC in US bath			SPEX single standard, 1000 mg/L certified		

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
8	Ca, Co, Fe, K, Mg, Mn, Na, Se, Zn	An aliquot of ERM-BD150 and ERM-BD151 was pelletized in diameter 10 mm and 2.5 mm high. A sample and standard Al-0.1%Au (IRMM-530R) were stack together, fixed in the polyethylene vial in sandwich form	k_0-INAA: Irradiation for about 13 h (two independent irradiations) in the carousel facility of the TRIGA reactor with a thermal neutron flux of $1.1x10^{12}$ cm^{-2} s^{-1}.	k_0-standardization method of instrumental neutron activation analysis (k_0-INAA)	IRMM-530R (Al-0.1%Au alloy)	NIST SRM-1547 Peach Leaves	EURACHEM/CITAC Guide (2000), Quantifying Uncertainty in Analytical Measurement and uncertainties of input parameters relevant for technique. Expanded uncertainty with a coverage factor k=2 is given for each determination.
	Cl		As above but with short irradiation (3-5 minutes, two independent irradiations)				

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
9	Hg	none	thermal combustion, amalgamation and detection of Hg^0 vapour with atomic absorption spectrometry (DMA-80)	calibration curve (10 calibration points); linear regression	aqueous Hg solution traceable to NIST (HACH LANGE GmbH, Batch No. AO267)	Certified reference material BCR 150 (Skimmed milk powder) was used. Measured values were in good agreement with certified value.	EURACHEM/CITAC Guide (2000), Quantifying Uncertainty in Analytical Measurement and uncertainties of input parameters relevant for technique. Expanded uncertainty with a coverage factor k=2 is given for each determination.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
10	I	Samples were analysed as received – samples of about 300 mg were weighed in a cleaned polyethylene ampoule and sealed.	RNAA: simultaneous irradiation of the sample and an iodine standard solution for about 5 minutes (Φth = $4.0x10^{12}$ cm^{-2} s^{-1}). The irradiated sample and 90-100 mg of iodine carrier were then combusted in an oxygen atmosphere and iodine separated with $CHCl_3$. The induced ^{128}I was measured in a well type HPGe detector. The chemical yield was determined spectrophoto-metrically at 517 nm.	Relative method	Iodine working standard solution of known concentration (10 µg I g^{-1}), used for irradiation, was prepared from KIO_3 (Merck, purity 99.5 %).	NIST SRM-1549 Non-fat milk powder was used for quality assurance.	Using the commercially available software program GUM Workbench and the recommendations of the Eurachem/CITAC Guide, we evaluated the uncertainty budget and calculated the expanded uncertainty with a coverage factor of k = 2 for used RNAA.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
11	Cd, Cu, Pb Se, Zn	Microwave digestion of sample with HNO_3/H_2O_2	ICP MS	External calibration	ICP Multi Element Standard solution XVI CertiPUR, Merck Lot.No. HC956983	NIST 1549 (Non fat milk powder) and NIST 8435 (Whole milk powder) (Cu, Pb, Se, Zn only)	EURACHEM/CITAC Guide (2000), Quantifying Uncertainty in Analytical Measurement and uncertainties of input parameters relevant for technique. Expanded uncertainty with a coverage factor k=2 is given for each determination.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
12	Ca	microwave digestion	ICP-OES	external calibration	ICP/DCP Standard Alfa Aesar Lot. 61000473 traceable to NIST SRM 3109a	For quality assurance the standard reference material NIST 1549 and digestion blanks were prepared and analysed in the same manner as samples.	Estimation of uncertainty was performed using SRM 1643e and SRM 1549. The uncertainty covers the whole analytical process (sample preparation, digestion, dilution, measurement procedure). For combined uncertainty (see average +/- uncertainty) bias, uncertainty of reference material and relative standard deviation of at least 6 independent measurements was taken into account.
	K				Plasma Standard Specpure Lot. 61000579 traceable to NIST SRM 3141a		
	Mg				ICP/DCP Standard Alfa Aesar Lot. 158130610 traceable to NIST SRM 3131a		
	Na				ICP/DCP Standard Alfa Aesar Lot. 106101210 traceable to NIST SRM 3152a		
	P				ICP Standard CertiPUR Lot. HC112471 traceable to NISt SRM 3139a		
	Zn				Baker Instra Analyzed Lot. J00510 traceable to NIST SRM 3168a		

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
13	Ca	microwave digestion	ICP-MS	external calibration	ICP/DCP Standard Alfa Aesar Lot. 61000473 traceable to NIST SRM 3109a	For quality assurance the standard reference material NIST 1549 and digestion blanks were prepared and analysed in the same manner as samples.	Estimation of uncertainty was performed using SRM 1643e and SRM 1549. The uncertainty covers the whole analytical process (sample preparation, digestion, dilution, measurement procedure). For combined uncertainty (see average +/- uncertainty) bias, uncertainty of reference material and relative standard deviation of at least 6 independent measurements was taken into account.
	Cu				ICP Standard Baker Instra Analyzed Lot. J00485 traceable to NIST SRM 3114		
	Fe				traceable to NIST SRM 3126a		
	K				Plasma Standard Specpure Lot. 61000579 traceable to NIST SRM 3141a		
	Mg				ICP/DCP Standard Alfa Aesar Lot. 158130610 traceable to NIST SRM 3131a		
	Mn				ICP Standard Baker Instra Analyzed Lot. J01015 traceable to NIST SRM 3132		
	Na				ICP/DCP Standard Alfa Aesar Lot. 106101210 traceable to NIST SRM 3152a		
	Pb				ICP Standard Baker Instra Analyzed Lot. K00652 traceable to NIST SRM 3128		
	Zn				Plasma Standard Specpure Lot. 61000263 traceable to NIST SRM 3168a		
	Hg	as above	CVAAS	as above	traceable to NIST SRM 3133	as above	as above

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
14	Cu	microwave digestion	GF-AAS	external calibration	ICP Standard Baker Instra Analyzed Lot. J00485 traceable to NIST SRM 3114	For quality assurance the standard reference material NIST 1549 and digestion blanks were prepared and analysed in the same manner as samples.	Estimation of uncertainty was performed using SRM 1643e and SRM 1549. The uncertainty covers the whole analytical process (sample preparation, digestion, dilution, measurement procedure). For combined uncertainty (see average +/- uncertainty) bias, uncertainty of reference material and relative standard deviation of at least 6 independent measurements was taken into account.
	Hg		CV-AAS	external calibration	ICP Standard Baker Instra Analyzed Lot. K00200 traceable to NIST SRM 3133		
	Se		Hydride-AAS	external calibration	ICP Standard Baker Instra Analyzed Lot. J00739 traceable to NIST SRM 3149		
	Zn		GF-AAS	external calibration			

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
15	I	Digestion by combustion under oxygen atmosphere, absorption in alkaline solution	Determination of iodide by HPLC-ICPMS	external calibration	Ultra Scientific Iodide Standard Lot.G00022	For quality assurance the standard reference material NIST 1549 and digestion blanks were prepared and analysed in the same manner as samples.	Estimation of uncertainty was performed using SRM 1549. The uncertainty covers the whole analytical process (sample preparation, digestion, dilution, measurement procedure). For combined uncertainty (see average +/- uncertainty) bias, uncertainty of reference material and relative standard deviation of at least 6 independent measurements was taken into account.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
16	Cl	Digestion by combustion under oxygen atmosphere, absorption in alkaline solution	Determination of chloride by IC	6 point external calibration, quadratic calculation	Merck Certipur; 995-1005mg/l Cl-, HC064913; traceable to NIST SRM 999a	10 % duplicate samples, QA Samples (2 levels / n= 10) over the periode of measurement (ULTRAgrade IC Solution 1001 +/- 2 µg/ml Cl-, L01329, traceable to NIST SRM 3182)	Estimation of uncertainty was performed using SRM 1549. The uncertainty covers the whole analytical process (sample preparation, digestion, dilution, measurement procedure). For combined uncertainty (see average +/- uncertainty) bias, uncertainty of reference material and relative standard deviation of independent measurements was taken into account.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
17	Ca, Cl, Co, Fe, Hg, I, K, Mg, Mn, Na, Se, Zn	Samples were transferred into standard High Density Polyethylene vials. After irradiation no other sample treatment nor transfer of the samples into non irradiated vials was performed	k0-Neutron Activation Analysis	Absolute method using k0 nuclear data as defined by De Corte et al.	IRMM 530R used as standard for flux estimation	SMELS I, SMELS II, SMELS III, BCR-176R, CRM-278R, CRM-063R, BCR-151	GUM-approach as discussed by P. Robouch et al.: "Uncertainty Budget for k0-NAA", Journal of Radioanalytical and Nuclear Chemistry, Vol. 245, No. 1 (2000) 195-197

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
18	Ca	Precision weighing into polyethylene capsules only.	NAA: 9 hour irradiation in ~6.5x10^12 cm^-2s^-1 neutron flux. 4-8 hour gamma spectrometry after 2-3 week decay.	k0 method	IRMM-530R Al-Au wire	Balances calibrated to NATA standard; Gamma spectrometers calibrated against certified radioactive standards; reference material included in each batch.	Calculated by NAA software (k0 for Windows), validated against independent calculations.
	Cl		NAA: 1 minute irradiation in ~2.1x10^13 cm^-2s^-1 neutron flux. 12-18 minute gamma spectrometry after 10 minute decay.		NIST 3121 Au solution on filter paper		
	K		NAA: 9 hour irradiation in ~6.5x10^12 cm^-2s^-1 neutron flux. 1 hour gamma spectrometry after 4-6 day decay.		IRMM-530R Al-Au wire		
	Mg		NAA: 1 minute irradiation in ~2.1x10^13 cm^-2s^-1 neutron flux. 12-18 minute gamma spectrometry after 10 minute decay.		NIST 3121 Au solution on filter paper		
	Na		NAA: 1 minute irradiation in ~2.1x10^13 cm^-2s^-1 neutron flux. 12-18 minute gamma spectrometry after 10 minute decay.		NIST 3121 Au solution on filter paper		
	Zn		NAA: 9 hour irradiation in ~6.5x10^12 cm^-2s^-1 neutron flux. 4-8 hour gamma spectrometry after 2-3 week decay.		IRMM-530R Al-Au wire		

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
19	Cu	Digestion of sample spiked with ^{65}Cu in presence of 5 ml HNO_3 + 1 ml H_2O_2 in a micowave oven and closed vessel. Then ad hoc dilution	quadrupole ICP/MS	Double Isotope Dilution Mass Spectrometry IDMS	^{65}Cu spike (99.61 % Teknolab) characterised against high purity standard solution in house prepared from digestion of high purity solid (99.99999 % Prolabo).	IDMS analysis accredited 2.54 Cofrac	An uncertainty budget had been established in compliance with the GUM comprising uncertainties for weighing, ratio meaurements, fidelity, isotope abundances and corrections for blank . Our software calculate uncertainties propagation and the expanded final uncertainty (k=2)
	Hg	Digestion of sample spiked with ^{202}Hg in presence of 5 ml HNO_3 + 1 ml H_2O_2 in a micowave oven and closed vessel. Then ad hoc dilution	sector field ICP/MS with cold vapour generation; mercury was stabilized with BrCl (according to the EPA standard, 1631 E)		^{202}Hg spike (97.7% IRMM-ERM-AE640) characterised against high purity standard solution in house prepared from digestion of high purity solid (99.9999 % Merck). Used of ERM-AE639 for mass bias correction		
	Pb	Digestion of sample spiked with ^{206}Pb in presence of 5 ml HNO_3 + 1 ml H_2O_2 in a micowave oven and closed vessel. Then ad hoc dilution	sector field ICPMS		^{206}Pb spike (99.3 % Euriso-top) characterised against high purity standard solution in house prepared from digestion of high purity solid (99.99999 % Prolabo). Used NIST SRM 981 and 982 for mass bias correction		
	Se	Digestion of sample spiked with ^{77}Se in presence of 5 ml HNO_3 + 1 ml H_2O_2 in a micowave oven and closed vessel. Then ad hoc dilution	quadrupole ICP/MS with collision cell (He 1.5 ml/min + H_2 1.5 ml/min		^{77}Se spike (99.2 % Eurisotop) characterised against high purity standard solution in house prepared from digestion of high purity solid (99.999 % Alfa Aesar).		

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
20	Ca, Cu, Fe, K, Mg, Mn, Na, P, Zn	Microwave assisted digestion (UltraClave)	ICP-OES	external calibration; ionisation compensation with $CsCl_2$-sol. 1%	Multi-element standard IV (Merck)	Control standards (from independent stock solution) at the beginning, in the middle and the end of sample sequence; muva RVQS 437 test material	Estimation of the combined uncertainties from sample result and instrumentation
	Cd, Pb	Microwave assisted digestion	GF-AAS	Standard-Addition	Titrisol-standard (Merck)	Control standards (from independent stock solution) at the beginning, in the middle and the end of sample sequence; test material from pt FAPAS 1865	
	Cl	VDLUFA Vol.6C 10.6.2	titrimetric, $AgNO_3$		Cl-standard 0,1 mol/l; secondary ref.mat., Based on a NIST SRM (B.Kraft)		
	Co, Se	Microwave assisted digestion (UltraClave)	ICP-MS	IS Rhodium	Multi-element standard VI (Merck)	Control standards (from independent stock solution) at the beginning, in the middle and the end of sample sequence;	
	I	Microwave assisted digestion (UltraClave)	ICP-MS		Anion-standard (B.Kraft)	Control standards (from independent stock solution) at the beginning, in the middle and the end of sample sequence; test material from pt FAPAS 1865	
	Hg	no sample preparation	DMA (Direct Mercury Analyser)		Certipur-standard (Merck)	Control standards (from independent stock solution) at the beginning, in the middle and the end of sample sequence; test material from pt FAPAS 07172	

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
21	Ca, Cu, Fe, K, Mg, Na, P, Zn	Microwave assisted digestion in 5 mL nitric acid (conc.), diluted in water to 2 % acid.	ICP-OES	External with minimum 4 standards	Merck Certipur	Measurement of SRM-1549 and BCR-063r	Through a validation study. Includes uncertainty contributions from trueness, intermediate precision and repeatability.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
22	Cd, Co, Cu, Mn, Pb, Se, Zn	Microwave assisted digestion in 5 mL nitric acid (conc.) diluted in water to 2 % acid.	ICP-MS collision cell with He	External with minimum 4 standards	Merck Certipur	Measurement of SRM-1549 and BCR-063r	Through a validation study. Includes uncertainty contributions from trueness, intermediate precision and repeatability.

Lab Code	Element	Sample preparation method	Measurement technique	Calibration method	Standard or reference material used for calibration	Quality Assurance	Uncertainty estimation
23	Cd, Co, Cu, Mn, Pb, Se, Zn	Microwave assisted digestion in 5 mL nitric acid (conc.), evaporation of residue and dissolution in 5 % ethanoic acid	ICP-MS collision cell with H_2	External with minimum 4 standards	Merck Certipur	Measurement of SRM-1549 and BCR-063r	Through a validation study. Includes uncertainty contributions from trueness, intermediate precision and repeatability.

CERTIFICATION REPORT

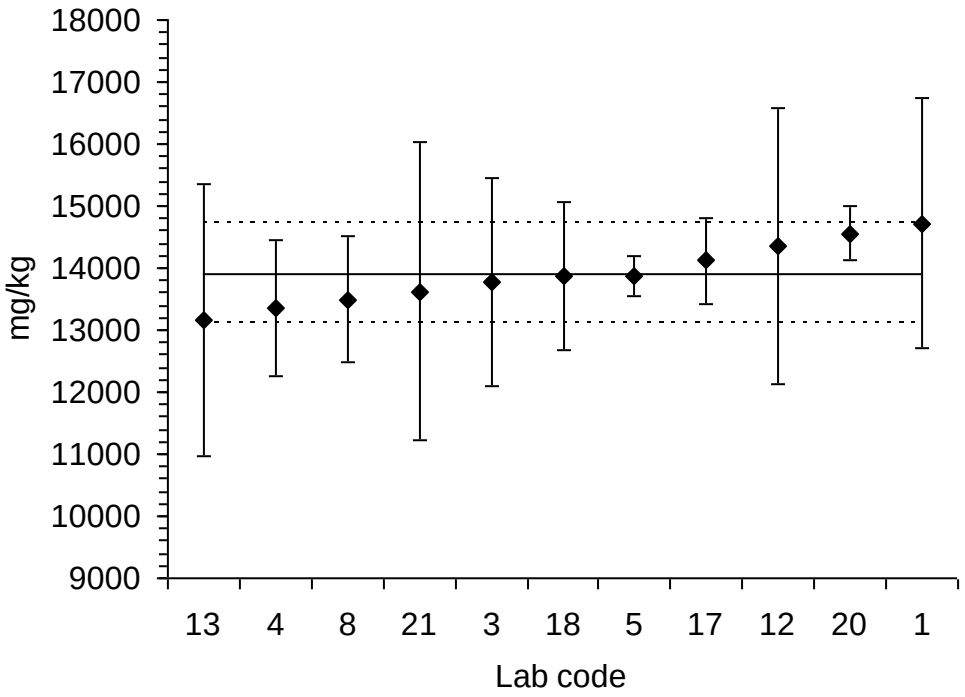
The certification of the mass fractions of elements in skimmed milk powders: ERM BD150 and ERM BD151

Annex E: Results of the characterisation measurements

Tables present the results of characterisation measurements (corrected to dry mass) and the estimated uncertainties of the measurements, as reported by participants. Some reported values were rounded for formatting reasons. Graphs show expanded uncertainties as stated by the laboratories and the certified range, and are given for the accepted datasets only.

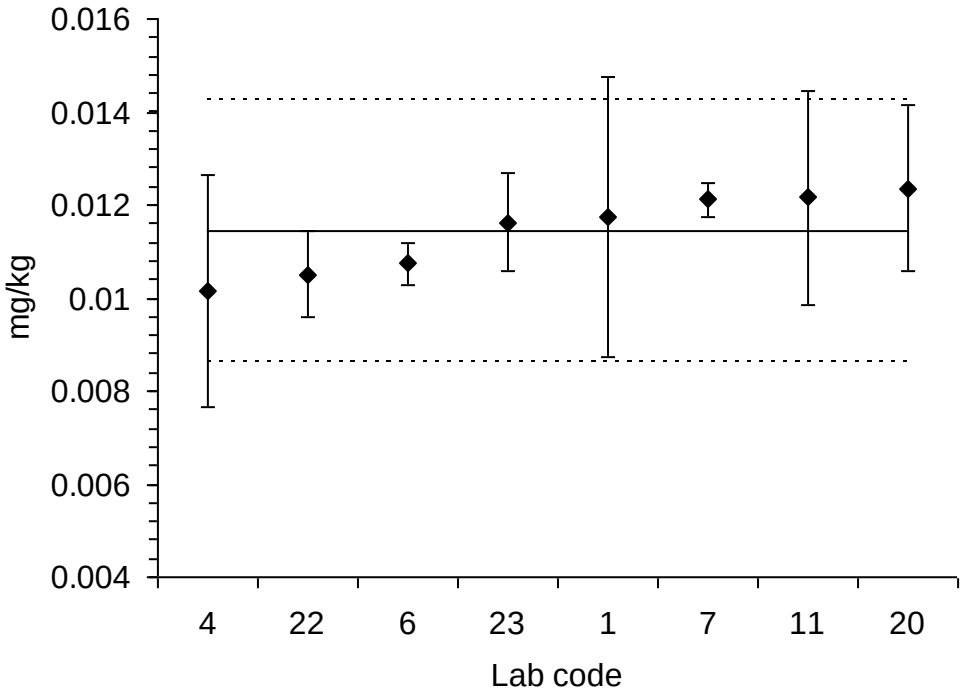
Ca in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	14327	14563	14003	14923	15574	14946	14723	2025
3	FAAS	13683	13634	13975	13620	13898	13909	13787	1677
4	ICP-SFMS	13500	13400	13300	13300	13400	13200	13350	1100
5	ICP-OES	13713	14034	13713	13927	13820	14034	13874	333
8	k0-INAA	13549	13894	13377	13471	13568	13064	13487	1013
12	ICP-OES	14400	14400	14100	14400	14100	14800	14367	2230
13	ICP-MS	14000	13000	12000	14000	13000	13000	13167	2200
17	k0-INAA	14100	14200	14200	14300	14400	13500	14117	700
18	k0-INAA	13440	14190	13850	14010	13250	14460	13867	1190
20	ICP-OES	14445	14465	14770	14340	14575	14780	14562	449
21	ICP-OES	13676	13721	13790	13641	13471	13444	13624	2413



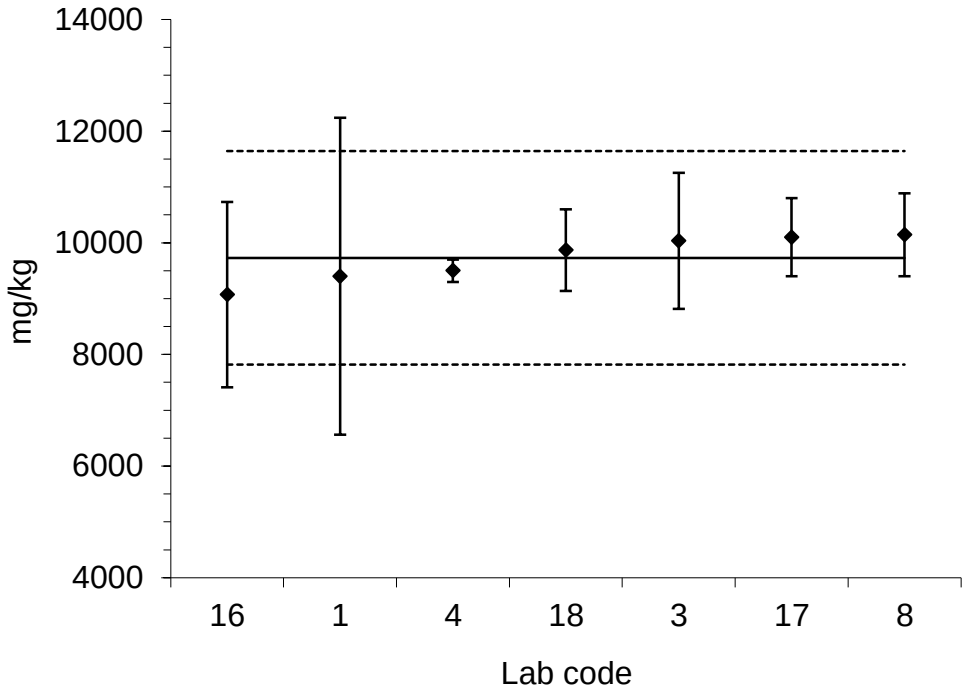
Cd in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.0102	0.0116	0.0114	0.016	0.0108	0.0104	0.0117	0.0030
4	ICP-SFMS	0.0104	0.0097	0.0102	0.0102	0.0101	0.0103	0.0102	0.0025
6	ICP-MS	0.01073	0.01084	0.01105	0.01062	0.01084	0.01040	0.0107	0.0005
7	ICP-SFMS	0.01232	0.01211	0.01221	0.01211	0.01221	0.01178	0.0121	0.0004
11	ICP-MS	0.0125	0.0123	0.0124	0.0127	0.0114	0.0117	0.0122	0.0023
20	GFAAS	0.01196	0.01138	0.01280	0.01290	0.01237	0.01274	0.0124	0.0018
22	ICP-MS	0.01065	0.01026	0.01023	0.01129	0.01004	0.01061	0.0105	0.0009
23	ICP-MS	0.01257	0.01159	0.01106	0.01133	0.01108	0.01214	0.0116	0.0010



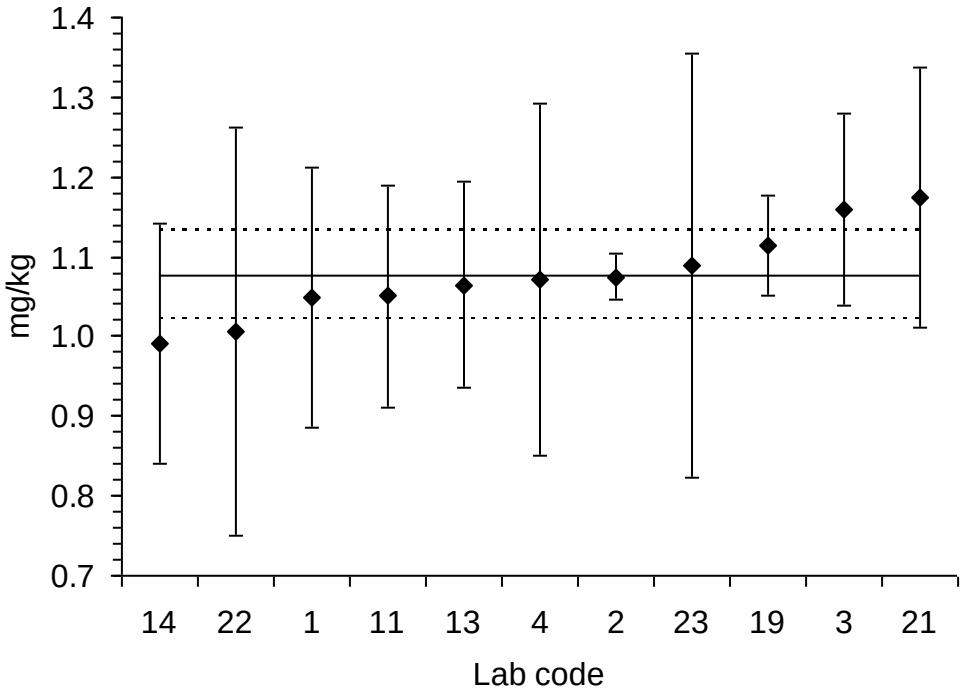
Cl in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	9197	8595	11357	8329	8485	10432	9399	2839
3	titrimetric	9969	10104	9981	10157	9985	9998	10032	1219
4	ICP-SFMS	9650	9570	9580	9370	9340	9490	9500	200
8	k0-INAA	10142	10037	10102	10220	10040	10315	10143	742
16	IC	9060	9070	8870	9210	9030	9170	9068	1660
17	k0-INAA	10100	10300	9900	10200	10200	9900	10100	700
18	k0-INAA	9910	9620	10160	9740	10080	9690	9867	730
Results not included in the characterisation dataset									
5	ICP-OES	11463	11356	11249	11570	11463	11470		
20	titrimetric	10682	9961	9377	9628	10059	10210		



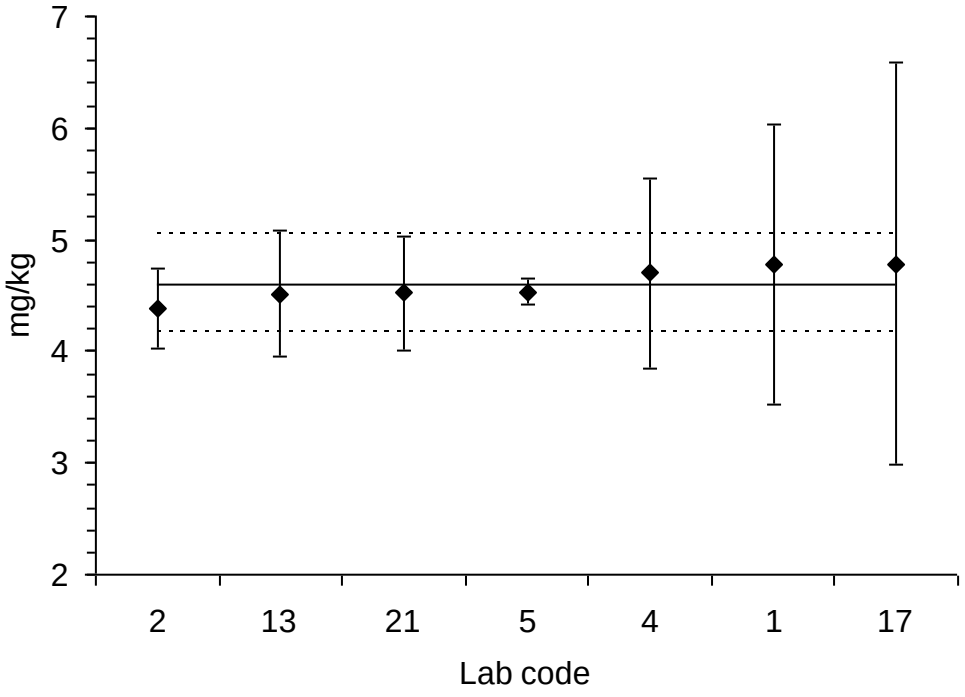
Cu in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	1.043	1.089	1.05	1.024	1.046	1.044	1.049	0.163
2	ID-ICP-MS	1.0839	1.0650	1.0498	1.0750	1.0885	1.0847	1.074	0.029
3	GFAAS	1.19	1.13	1.15	1.19	1.14	1.15	1.158	0.120
4	ICP-SFMS	1.08	1.08	1.07	1.07	1.06	1.07	1.072	0.220
11	ICP-MS	1.073	1.022	1.044	1.043	1.071	1.049	1.050	0.139
13	ICP-MS	1.1	1.1	0.99	1.1	1	1.1	1.065	0.130
14	ET-AAS	1.03	1.02	1.01	0.99	0.93	0.97	0.992	0.150
19	ID-ICP-MS	1.093	1.104	1.159	1.109	1.058	1.16	1.114	0.062
21	ICP-OES	1.2096	1.1894	1.1930	1.1340	1.1686	1.1484	1.174	0.163
22	ICP-MS	1.0819	1.0783	1.0799	0.9496	0.8896	0.9590	1.006	0.255
23	ICP-MS	1.1303	1.1042	1.1011	1.0621	1.0538	1.0837	1.089	0.267
Results not included in the characterisation dataset									
5	ICP-OES	0.92	0.946	0.916	0.929	0.945	0.962		
6	ICP-MS	0.9471	0.9439	0.9535	0.9471	0.9642	0.9407		
7	ICP-SFMS	0.9330	0.9330	0.9482	0.9330	0.9330	0.9482		
20	ICP-OES	1.4786	1.3119	1.4006	1.2724	1.2257	1.2493		



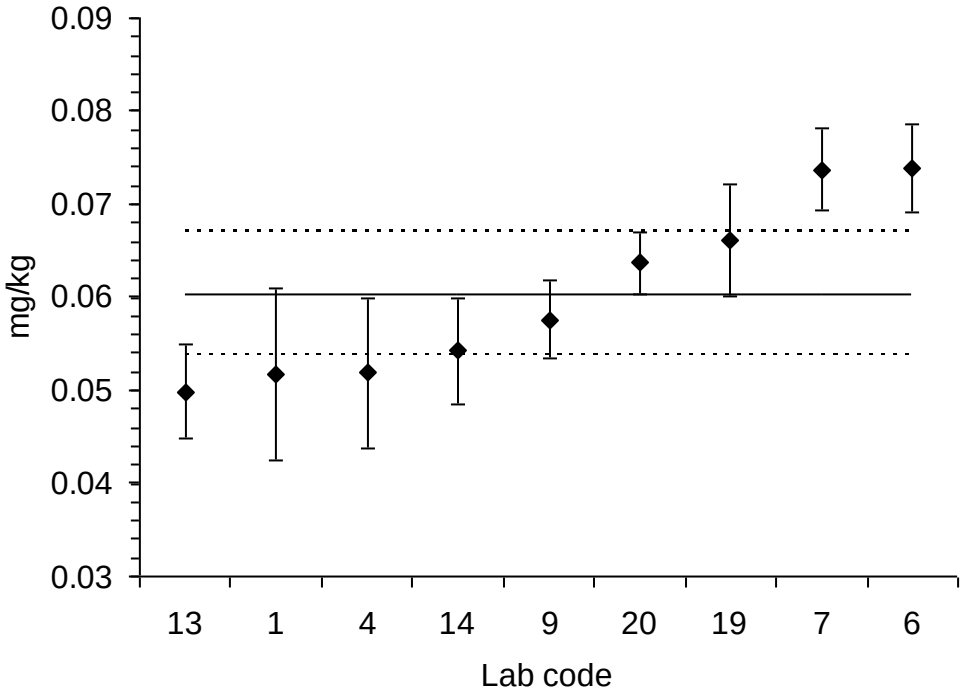
Fe in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	6.256	5.313	4.389	4.132	4.503	4.052	4.77	1.25
2	ID-ICP-MS	4.4140	4.3362	4.3801	4.3421	4.5348	4.3327	4.39	0.36
4	ICP-SFMS	4.72	4.74	4.66	4.68	4.74	4.65	4.70	0.85
5	ICP-OES	4.53	4.48	4.65	4.51	4.53	4.51	4.54	0.12
13	ICP-MS	4.7	4.5	4.5	4.3	4.4	4.7	4.52	0.56
17	k0-INAA	3.8	5.6	5.1	4.1	5.3	<3.6	4.78	1.80
21	ICP-OES	4.3711	4.4044	4.4333	4.6662	4.7395	4.4983	4.52	0.52
Results not included in the characterisation dataset									
3	FAAS	5.76	5.36	4.99	4.75	5.42	4.68		
20	ICP-OES	5.6437	4.6606	5.1295	5.7738	5.4762	4.7407		



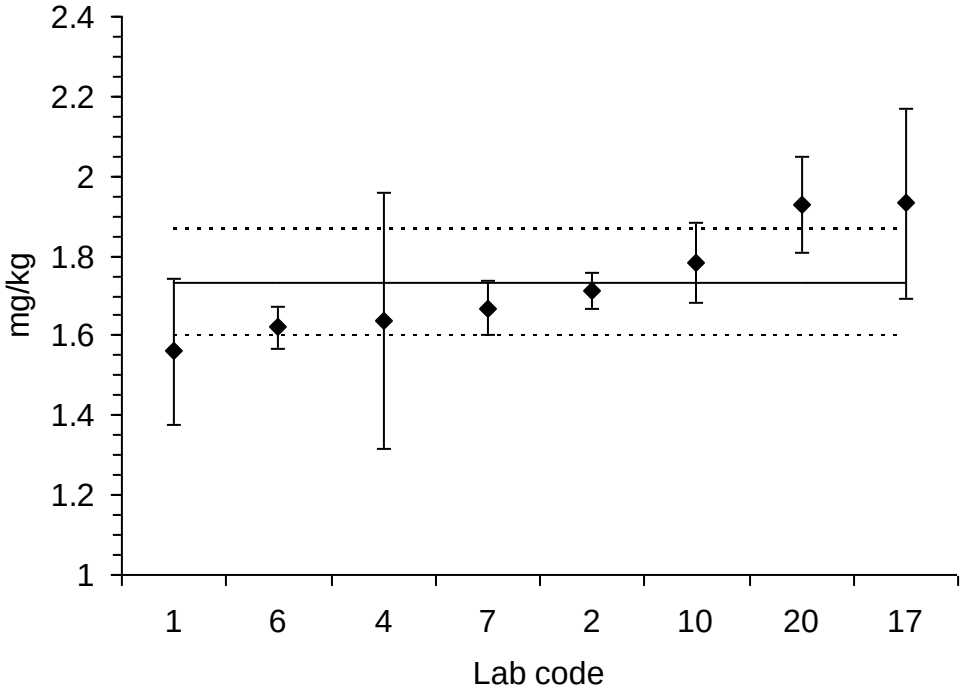
Hg in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.0546	0.0576	0.0533	0.0492	0.0474	0.0481	0.0517	0.0092
4	ICP-SFMS	0.052	0.05	0.053	0.052	0.051	0.053	0.0518	0.0080
6	ICP-MS	0.0764	0.0733	0.0697	0.0756	0.0719	0.0763	0.0739	0.0131
7	ICP-SFMS	0.0772	0.0746	0.0780	0.0712	0.0710	0.0702	0.0737	0.0131
9	DMA	0.0578	0.0577	0.0572	0.0578	0.0574	0.0577	0.0576	0.0042
13	CV-AFS	0.0504	0.0498	-	0.05	0.049	0.05	0.0498	0.0089
14	CV-AAS	0.0569	0.0547	0.0548	0.0524	0.0529	0.0541	0.0543	0.0057
19	ID-ICP-MS	0.066	0.069	0.069	0.067	0.063	0.063	0.0662	0.0060
20	DMA	0.0648	0.0627	0.0637	0.0634	0.0624	0.0650	0.0637	0.0032



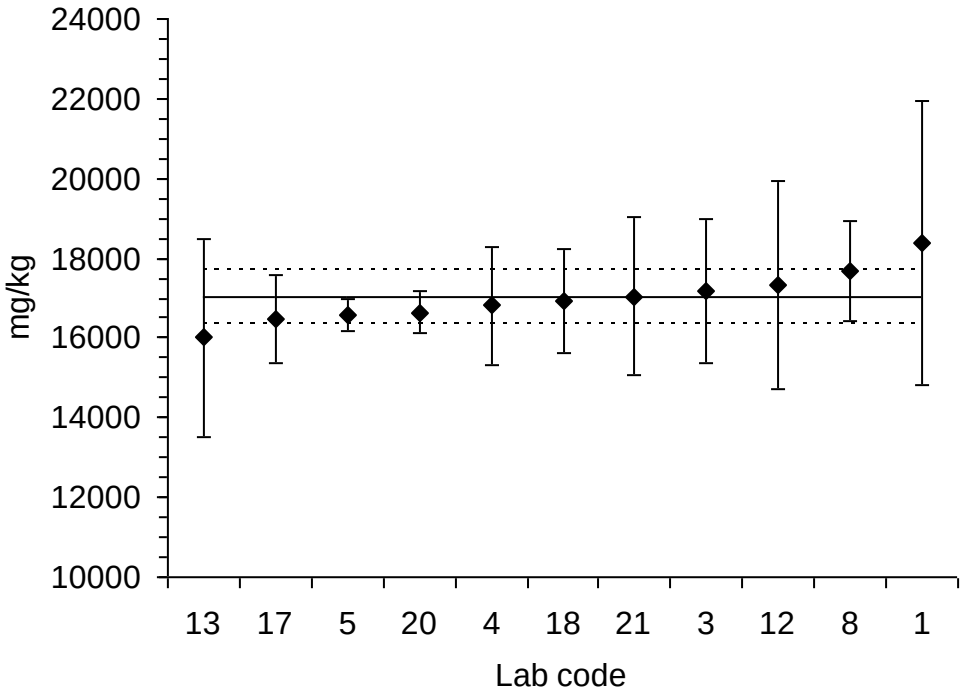
I in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	1.572	1.498	1.591	1.645	1.525	1.527	1.560	0.181
2	ID-ICP-MS	1.7269	1.7054	1.7040	1.7254	1.6516	1.7709	1.714	0.045
4	ICP-SFMS	1.62	1.61	1.66	1.61	1.63	1.69	1.637	0.320
6	ICP-MS	1.62	1.62	1.60	1.64	1.64	1.62	1.621	0.052
7	ICP-SFMS	1.72	1.64	1.69	1.66	1.68	1.63	1.669	0.067
10	RNAA	1.72	1.78	1.70	1.86	1.82	1.81	1.782	0.100
17	k0-INAA	2.11	1.73	1.94	1.91	1.9	2	1.932	0.240
20	ICP-MS	1.9026	1.9109	1.9981	1.9660	1.8774	1.9172	1.929	0.232
Results not included in the characterisation dataset									
15	HPLC-ICP-MS	0.429	0.498	0.38	0.367	0.431	0.494		



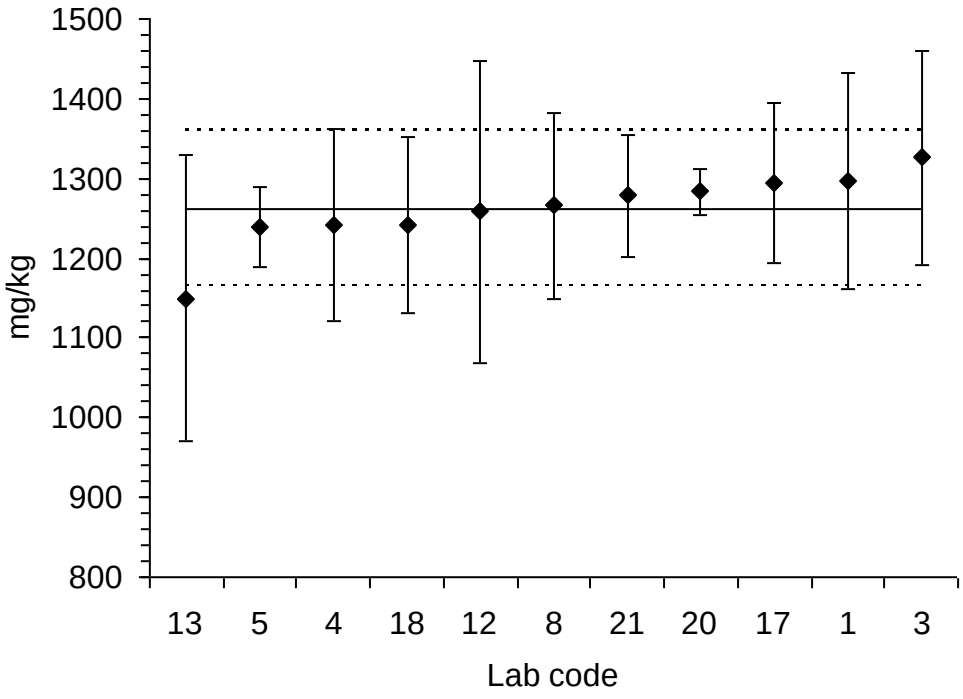
K in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	16991	17467	17167	19828	19524	19275	18375	3569
3	FAAS	16649	16826	17201	18034	17033	17250	17166	1803
4	ICP-SFMS	16900	16700	16300	16700	16900	17300	16800	1500
5	ICP-OES	16392	16606	16392	16820	16820	16499	16588	398
8	k0-INAA	17919	17736	17499	17662	17426	17747	17665	1263
12	ICP-OES	17400	17500	17100	17500	17200	17200	17317	2620
13	ICP-MS	16000	16000	15000	16000	16000	17000	16000	2500
17	k0-INAA	16500	16500	16700	16500	16500	16200	16483	1100
18	k0-INAA	16500	16700	16900	16800	17000	17700	16933	1300
20	GFAAS	16365	16725	16540	16505	16855	16870	16643	514
21	ICP-OES	16895	16855	16917	17286	17213	17113	17046	1986



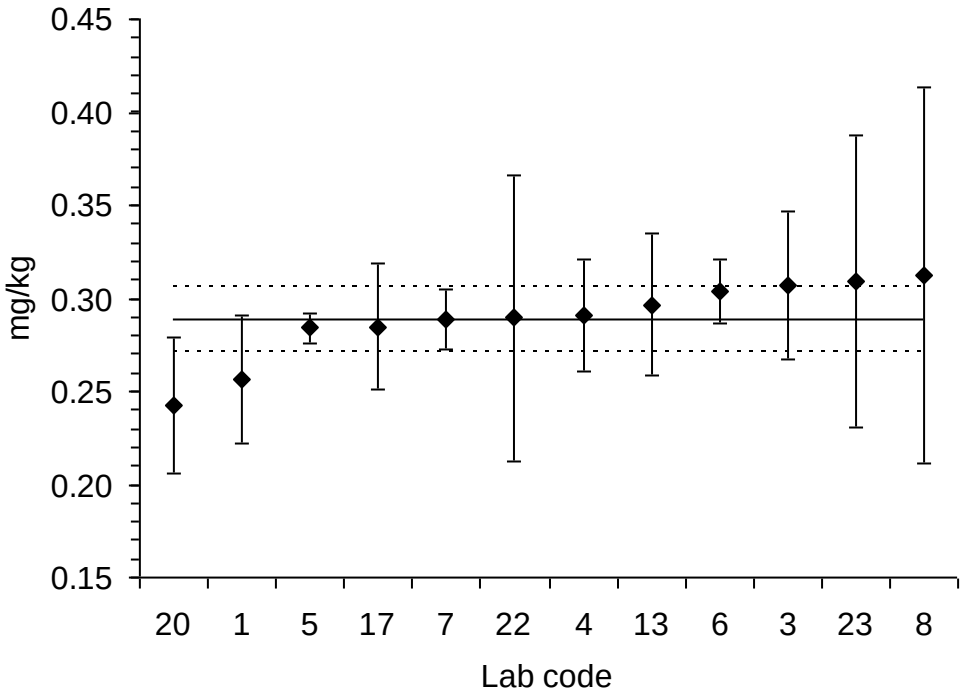
Mg in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	1227	1265	1238	1352	1361	1341	1297	136
3	ET-/F-AAS	1348	1297	1318	1325	1327	1340	1326	135
4	ICP-SFMS	1250	1250	1240	1240	1220	1250	1242	120
5	ICP-OES	1232	1200	1264	1264	1253	1221	1239	50
8	k0-INAA	1196	1222	1305	1277	1236	1362	1266	117
12	ICP-OES	1280	1230	1280	1240	1230	1290	1258	190
13	ICP-MS	1200	1200	1100	1100	1100	1200	1150	180
17	k0-INAA	1280	1320	1310	1280	1310	1270	1295	100
18	k0-INAA	1240	1240	1260	1210	1300	1200	1242	110
20	ICP-OES	1288	1292	1272	1274	1277	1297	1283	29
21	ICP-OES	1277	1279	1287	1284	1276	1266	1278	77



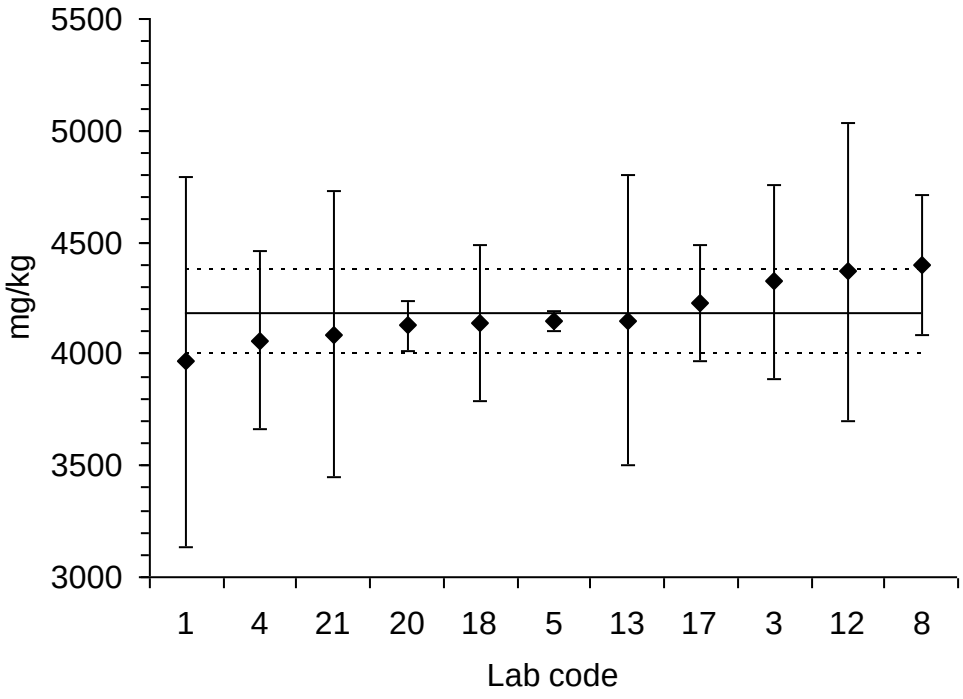
Mn in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.2519	0.2596	0.2509	0.2579	0.2638	0.2527	0.256	0.034
3	FAAS	0.3	0.31	0.3	0.32	0.3	0.31	0.307	0.040
4	ICP-SFMS	0.292	0.291	0.291	0.291	0.288	0.293	0.291	0.030
5	ICP-OES	0.27855	0.27963	0.29034	0.28713	0.29248	0.27534	0.284	0.009
6	ICP-MS	0.31284	0.30534	0.30534	0.31177	0.29462	0.29248	0.304	0.017
7	ICP-SFMS	0.29248	0.28820	0.29141	0.29784	0.28605	0.27427	0.288	0.016
8	k0-INAA	0.349	0.347	0.307	0.257	0.29	0.326	0.313	0.101
13	ICP-MS	0.28	0.29	0.3	0.3	0.29	0.32	0.297	0.038
17	k0-INAA	0.283	0.293	0.261	0.286	0.287	0.299	0.285	0.034
20	ICP-OES	0.25669	0.23010	0.24438	0.25255	0.23981	0.23021	0.242	0.048
22	ICP-MS	0.31259	0.29040	0.29426	0.28273	0.26684	0.28903	0.289	0.077
23	ICP-MS	0.30969	0.31953	0.30937	0.30180	0.29506	0.31687	0.309	0.079



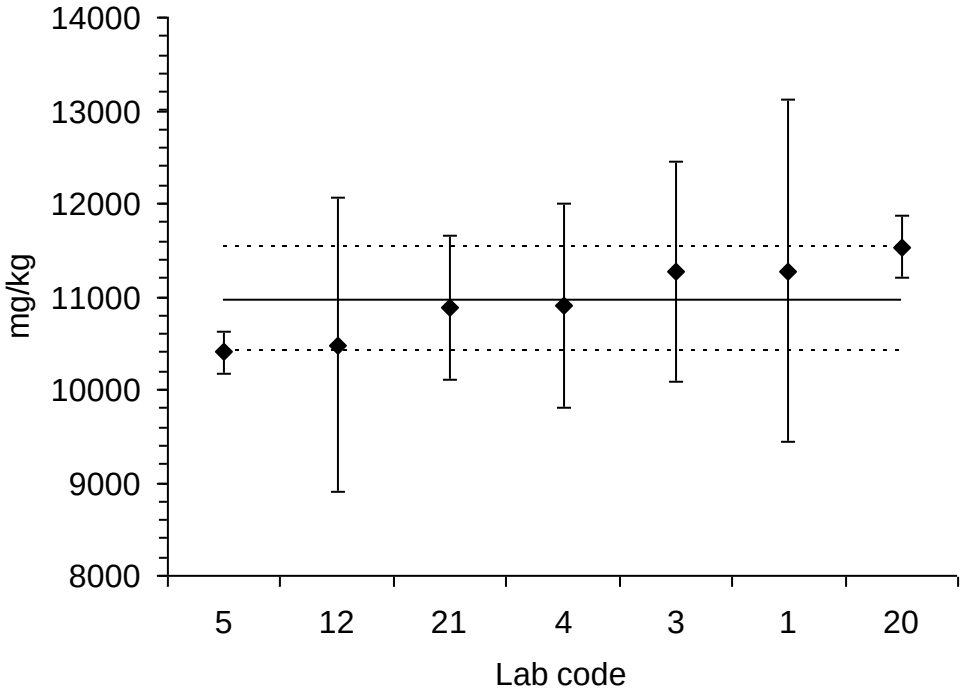
Na in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	3733	3928	3829	4144	4090	4080	3967	829
3	FAAS	4333	4300	4366	4275	4335	4324	4322	437
4	ICP-SFMS	4100	4060	4050	4040	4000	4120	4062	400
5	ICP-OES	4135	4146	4168	4146	4146	4135	4146	41
8	k0-INAA	4462	4439	4313	4403	4370	4395	4397	313
12	ICP-OES	4310	4330	4440	4380	4340	4400	4367	670
13	ICP-MS	4300	4300	3900	4100	4000	4300	4150	650
17	k0-INAA	4250	4280	4170	4200	4250	4200	4225	260
18	k0-INAA	4210	4000	4270	4060	4260	4040	4140	350
20	ICP-OES	4102.2	4152.9	4108.5	4061.0	4149.6	4180.1	4126	109
21	ICP-OES	4048.5	4041.0	4059.1	4138.1	4116.4	4106.6	4085	641



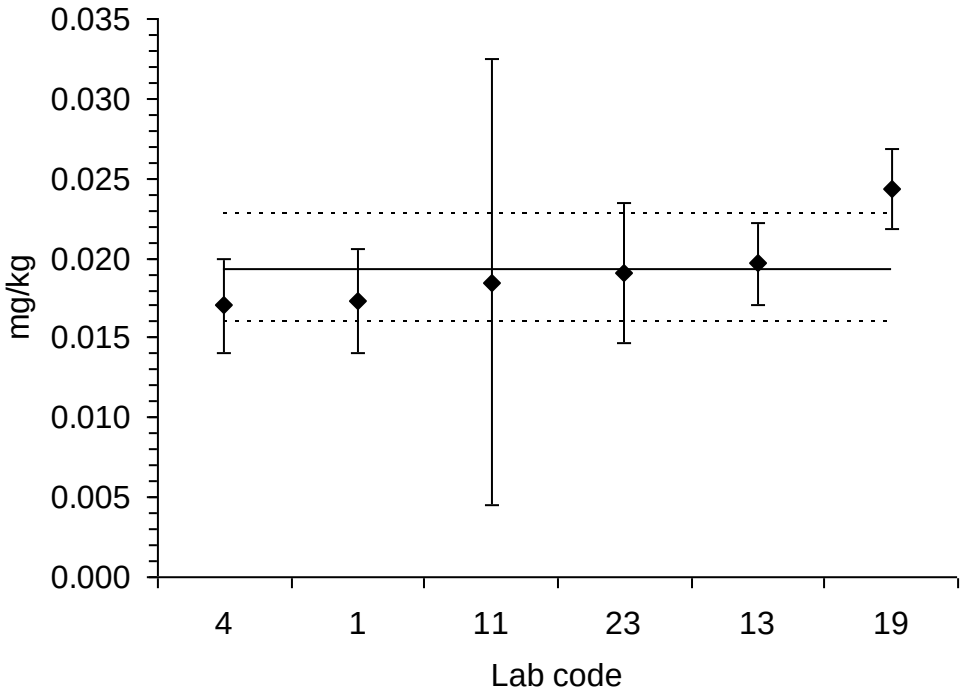
P in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	10967	11524	11411	11349	11268	11157	11279	1844
3	FAAS	10843	10926	11353	11882	11201	11428	11272	1188
4	ICP-SFMS	10800	10800	10900	11000	10900	11000	10900	1100
5	ICP-OES	10553	10339	10392	10532	10242	10371	10405	229
12	ICP-OES	10600	10400	10600	10300	10500	10500	10483	1590
20	ICP-OES	11400	11505	11720	11360	11600	11620	11534	335
21	ICP-OES	10886	10918	10948	10916	10830	10780	10880	766



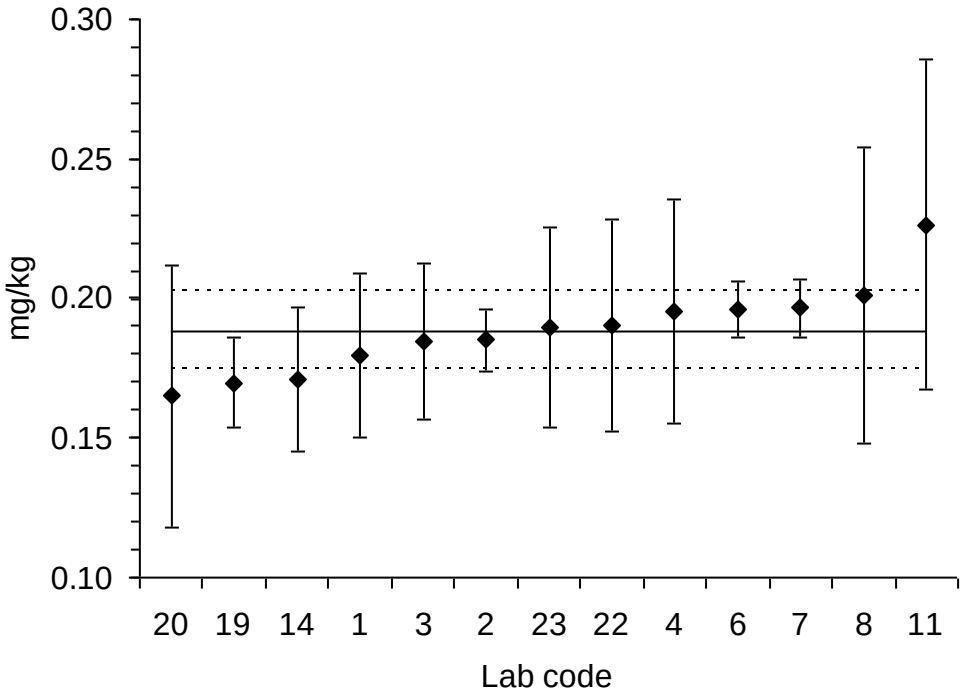
Pb in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.025	0.0169	0.0146	0.0163	0.0152	0.0159	0.0173	0.0033
4	ICP-SFMS	0.017	0.017	0.017	0.017	0.017	0.017	0.0170	0.0030
11	ICP-MS	0.028	0.016	0.012	0.023	0.016	0.016	0.0185	0.0140
13	ICP-MS	0.021	0.016	0.018	0.021	0.021	0.021	0.0197	0.0026
19	ID-ICP-MS	0.027	0.023	0.027	0.021	0.024	0.024	0.0243	0.0049
23	ICP-MS	0.01688	0.01901	0.01788	0.02591	0.01751	0.01707	0.0190	0.0044
Results not included in the characterisation dataset									
6	ICP-MS	0.01071	0.00964	0.00836	0.00836	0.01082	0.01061		
7	ICP-SFMS	0.00997	0.00889	0.00856	0.00769	0.00845	0.00910		
20	GFAAS	0.01515	0.01358	0.01410	0.01206	0.01573	0.01572		
22	ICP-MS	0.01219	0.01236	0.01219	0.01415	0.01790	0.01440		



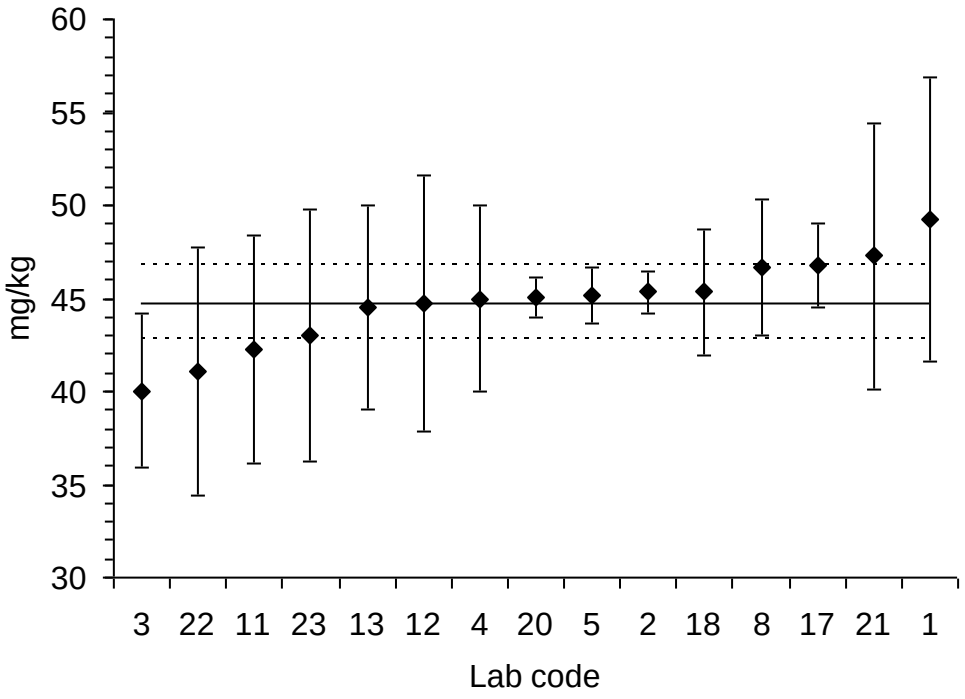
Se in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.1774	0.1839	0.1813	0.178	0.1819	0.1753	0.180	0.029
2	ID-ICP-MS	0.18430	0.17933	0.18162	0.18755	0.18710	0.18986	0.185	0.011
3	HG-AAS	0.184	0.184	0.187	0.182	0.184	0.185	0.184	0.028
4	ICP-SFMS	0.194	0.203	0.196	0.202	0.177	0.2	0.195	0.040
6	ICP-MS	0.19614	0.19397	0.19505	0.19722	0.19505	0.19830	0.196	0.010
7	ICP-SFMS	0.19392	0.19820	0.20677	0.19070	0.19285	0.19606	0.196	0.010
8	k0-INAA	0.178	0.189	0.216	0.221	0.171	0.233	0.201	0.053
11	ICP-MS	0.23	0.242	0.218	0.222	0.221	0.226	0.227	0.059
14	HG-AAS	0.167	0.171	0.171	0.176	0.169	0.172	0.171	0.026
19	ID-ICP-MS	0.166	0.176	0.168	0.157	0.174	0.177	0.170	0.016
20	ICP-OES	0.17841	0.16712	0.14483	0.17820	0.16191	0.15922	0.165	0.047
22	ICP-MS	0.19359	0.18810	0.18036	0.18622	0.19002	0.20361	0.190	0.038
23	ICP-MS	0.19369	0.19164	0.18800	0.18249	0.18923	0.19189	0.189	0.036
Results not included in the characterisation dataset									
17	k0-INAA	0.24	0.21	0	0.2	0	0		



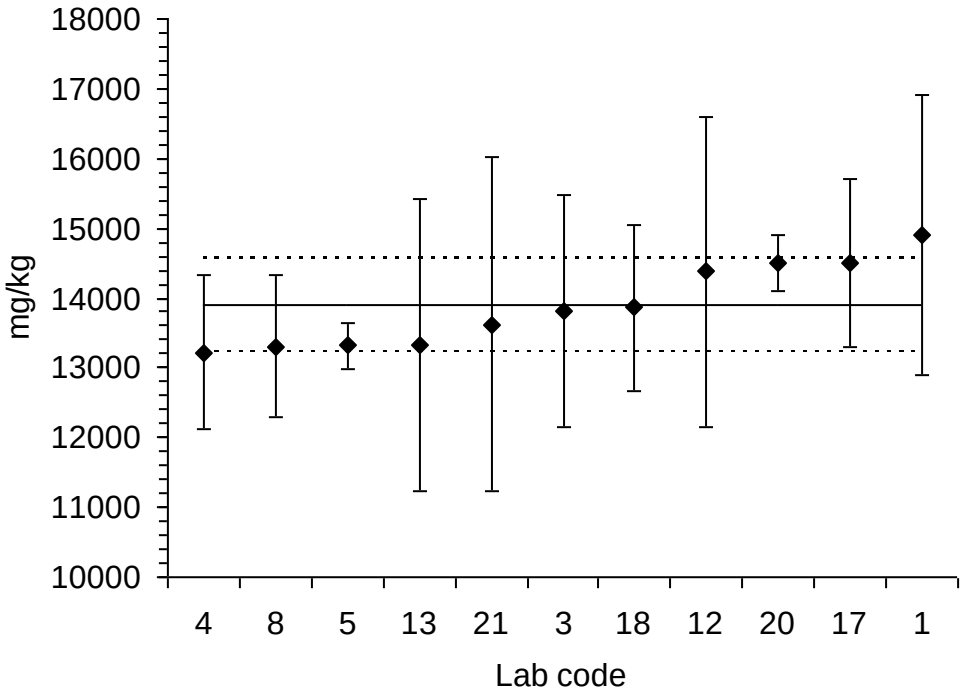
Zn in ERM-BD150

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	46.93	48.73	49.21	50.90	49.90	49.52	49.2	7.6
2	ID-ICP-MS	44.701	44.927	45.136	46.235	45.376	45.563	45.3	1.2
3	FAAS	40.1	39.9	40.7	40.1	40	39.5	40.1	5.4
4	ICP-SFMS	45.3	44.8	45	44.2	45.5	45.1	45.0	5.0
5	ICP-OES	46.07	45.75	44.89	44.78	44.68	44.68	45.1	1.5
8	k0-INAA	47.7	47	45.2	46.7	46.5	46.9	46.7	3.7
11	ICP-MS	44.1	41.5	41.8	42.1	41.8	42.1	42.2	6.1
12	ICP-OES	44.6	44.4	44.3	44.8	44.5	45.7	44.7	6.9
13	ICP-MS	45	45	43	44	44	46	44.5	5.5
17	k0-INAA	48.3	47.8	47	46.9	47.5	43.1	46.8	2.3
18	k0-INAA	43.8	46.3	45.8	45.7	44.2	46.3	45.4	3.4
20	ICP-OES	45.263	45.060	45.164	44.893	44.563	45.387	45.1	1.0
21	ICP-OES	47.694	47.658	47.972	46.294	47.395	46.538	47.3	7.1
22	ICP-MS	43.702	43.567	43.657	39.106	36.915	39.649	41.1	6.6
23	ICP-MS	44.410	43.710	44.721	41.744	41.331	42.256	43.0	6.8



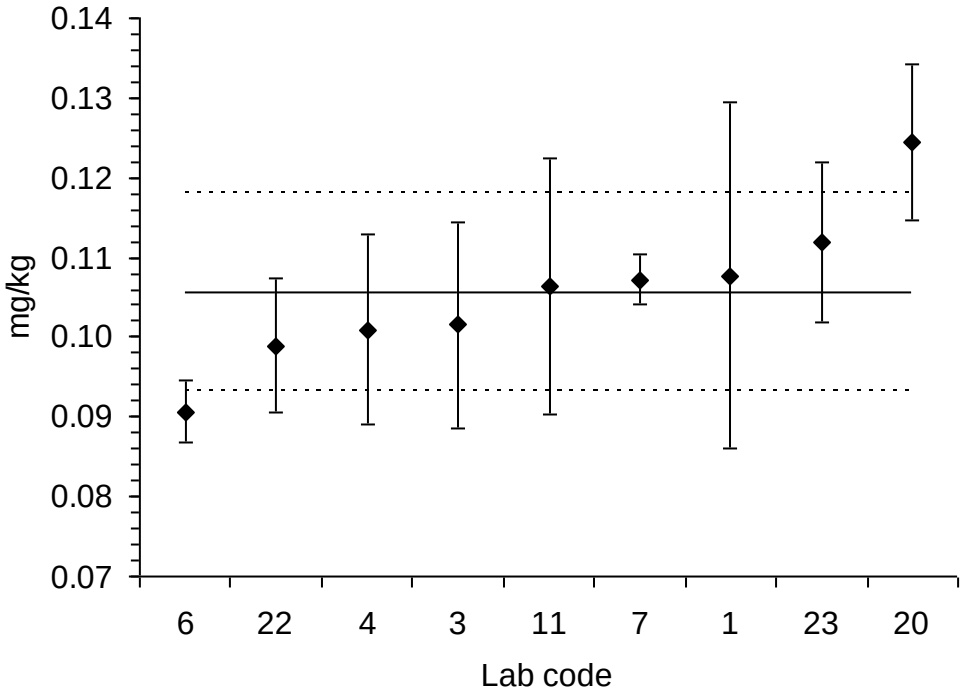
Ca in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	14515	14500	14987	15448	14917	15107	14912	2008
3	FAAS	13788	13807	13887	13735	13921	13759	13816	1670
4	ICP-SFMS	13400	13200	13200	13100	13200	13200	13217	1100
5	ICP-OES	13208	13313	13208	13102	13419	13630	13313	320
8	k0-INAA	13576	13586	12753	13606	13117	13213	13309	1018
12	ICP-OES	14200	13900	14600	14400	14400	14800	14383	2220
13	ICP-MS	14000	14000	13000	13000	13000	13000	13333	2100
17	k0-INAA	14100	14400	14600	14400	15000	14500	14500	1200
18	k0-INAA	13440	14190	13850	14010	13250	14460	13867	1190
20	ICP-OES	14250	14610	14530	14445	14730	14425.1	14498	403
21	ICP-OES	13737.9	13654.4	13727.4	13510.6	13641.1	13470.7	13624	2404



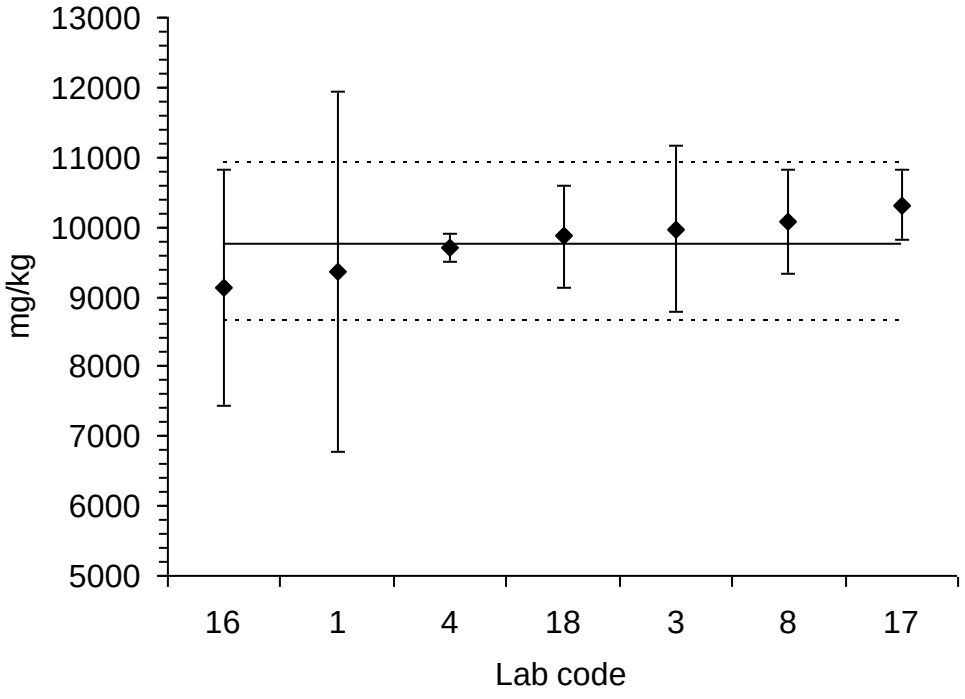
Cd in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.1074	0.1054	0.1144	0.1108	0.1045	0.1034	0.1077	0.0217
3	GFAAS	0.108	0.107	0.108	0.093	0.096	0.097	0.1015	0.0130
4	ICP-SFMS	0.102	0.0998	0.0999	0.102	0.1	0.102	0.1010	0.0120
6	ICP-MS	0.08740	0.09057	0.09025	0.09310	0.09194	0.09067	0.0907	0.0131
7	ICP-SFMS	0.10672	0.10556	0.10883	0.10778	0.10672	0.10778	0.1072	0.0032
11	ICP-MS	0.102	0.105	0.108	0.106	0.107	0.11	0.1063	0.0160
20	GFAAS	0.12002	0.13330	0.12008	0.12559	0.12552	0.12156	0.1243	0.0180
22	ICP-MS	0.10025	0.10111	0.09493	0.09915	0.09858	0.09962	0.0989	0.0084
23	ICP-MS	0.12122	0.11049	0.11066	0.11057	0.11065	0.10830	0.1120	0.0101



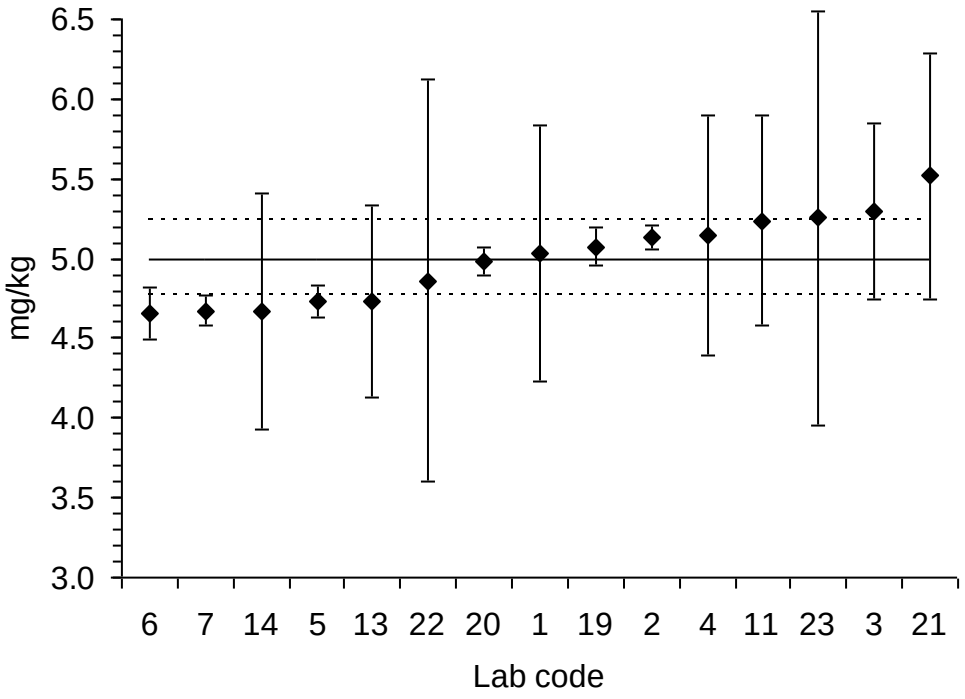
Cl in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	10342	9148	8407	10204	8811	9185	9350	2585
3	titrimetric	9955	9942	9999	9965	9970	9998	9972	1200
4	ICP-SFMS	9700	9710	10100	9520	9520	9730	9713	200
8	k0-INAA	10223	9996	9967	10358	9943	9973	10077	737
16	IC	9000	9110	8770	9320	9400	9100	9117	1690
17	k0-INAA	10100	10300	10300	10200	10700	10300	10317	500
18	k0-INAA	9910	9620	10160	9740	10080	9690	9867	730
Results not included in the characterisation dataset									
5	ICP-OES	11309	11196	11175	11161	11308	11189		
20	titrimetric	9560	10034	10341	9961	10439	9810		



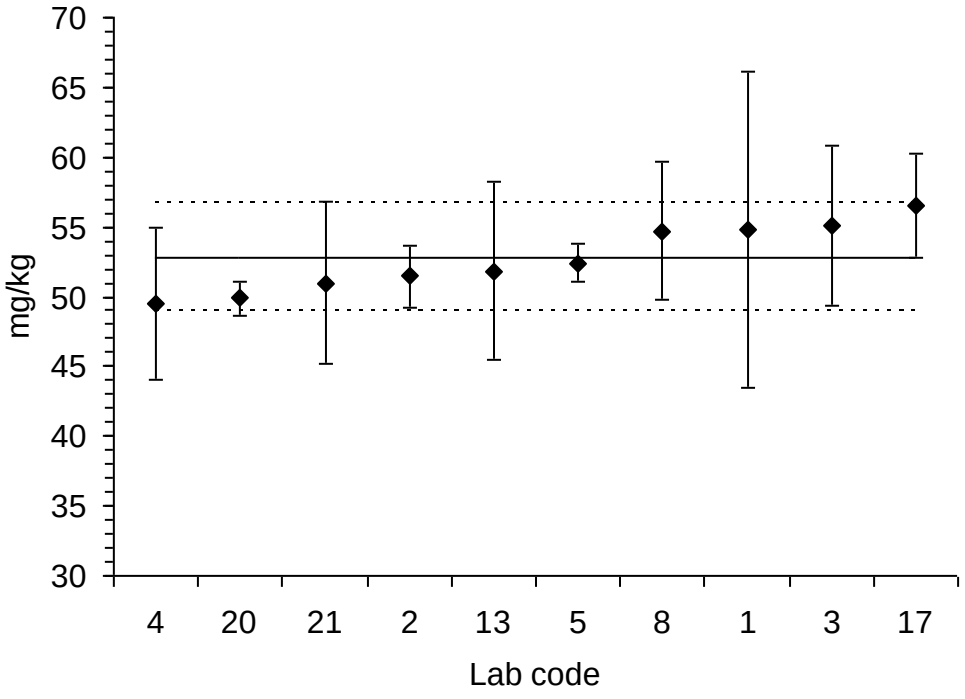
Cu in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	5.105	5.05	5.347	4.889	4.909	4.911	5.04	0.80
2	ID-ICP-MS	5.1034	5.1709	5.1106	5.1283	5.1271	5.1258	5.13	0.07
3	ET-AAS	5.39	5.43	5.47	5.1	5.18	5.18	5.29	0.55
4	ICP-SFMS	5.17	5.12	5.12	5.14	5.19	5.11	5.14	0.75
5	ICP-OES	4.72	4.77	4.66	4.81	4.71	4.72	4.73	0.95
6	ICP-MS	4.55	4.68	4.56	4.73	4.67	4.73	4.66	0.93
7	ICP-SFMS	4.67	4.70	4.65	4.64	4.70	4.65	4.67	0.93
11	ICP-MS	5.20	5.17	5.33	5.18	5.23	5.31	5.24	0.66
13	ICP-MS	4.8	5	4.8	4.7	4.5	4.6	4.73	0.60
14	GFAAS	4.82	4.78	4.49	4.93	4.53	4.47	4.67	0.74
19	ID-ICP-MS	5.002	5.107	5.085	5.144	4.992	5.119	5.07	0.12
20	ICP-OES	5.0041	4.9463	4.9473	5.0160	5.0071	4.9840	4.98	0.09
21	ICP-OES	5.7209	5.7193	5.7066	5.3665	5.3065	5.2974	5.52	0.77
22	ICP-MS	5.3406	5.3318	4.8060	4.5037	4.5322	4.6277	4.86	1.26
23	ICP-MS	5.3583	5.2172	5.4834	5.1716	5.1720	5.1186	5.25	1.29



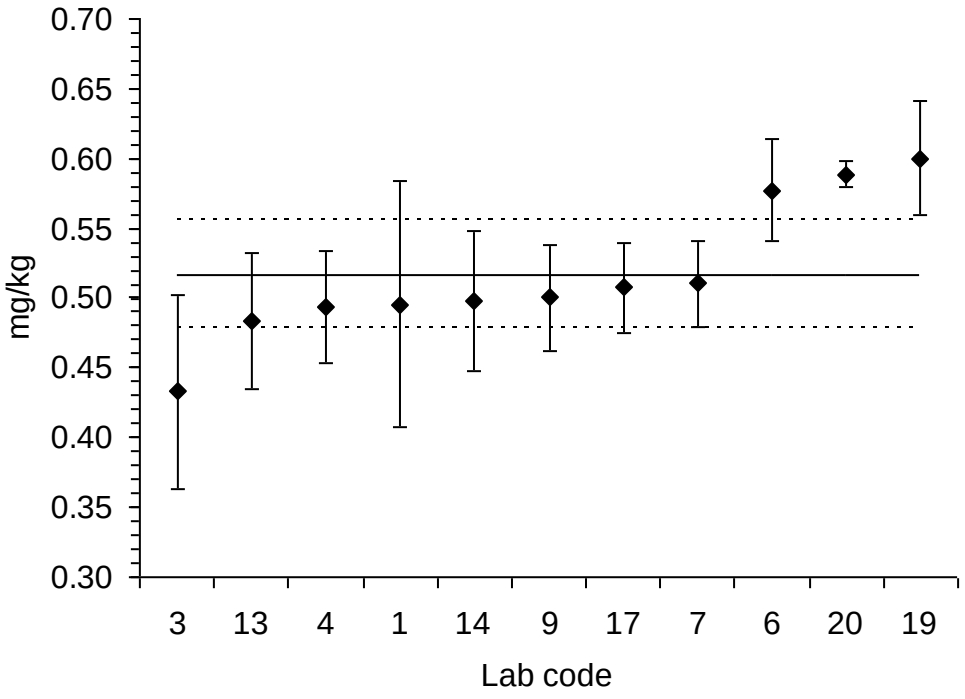
Fe in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	54.92	53.49	56.56	54.40	55.01	54.64	54.8	11.3
2	ID-ICP-MS	51.665	51.265	52.019	51.455	51.072	51.244	51.5	2.3
3	FAAS	51.2	53.7	53	57.8	57.6	57.2	55.1	5.8
4	ICP-SFMS	50.5	49.4	49.4	49.5	49.2	49.1	49.5	5.5
5	ICP-OES	53.36	52.94	51.88	51.99	52.09	52.20	52.4	1.4
8	k0-INAA	56.2	53.8	53.4	57.8	54.4	52.7	54.7	5.0
13	ICP-MS	52	52	53	51	51	52	51.8	6.4
17	k0-INAA	57.4	55.3	57.4	56.6	54.7	58	56.6	3.7
20	ICP-OES	49.468	49.568	50.990	49.605	49.814	49.909	49.9	1.2
21	ICP-OES	52.529	53.043	52.740	49.135	49.216	49.245	51.0	5.8



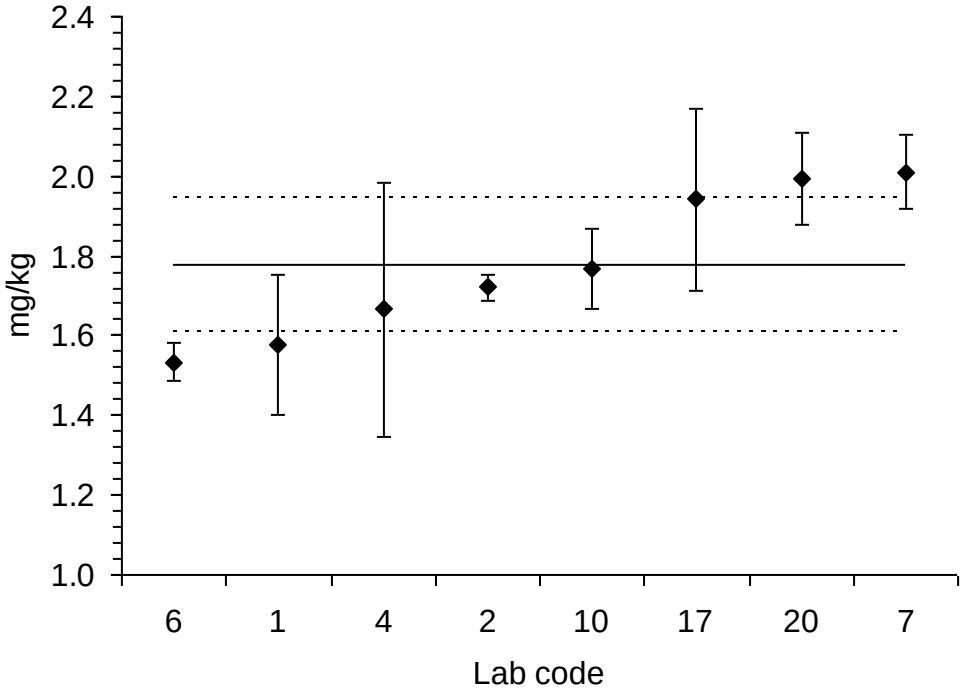
Hg in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.5255	0.5231	0.5507	0.465	0.4545	0.4524	0.495	0.088
3	CV-AAS	0.429	0.462	0.446	0.425	0.416	0.418	0.433	0.087
4	ICP-SFMS	0.5	0.496	0.483	0.49	0.498	0.494	0.494	0.040
6	ICP-MS	0.56848	0.56108	0.58433	0.58750	0.58855	0.57376	0.577	0.103
7	ICP-SFMS	0.50198	0.50410	0.51466	0.51149	0.51678	0.51361	0.510	0.031
9	DMA	0.5	0.498	0.501	0.498	0.501	0.504	0.500	0.038
13	ICP-MS	0.474	0.48	0.486	0.487	0.481	0.493	0.484	0.049
14	CV-AAS	0.504	0.498	0.496	0.498	0.49	0.5	0.498	0.050
17	k0-INAA	0.489	0.488	0.514	0.509	0.513	0.531	0.507	0.032
19	ID-ICP-MS	0.592	0.592	0.605	0.603	0.606	0.604	0.600	0.107
20	DMA	0.58129	0.58906	0.59125	0.59124	0.59392	0.58598	0.589	0.105



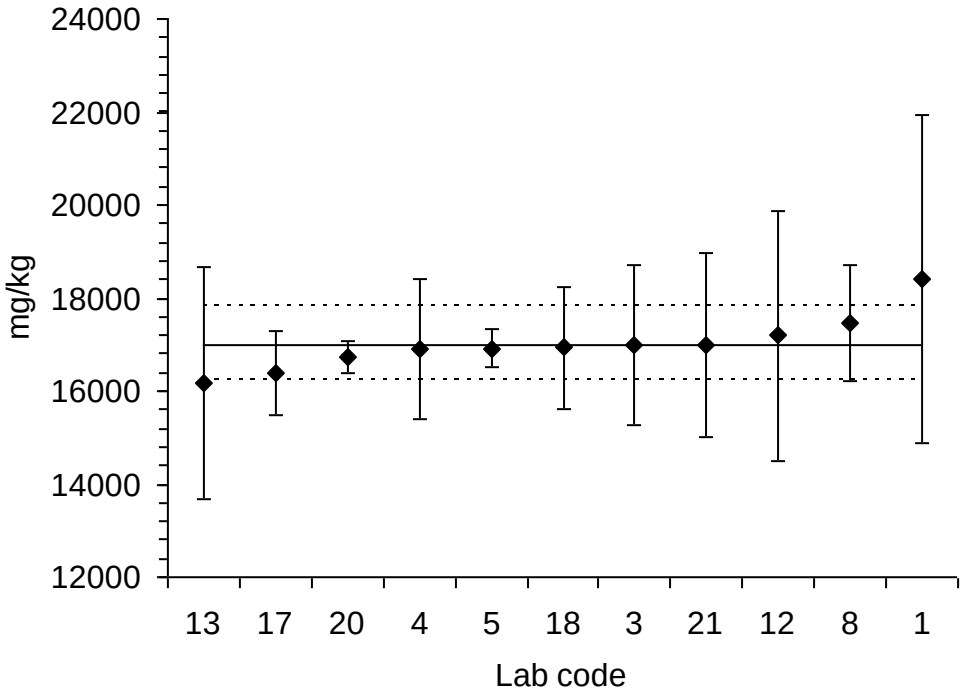
I in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	1.581	1.608	1.571	1.517	1.597	1.589	1.58	0.18
2	ID-ICP-MS	1.7202	1.7421	1.7517	1.6985	1.7019	1.7127	1.72	0.03
4	ICP-SFMS	1.64	1.68	1.66	1.62	1.7	1.69	1.67	0.32
6	ICP-MS	1.55	1.56	1.54	1.51	1.53	1.50	1.53	0.29
7	ICP-SFMS	1.99	2.00	2.02	2.03	2.05	1.98	2.01	0.23
10	RNAA	1.69	1.71	1.71	1.84	1.83	1.83	1.77	0.10
17	k0-INAA	1.82	2.09	1.87	1.88	2.01	1.98	1.94	0.23
20	ICP-MS	1.9398	1.9579	1.9950	1.9801	2.0620	2.0290	1.99	0.23
Results not included in the characterisation dataset									
15	HPLC-ICP-MS	0.648	0.713	0.525	0.495	0.674	0.607		



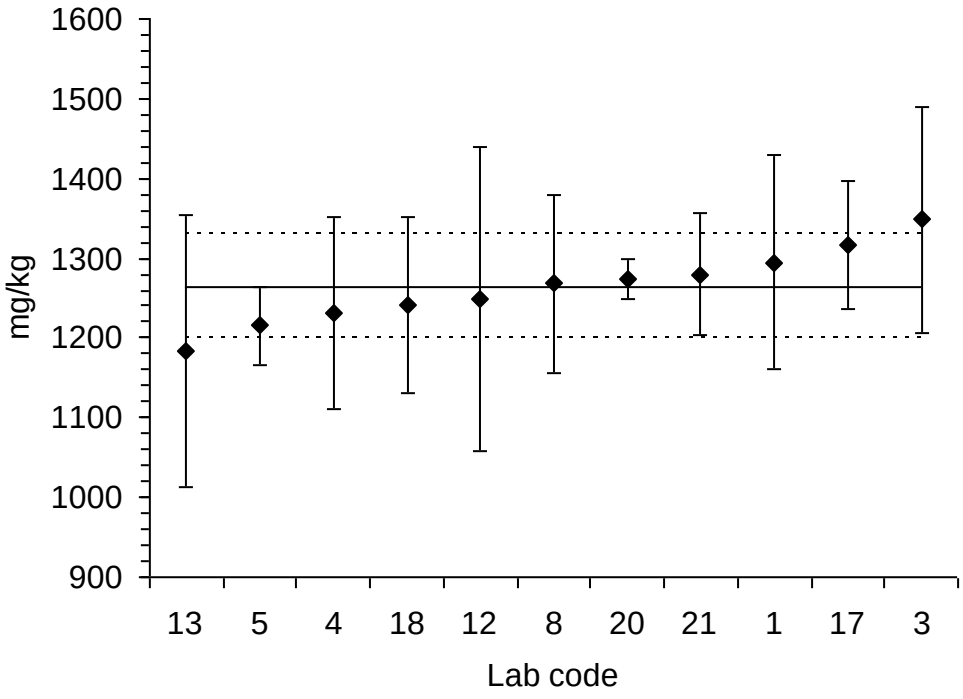
K in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	17006	17274	18264	19224	19595	19168	18422	3527
3	FAAS	16764	16878	17075	17021	17113	17133	16997	1713
4	ICP-SFMS	16800	16900	16700	16900	17000	17100	16900	1500
5	ICP-OES	17223	17012	16906	16801	16695	16801	16906	406
8	k0-INAA	17560	17688	17485	17472	17291	17185	17447	1246
12	ICP-OES	17400	17000	17800	17500	16600	16800	17183	2670
13	ICP-MS	16000	16000	16000	16000	16000	17000	16167	2500
17	k0-INAA	16200	16400	16400	16200	16900	16300	16400	900
18	k0-INAA	16500	16700	16900	16800	17000	17700	16933	1300
20	ICP-OES	16560	16640	16705	16790	16940	16825	16743	337
21	ICP-OES	16879	16686	16768	17183	17286	17213	17003	1986



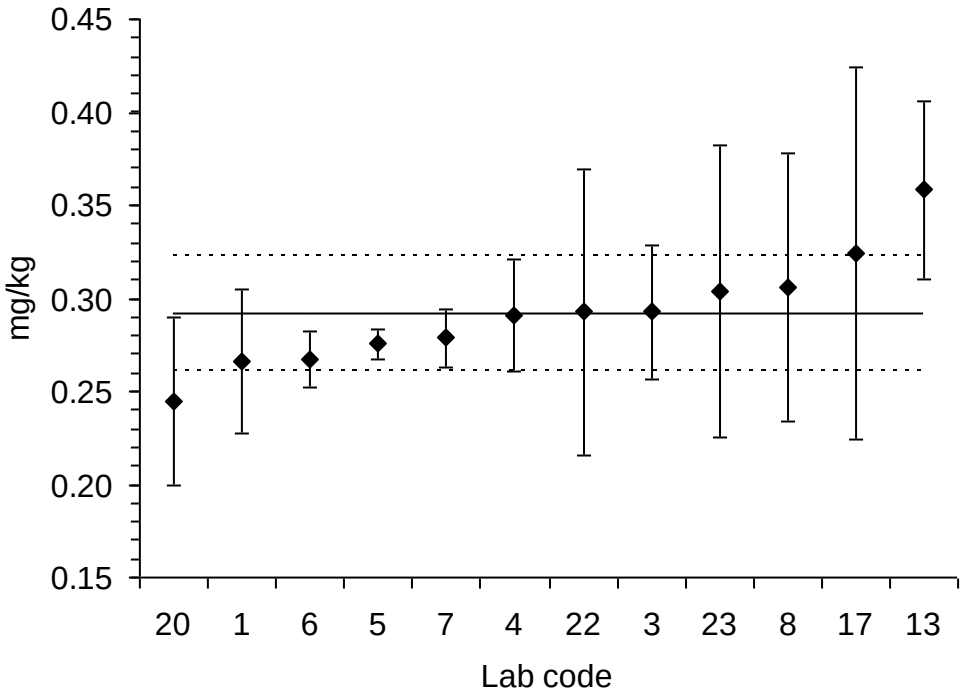
Mg in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	1229	1243	1300	1336	1345	1316	1295	134
3	FAAS	1318	1317	1415	1336	1351	1356	1349	142
4	ICP-SFMS	1230	1250	1230	1240	1220	1220	1232	120
5	ICP-OES	1205	1215	1215	1226	1205	1226	1215	49
8	k0-INAA	1274	1231	1251	1288	1276	1290	1268	112
12	ICP-OES	1230	1260	1250	1260	1230	1260	1248	190
13	ICP-MS	1200	1200	1200	1200	1100	1200	1183	170
17	k0-INAA	1300	1320	1340	1280	1340	1320	1317	80
18	k0-INAA	1240	1240	1260	1210	1300	1200	1242	110
20	ICP-OES	1280.6	1255.6	1273.3	1276.8	1279.9	1273.1	1273	26
21	ICP-OES	1284.2	1274.5	1282.6	1274.8	1284.3	1276.1	1279	77



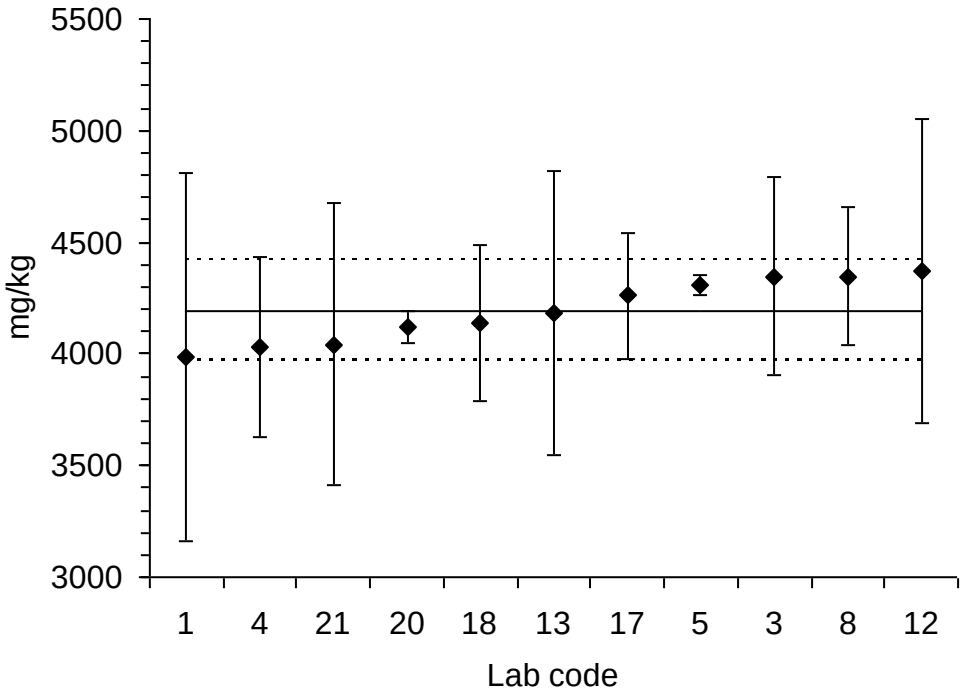
Mn in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.2618	0.251	0.2677	0.2655	0.2563	0.2945	0.266	0.038
3	ET-/F-AAS	0.297	0.296	0.283	0.297	0.291	0.293	0.293	0.036
4	ICP-SFMS	0.291	0.295	0.289	0.292	0.287	0.289	0.291	0.030
5	ICP-OES	0.27790	0.27578	0.27895	0.27261	0.27578	0.27156	0.275	0.008
6	ICP-MS	0.26839	0.26522	0.26416	0.27278	0.26944	0.26205	0.267	0.015
7	ICP-SFMS	0.28005	0.28322	0.27477	0.27583	0.27794	0.28111	0.279	0.016
8	k0-INAA	0.33	0.363	0.303	0.268	0.299	0.272	0.306	0.072
13	ICP-MS	0.35	0.36	0.35	0.33	0.40	0.36	0.358	0.072
17	k0-INAA	0.294	0.31	0.423	0.32	0.35	0.25	0.325	0.100
20	ICP-OES	0.23294	0.23785	0.24669	0.24456	0.23058	0.27448	0.245	0.045
22	ICP-MS	0.31259	0.30067	0.29040	0.28069	0.28171	0.28910	0.293	0.077
23	ICP-MS	0.32019	0.29150	0.30295	0.30322	0.30065	0.30442	0.304	0.079



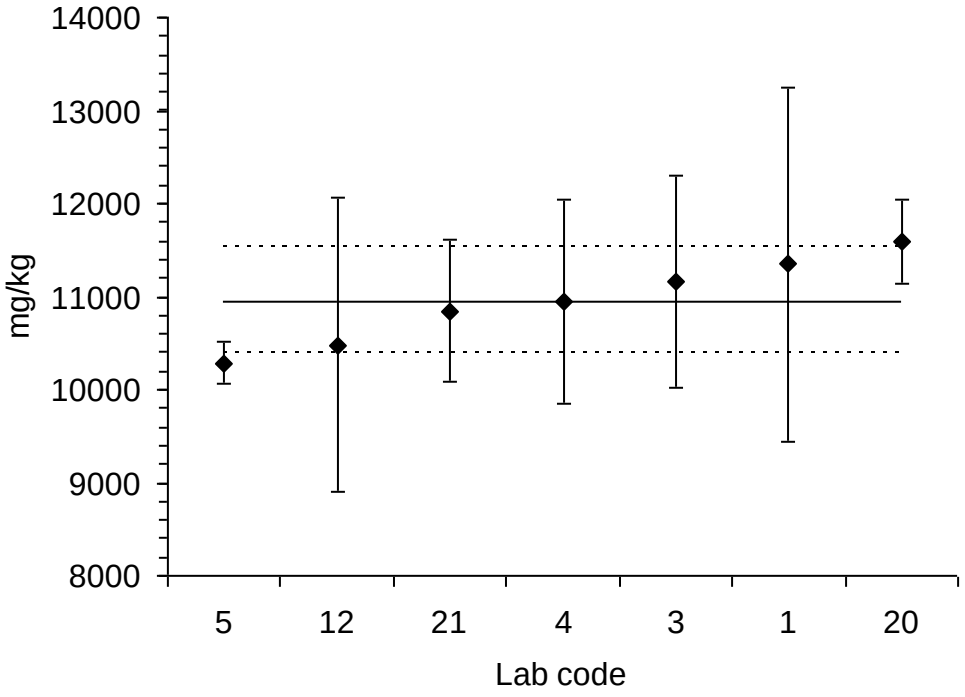
Na in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	3800	3820	4049	4118	4101	4045	3989	824
3	FAAS	4279	4284	4369	4314	4402	4429	4346	443
4	ICP-SFMS	4040	4070	4040	4040	4000	3990	4030	400
5	ICP-OES	4322	4311	4290	4332	4279	4301	4306	43
8	k0-INAA	4392	4386	4361	4363	4299	4286	4348	308
12	ICP-OES	4410	4300	4540	4370	4380	4240	4373	680
13	ICP-MS	4300	4200	4200	4200	4000	4200	4183	640
17	k0-INAA	4240	4330	4290	4190	4260	4250	4260	280
18	k0-INAA	4210	4000	4270	4060	4260	4040	4140	350
20	ICP-OES	4080.5	4118.5	4107.0	4126.0	4155.1	4140.6	4121	72
21	ICP-OES	4029.1	3983.9	3996.4	4077.7	4090.9	4081.1	4043	634



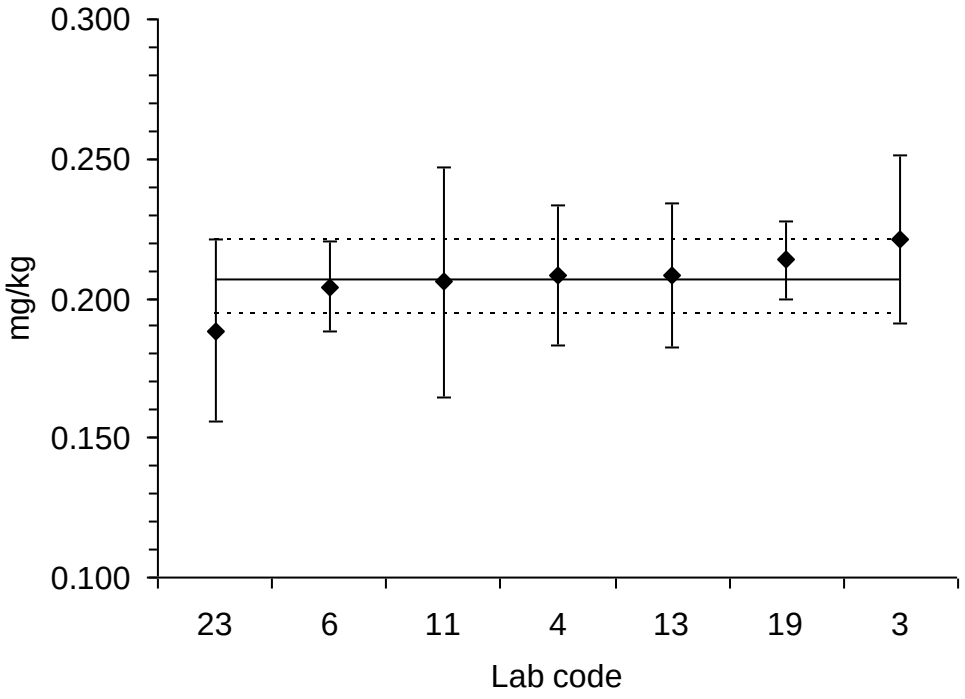
P in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	11240	11187	11944	11277	11237	11190	11346	1911
3	ET-/F-AAS	11210	10972	11428	10966	11221	11170	11161	1143
4	ICP-SFMS	10900	11000	11000	11000	10900	10900	10950	1100
5	ICP-OES	10345	10376	10419	10197	10249	10144	10288	2058
12	ICP-OES	10400	10500	10500	10500	10500	10500	10483	1580
20	ICP-OES	11295	11545	11560.1	11984.8	11619.9	11555	11593	456
21	ICP-OES	10886.2	10944.7	10918.4	10774.4	10796.4	10731.2	10842	766



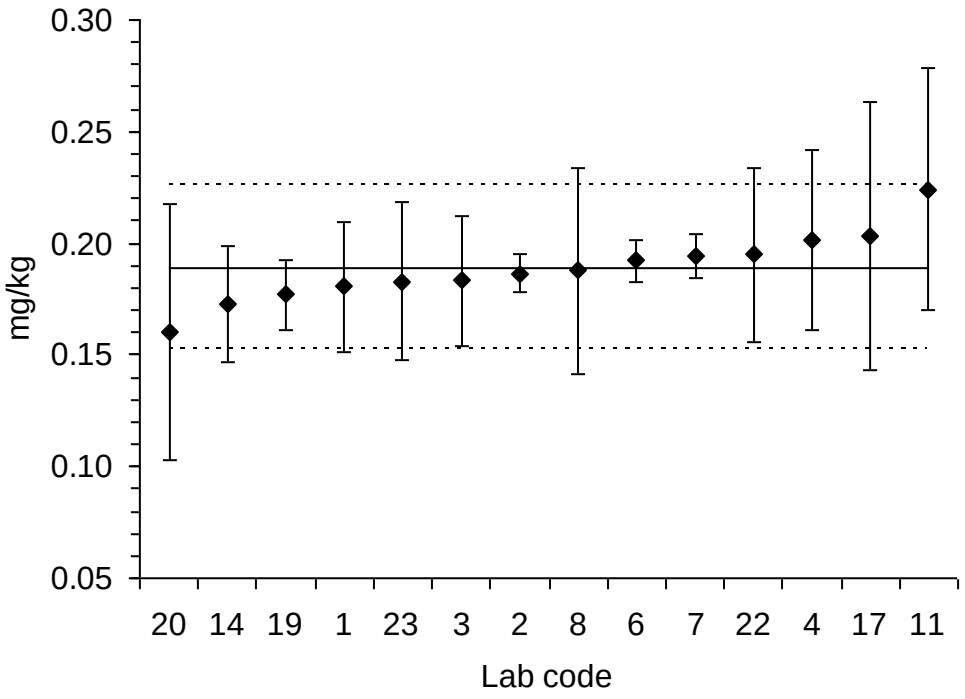
Pb in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
3	GFAAS	0.252	0.241	0.234	0.202	0.196	0.201	0.221	0.030
4	ICP-SFMS	0.205	0.212	0.209	0.209	0.208	0.206	0.208	0.025
6	ICP-MS	0.20499	0.20710	0.20499	0.19971	0.20393	0.20499	0.204	0.016
11	ICP-MS	0.211	0.198	0.204	0.208	0.201	0.213	0.206	0.041
13	ICP-MS	0.22	0.2	0.21	0.21	0.2	0.21	0.208	0.026
19	ID-ICP-MS	0.207	0.206	0.225	0.206	0.225	0.214	0.214	0.014
23	ICP-MS	0.18960	0.19442	0.19294	0.18501	0.18365	0.18542	0.189	0.033
Results not included in the characterisation dataset									
1	ICP-MS	0.2005	0.1997	0.2102	0.2058	0.1979	0.2004		
7	ICP-SFMS	0.15429	0.15641	0.15112	0.14901	0.14795	0.15007		
20	GFAAS	0.25475	0.26517	0.26256	0.25695	0.28092	0.27161		
22	ICP-MS	0.17993	0.18147	0.16952	0.17584	0.17262	0.17334		



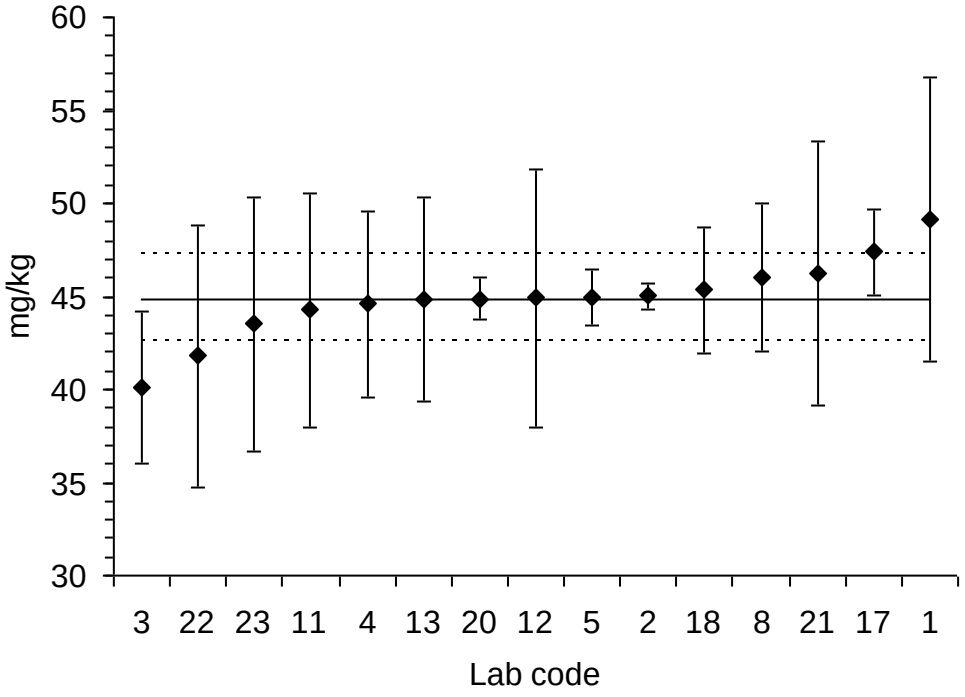
Se in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	0.1824	0.1843	0.1845	0.1781	0.1733	0.1799	0.180	0.030
2	ID-ICP-MS	0.18151	0.19133	0.18460	0.18906	0.19155	0.18106	0.187	0.009
3	HG-AAS	0.188	0.19	0.182	0.182	0.178	0.179	0.183	0.029
4	ICP-SFMS	0.2	0.202	0.198	0.211	0.207	0.19	0.201	0.040
6	ICP-MS	0.18703	0.19125	0.19020	0.19337	0.20182	0.18914	0.192	0.010
7	ICP-SFMS	0.19445	0.19234	0.19551	0.19974	0.19762	0.18705	0.194	0.010
8	k0-INAA	0.175	0.223	0.168	0.208	0.188	0.165	0.188	0.046
11	ICP-MS	0.22	0.227	0.219	0.228	0.217	0.234	0.224	0.054
14	HG-AAS	0.176	0.173	0.172	0.173	0.171	0.17	0.173	0.026
17	k0-INAA	0.227	0.19	0.212	0.21	0.18	0.2	0.203	0.060
19	ID-ICP-MS	0.16	0.182	0.178	0.181	0.176	0.184	0.177	0.016
20	ICP-MS	0.17975	0.16639	0.16172	0.16404	0.15527	0.13397	0.160	0.057
22	ICP-MS	0.17863	0.19662	0.17467	0.20788	0.20255	0.20905	0.195	0.195
23	ICP-MS	0.18982	0.17740	0.18052	0.18602	0.18109	0.18287	0.183	0.183



Zn in ERM-BD151

Lab code	Technique	replicate 1 [mg/kg]	replicate 2 [mg/kg]	replicate 3 [mg/kg]	replicate 4 [mg/kg]	replicate 5 [mg/kg]	replicate 6 [mg/kg]	mean [mg/kg]	Expanded uncertainty [mg/kg]
1	ICP-MS	48.11	47.22	50.83	49.65	50.07	49.16	49.17	7.62
2	ID-ICP-MS	44.909	44.826	44.966	45.225	45.091	45.078	45.02	0.73
3	FAAS	40	39.8	40.3	41.3	39.5	39.8	40.12	8.02
4	ICP-SFMS	44.9	44.6	44.6	44.3	44.3	44.9	44.60	5.00
5	ICP-OES	45.75	45.75	44.91	44.17	45.12	43.96	44.94	1.53
8	k0-INAA	46.5	46.6	45.1	46.5	46	45.6	46.05	4.00
11	ICP-MS	44	45.8	43	43.3	45.9	43.5	44.25	6.30
12	ICP-OES	45.1	43.5	46.3	44.4	44.3	45.8	44.90	6.90
13	ICP-MS	46	46	45	45	43	44	44.83	5.50
17	k0-INAA	47.5	46.8	48.6	47.3	46.6	47.5	47.38	2.30
18	k0-INAA	43.8	46.3	45.8	45.7	44.2	46.3	45.35	3.40
20	ICP-OES	44.248	44.248	44.811	45.099	45.510	45.385	44.88	1.10
21	ICP-OES	47.732	47.680	47.623	44.605	44.774	45.039	46.24	7.11
22	ICP-MS	45.199	46.085	41.608	38.705	38.981	40.126	41.78	7.00
23	ICP-MS	42.717	42.097	44.918	43.502	43.795	44.015	43.51	6.83



European Commission

EUR 26108 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: The certification of the mass fractions of elements in skimmed milk powders: ERM-BD150 and ERM-BD151
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Abstract
This report describes the production of ERM BD150 and ERM BD151, skimmed milk powder materials certified for the mass fractions of elements. The material was produced following ISO Guide 34:2009.
The starting material was 1000 L of fresh raw milk. The milk was skimmed and pasteurised, and divided in two batches of about 500 L. Spike solutions of Cd, Cu, Fe, Hg and Pb were added to each batch. The batches were again pasteurised, concentrated by evaporation, and spray dried to produce fine powders.
Between unit-homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006. Within-unit homogeneity was quantified to determine the minimum sample intake.
The material was characterised by an inter-comparison 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, instability and characterisation.
The materials are intended for quality control and assessment of method performance. As any reference material, they can be used for control charts or validation studies. The CRMs are available in glass bottles containing 20 g of dried powder. The minimum amount of sample to be used is 500 mg for Fe and 200 mg for all other elements.
The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

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Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security, including nuclear; all supported through a cross-cutting and multi-disciplinary approach.

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