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European Reference Materials

CERTIFICATION REPORT

Certification of the mass fractions of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn in rye grass

Certified Reference Material ERM®-CD281

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CERTIFICATION REPORT

Certification of the mass fractions of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn in rye grass

Certified Reference Material ERM®-CD281

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Summary

This report describes the preparation and certification of the rye grass Certified Reference Material (CRM) ERM-CD281. This CRM replaces the exhausted predecessor BCR-281. ERM-CD281 was processed and certified by the European Commission, Directorate General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

ERM-CD281 has been certified for its content of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn.

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

The following values were assigned:

Element	Mass Fraction	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
As	0.042	0.010
B	5.5	0.5
Cd	0.120	0.007
Cr	24.8	1.3
Cu	10.2	0.5
Hg	0.0164	0.0022
Mn	82	4
Mo	2.22	0.12
Ni	15.2	0.6
Pb	1.67	0.11
Sb	0.042	0.007
Se	0.023	0.004
Sn	0.062	0.011
Zn	30.5	1.1

1) The value is the unweighted mean of accepted sets of data, each set being obtained in a different laboratory and/or with a different method. The certified values are reported on dry mass basis and are traceable to the SI.

2) Expanded uncertainty with a coverage factor k = 2 according to the Guide to the Expression of Uncertainty in Measurement (GUM), corresponding to a level of confidence of about 95 %.

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Glossary

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
ANOVA	Analysis of variance
BCR	Community Bureau of Reference
CC	Collision cell
CCT	Collision Cell Technology
CRMs	Certified Reference Materials
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 Analyzer
DRC	Dynamic Reaction Cell
ERM®	Trade mark of European Reference Materials
ET-AAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
HG-AFS	Hydride Generation Atomic Fluorescence Spectrometry
HR	High resolution
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-QMS	Inductively Coupled Plasma Quadrupole Mass Spectrometry
ICP-SFMS	Inductively Coupled Plasma Sector Field Mass Spectrometry
ID	Isotope dilution
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
k	Coverage factor
k_0-INAA	k_0-Instrumental Neutron Activation Analysis
k_0-NAA	k_0-Neutron Activation Analysis
LR	Low resolution
wt. %	Weight percentage
MR	Medium resolution
MS_{between}	Mean squares between-bottle from an ANOVA
MS_{within}	Mean squares within-bottle from an ANOVA
n	Number of replicates per vial
n_{ns}	Number of measurements on normal stock samples
n_{ref}	Number of measurements on reference samples
N/A	Not applicable
n.c.	Not calculated
NIST	National Institute of Standards and Technology
QC	Quality Control
RM Unit	Reference Materials Unit

RNAA	Radiochemical Neutron Activation Analysis
RSD	Relative Standard Deviation
s	Standard deviation
s_{bb}	Between-bottle standard deviation
$s_{\mathrm{bb,\ rel}}$	Between-bottle relative standard deviation
s_{ns}	Standard deviation of results of normal stock samples
s_{ref}	Standard deviation of results of reference samples
SI	International System of Units
u_{bb}	Standard uncertainty related to a possible between-bottle heterogeneity
$u_{\mathrm{bb,\ rel}}$	Relative standard uncertainty related to a possible between-bottle heterogeneity
u^*_{bb}	Standard uncertainty related to a maximum heterogeneity that could be hidden by method repeatability
$u^*_{\mathrm{bb,\ rel}}$	Relative standard uncertainty related to a maximum heterogeneity that could be hidden by method repeatability
u_{char}	Standard uncertainty of the material characterisation
$u_{\mathrm{char,\ rel}}$	Relative standard uncertainty of the material characterisation
u_{rec}	Standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
$u_{\mathrm{rec,\ rel}}$	Relative standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
U_{CRM}	Expanded uncertainty of the certified value
$U_{\mathrm{CRM,\ rel}}$	Expanded relative uncertainty of the certified value
u_{lts}	Standard uncertainty of the long-term stability
U_{meas}	Expanded measurement uncertainty
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}
V-KFT	Volumetric Karl Fischer titration
t_{sl}	Proposed shelf life
$\overline{x}$	Average of all results of the homogeneity study
$\overline{x_{\mathrm{ns}}}$	Average of all results of normal stock samples
$\overline{x_{\mathrm{ref}}}$	Average of results of reference samples
x_i	Time point for each replicate

1 Introduction

Animal feed quality has a significant impact on the quality of the food products derived from animals and thus on human health and is one of work areas of the EU legislation, e.g. Regulation (EC) No 1881/2006, Directive 2001/22/EC and Directive 2002/32/EC. There are several elements of high importance owing to their nutritional or toxic properties [1, 2]. Elements such as B, Cu, Cr, Mg, Mn, K, Ni, P, Se, Sn and Zn are classified as elements of nutritional quality. However, their dietary role depends on their content in animal feed. Too high intakes of a nutrient can cause toxic effects. The tolerance limit of the nutrient depends both on the animal species and on their diet composition. A number of important nutritional and biochemical interactions between feed components have been recognised. For instance, Cu metabolism is strongly related to the Mo content, and coexistence of vitamin E and Se provide protection against metals such as Cd, Hg, As or Pb. It becomes clear that the information about the content of nutritional elements in animal feed helps to design a well-balanced diet for animals.

On the other hand, examples of elements, which represent a potential risk for human or animal health are As, Cd, Hg and Pb. In order to avoid negative effects on the health of domestic animals, the detection of this kind of elements is necessary. Failure to detect these elements could lead to a lower production (economic loss) or cause damage to the health of consumers of animal products (milk, meat, cheese, etc.). Some elements such as Sb are more often found in the environment because of human activities. Since they can play significant role for human and animal health in the future, their precise and careful control in feed is required. The measurement of some of the elements (e.g. Pb or Cd) is also relevant for the environmental monitoring and pollution control.

BCR-281 (Certified Reference Material for trace elements in rye grass) that was used in routine analysis of animal feed is out of stock. Therefore, ERM-CD281 Rye Grass certified for the total content of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn has been produced. This report describes the preparation and certification of the ERM-CD281.

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-TEST)

2.2 Processing

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(accredited to ISO/IEC 17025 for measurement of elements in soils, BELAC No 045-TEST)

3 Processing of the material

The rye grass used for ERM-CD281 was harvested in 1983 [3-5]. In 1988-1989, one part became the now sold-out BCR-281 and another part BCR-129 [3-5]. Some of the remaining material was processed by jet milling in 1994 and thereafter made available in 25 g portions [6]. The finely ground powder from 1994 was further processed at IRMM in 2006. The further processing consisted of drying at 50 °C (to reach the water content below 4 wt. %), homogenisation, filling into amber 60 mL glass vials with a lyo-insert and an aluminium cap under argon atmosphere. Capping and labelling was performed according to the filling sequence. A total of 2422 units were produced, each containing about 10 g of the rye grass material.

The particle size distribution of the final product was assessed using a Sympatec Helos laser diffraction instrument (Clausthal-Zellerfeld, DE). A typical particle size distribution is presented in Figure 1. The maximum particle size was shown to be 175 µm. However, a sieve analysis demonstrated presence of larger particles of 200 µm - 3 mm, see Figure 2 (d). In relation to the total number of particles, their relative abundance is much below 1 %.

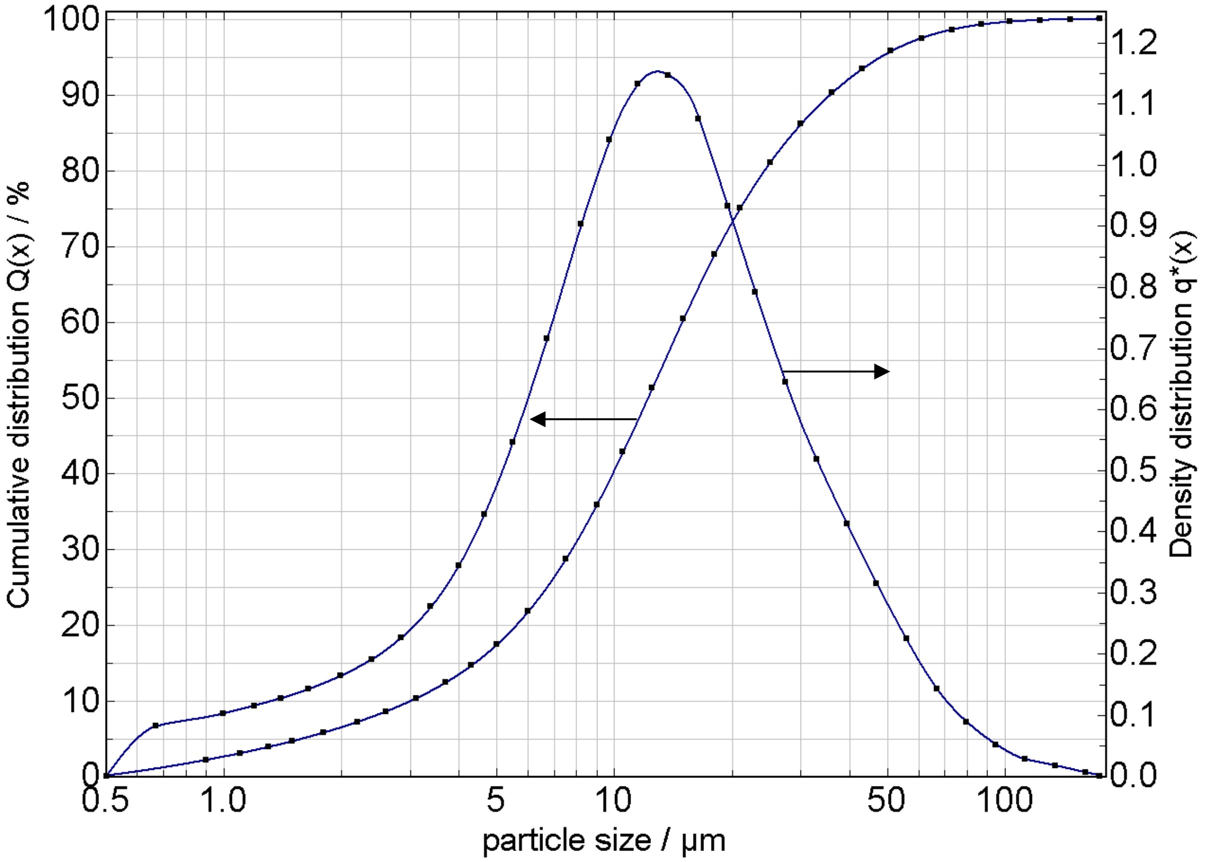

Figure 1: Typical particle size distribution of ERM-CD281 (average of triplicate measurements on three vials). Instrument: Sympatec Helos laser diffraction instrument (Clausthal-Zellerfeld, DE), optical concentration: 15 % - 25 % using the cuvette, and dispersant: 2-propanol.

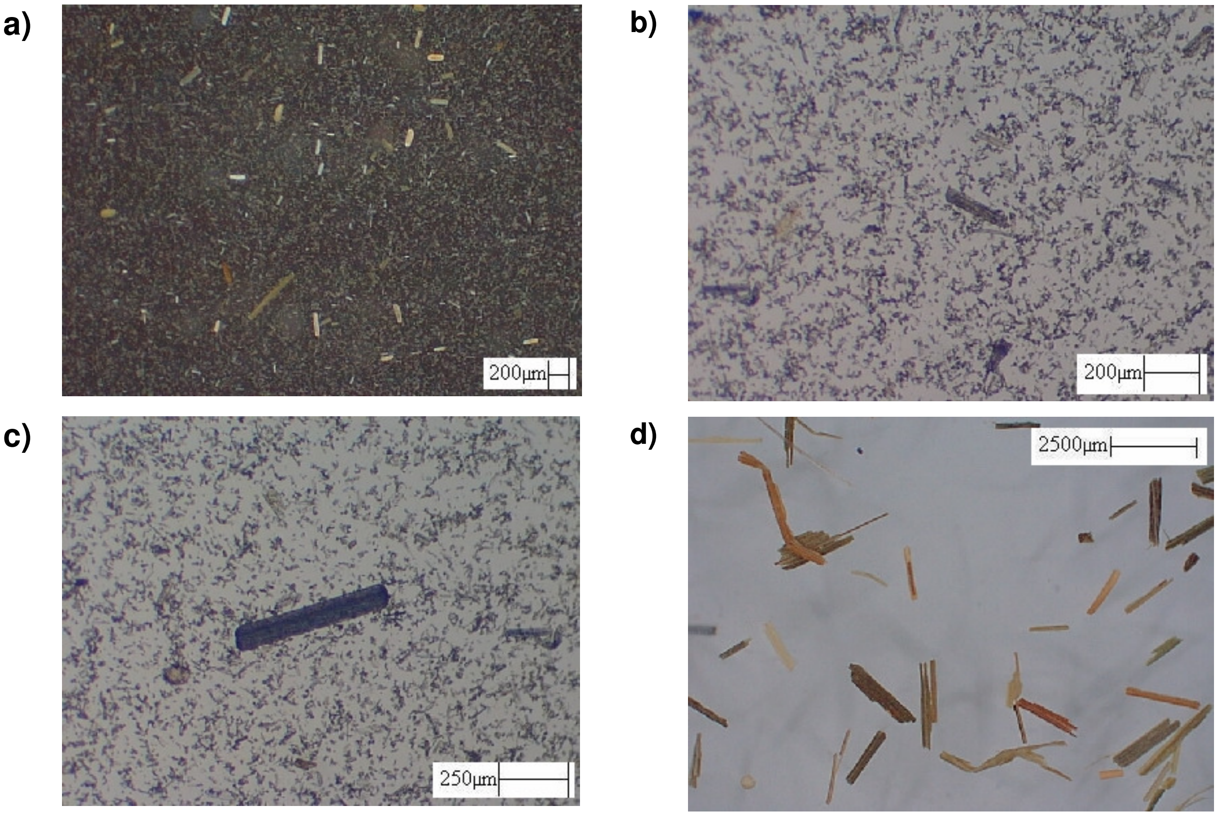

Figure 2: Micrographs of the final product, ERM-CD281 (a – c), and micrograph of the particles remaining on a 250 µm sieve after sieve analysis of ERM-CD281 (d).

The water content determined in the final product using volumetric Karl Fischer titration (V-KFT, Metrohm Ltd, Herisau, CH) was 2.68 wt. % ± 0.30 wt. % (average of triplicate measurements on ten vials, expanded uncertainty with a coverage factor of *k* = 2). The water content was also monitored by high speed Acousto-Optical Tunable Filter Near Infrared Spectrometry (AOTF-NIR) during capping of the vials. As shown in Figure 3 the water content over the whole batch was constant. The few observed outliers were associated with a bad ratio of the signal to the noise.

The water activity determined in the final product by means of a water activity meter (Aqualab CX3, Decagon, USA) was 0.107 (average of triplicate measurements on one vial).

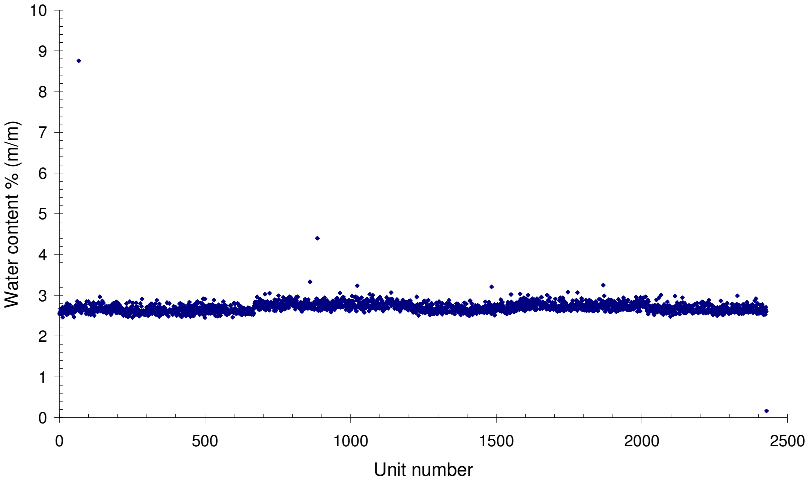

Figure 3: Results of the water content monitoring during capping of ERM-CD281. The visibly outlying data are due to a bad ratio of the signal to the noise.

4 Homogeneity

4.1 Between-bottle homogeneity

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

For the homogeneity test, fifteen vials were selected using a random stratified sampling scheme. The number of selected vials corresponds to approximately the cubic root of the total number of the produced units. The batch was divided into fifteen groups (with similar number of vials) and one vial was randomly selected from each group.

From each vial, three samples were prepared by digestion in a microwave oven using 5 mL HNO_3 and 0.5 mL HCl. The samples were analysed by means of ICP-OES (B, Cr, Cu, Mn, Mo, Ni and Zn), ICP-SFMS (MR: As and LR: Cd, Hg, Pb, Sb and Sn) and ICP-QMS with NH_3 DRC (Se). 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 determined in each vial once (see Section 6.2).

In case of As, Hg and Se it turned out that the homogeneity results were not in agreement with those from the characterisation exercises (about 10, 2 and 10 times higher, respectively). Based on some further investigations the laboratory confirmed these findings giving interference problems as an explanation. In case of As applying too low mass resolution could be a reason as well. Therefore, the homogeneity results for those elements were not used and the material homogeneity was evaluated using data from the short-term stability study (this approach is correct when no influence for the conditions tested in the stability study is present, as shown in Section 5.1). This resulted in a dataset with measurements on fourteen vials. The vials were analysed in triplicate by means of ICP-SFMS (HR: As and Se) and CV-AFS (Hg) after digestion in a microwave oven using 6 mL HNO_3 and 2 mL HCl. The measurements were performed under repeatability conditions, and in a randomised manner. The results were corrected for the water content determined in each vial twice (see Section 6.2).

The results of these measurements were evaluated using a method described by Linsinger *et al.* [7] as described in the following paragraphs:

The obtained data were first tested whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms (if the data do not follow at least a unimodal distribution, the calculation of standard deviations would be inappropriate). All individual results were normally and unimodally distributed.

Grubbs-tests were performed to detect potentially outlying individual results as well as outlying vial averages. Some outlying individual results and outlying vial averages for both homogeneity and stability results were found, see Annex A (homogeneity) and Table 3 (outlying individual values in stability measurements). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Furthermore, 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. However, some trends in the analytical sequence were visible, pointing at instability of the analytical system (As, Cd, Cu, Mn, and Sn). Since the uncertainty of homogeneity was very low for Cd, Cu and Mn (see Table 1), and in case of As and Sn the drift correction would not significantly affect the uncertainty, the drift correction was not applied.

The results were then evaluated by a one-way analysis of variance (ANOVA). From the results of the ANOVA calculation, the following figures were determined:

Between-bottle standard deviation (s_{bb}) as given by:

$$s_{\mathrm{bb}} = \sqrt{\frac{MS_{\mathrm{between}} - MS_{\mathrm{within}}}{n}}, \tag{1}$$

where:

MS_{between}:	mean squares between-bottle from an ANOVA
MS_{within}:	mean squares within-bottle from an ANOVA
n:	average number of replicates per vial

The maximum heterogeneity that can be hidden by the method repeatability (which is used as the minimum uncertainty contribution from homogeneity) defined by:

$$u_{\mathrm{bb}}^{*} = \sqrt{\frac{MS_{\mathrm{within}}}{n}} \sqrt[4]{\frac{2}{v_{\mathrm{MSwithin}}}}, \tag{2}$$

where:

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

The larger value of s_{bb} or u_{bb}^{*} was used as uncertainty contribution from the homogeneity, u_{bb}. However, a different approach was adopted for As and Pb for which one outlying vial average was detected. In this case between-bottle heterogeneity was modelled as a rectangular distribution limited by the largest outlying vial average, and the rectangular standard uncertainty of homogeneity was estimated as given by:

$$u_{\mathrm{rec}} = \frac{\left| \text{largest outlying vial average} - \overline{x} \right|}{\sqrt{3}}, \tag{3}$$

where:

$\overline{x}$: average of all results of the homogeneity study

However, it should be mentioned that the outlying vial averages are a result of presence of outlying individual values and do not necessarily reflect the real distribution of these elements in the material.

The results of the measurements are shown in Annex A (homogeneity study) and D (long-term stability study). The results of the evaluation of the between-bottle variation are summarised in Table 1. In most cases, the uncertainty contribution for homogeneity was determined by the method repeatability.

Table 1: Results of the homogeneity study

Element	$s_{\text{bb, rel}}$ [%]	$u^*_{\text{bb, rel}}$ [%]	$u_{\text{rec, rel}}$ [%]	$u_{\text{bb, rel}}$ [%]
As[b]	N/A	N/A	9.4	9.4
B[a]	0.4	0.8		0.8
Cd[a]	n.c.	0.8		0.8
Cr[a]	0.6	0.5		0.6
Cu[a]	n.c.	0.6		0.6
Hg[b]	3.3	1.8		3.3
Mn[a]	0.5	0.4		0.5
Mo[a]	n.c.	1.4		1.4
Ni[a]	0.7	0.6		0.7
Pb[a]	N/A	N/A	2.3	2.3
Sb[a]	n.c.	1.5		1.5
Se[b]	n.c.	3.4		3.4
Sn[a]	n.c.	2.9		2.9
Zn[a]	0.3	0.3		0.3

n.c.: cannot be calculated as $MS_{\text{between}} < MS_{\text{within}}$

[a]: based on the data from the dedicated homogeneity study

[b]: based on the data from the short-term stability study

N/A not applicable

The potential between-unit variation is generally below 1 – 3 %. Some exceptions were noted for As (9.4 %), Hg (3.3 %) and Se (3.4 %). The high value for As is a result of presence of the outlier. This between-unit variation is small enough compared to the method variability usually observed (average up to 10 % was obtained by the participants of the characterisation measurements for these three elements). This material is therefore sufficiently homogeneous to be suitable as reference materials.

4.2 Minimum sample intake

The minimum sample intake is the minimum amount of sample that is representative for the whole unit thus can be used in an analysis. Samples equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

To estimate of the minimum sample intake series of measurements with decreasing amount of sample for one randomly selected vial were performed. The following sample intakes were tested: 200 mg, 100 mg and 50 mg. For each sample intake 6 samples were prepared by digestion in a microwave oven using 3 mL HNO_3. Each sample intake was prepared in one independent microwave run. All the samples were analysed together by means of ICP-QMS (B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Sn and Zn) and ICP-SFMS (HR: As and Se) under repeatability conditions, and in a randomised manner. The measurement method was robust over the whole range of the sample intake tested and its repeatability was in the same range or below the repeatability achieved during the material characterisation (see Section 6).

The obtained data sets (all sample intakes taken together) were first tested whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms (if the data do not follow at least a unimodal distribution, the calculation of standard deviations is doubtful or impossible). All results were normally and unimodally distributed.

Furthermore, the results (all sample intakes taken together) were scrutinised for outliers using single Grubbs-test. One outlier for Cu was found. This outlier was significant on a 95 %, but not on a 99 % confidence level. Since no technical reason for the outlier could be found, the result was retained. In any case, its removal would not affect results of the minimum sample intake determination.

The minimum sample intake was established by comparison of variances obtained for 100 mg and 50 mg sample intakes with the variance obtained for 200 mg sample intake. It was done using F-test for equality of two samples for variances with degrees of freedom of 5 and a confidence level of 95 %.

The obtained results are presented in Annex B and the minimum sample intakes are summarised in Table 2.

Table 2: Results of the minimum sample intake determination

Element	Minimum sample intake [mg]
As	50
B	100
Cd	200
Cr	50
Cu	200
Hg	50
Mn	100
Mo	100
Ni	100
Pb	50
Sb	200
Se	100
Sn	50
Zn	100

As shown above, the minimum sample intake representative for all elements is 200 mg. However, lower sample intakes can be also applied, i.e. 100 mg for As, B, Cr, Hg, Mn, Mo, Ni, Pb, Se, Sn and Zn and 50 mg for As, Cr, Hg, Pb and Sn.

5 Stability

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, quite high temperatures can be reached. The stability studies have been carried out using an isochronous design [8]. 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. Time, temperature and light (UV-radiation) were regarded as the most relevant influences on stability of the material. The influence of UV-radiation was minimised by the choice of a brown glass vials, which eliminate most of the incoming light. In addition, materials are stored and dispatched in the dark, thus practically eliminating the possibility of degradation by UV-radiation. Therefore, only the influences of time and temperature needed to be investigated. Elements are not subject to thermal degradation at temperatures encountered during everyday life. However, it is known that some organometallic compounds have a low boiling point, e.g. tetracarbonyl nickel. Moreover, if an element is certified for its mass fraction, degradation of the matrix would affect this mass fraction as well. Therefore, assessment of the material stability under certain temperature and time conditions was required.

5.1 Short-term stability study

For the short-term stability study, samples have been 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 samples per storage time were selected using a random stratified sampling scheme. From each vial, three samples were prepared by digestion in a microwave oven using 5 mL HNO_3 and 0.5 mL HCl (exception: for 60 ºC test temperature, 1 week storage time only two samples were prepared from one vial). All samples were analysed with respect to the content of all elements by means of ICP-OES (B, Cr, Cu, Mn, Mo, Ni, Zn,) ICP-SFMS (MR: As, and LR: Cd, Hg, Pb, Sb and Sn) and ICP-QMS with NH_3 DRC (Se). The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the water content determined in each vial once (Section 6.2).

Similarly to the homogeneity study, the results for As, Hg and Se were not in agreement with those of the material characterisation (see Section 6). Therefore, additional measurements for those elements have been carried out. A new set of samples was analysed in triplicate by means of ICP-SFMS (HR: As and Se) and CV-AFS (Hg) after digestion in a microwave oven using 6 mL HNO_3 and 2 mL HCl. The measurements were performed under repeatability conditions, and in a randomised manner. The results were corrected for the water content determined in each vial twice (Section 6.2).

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 (see Table 3). 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 the regression lines were calculated. The slope of the regression lines was then tested for statistical significance (loss/increase due to shipping conditions). For all elements, the slopes of the regression lines were not significantly different from 0 (on 95 % and 99 % confidence level) for both 18 °C and 60 °C.

The results of the measurements are shown in Annex C. The results of the evaluation of the material short-term stability are summarised in Table 3.

Table 3: Results of the short-term stability tests

Element	Number of individual outlying results		Measurement technique	Significance on 95 % and 99% confidence level	
	18 ºC	60 ºC		18 ºC	60 ºC
As	1[a]	0	ICP-SFMS	No	No
B	0	0	ICP-OES	No	No
Cd	0	0	ICP-SFMS	No	No
Cr	0	0	ICP-OES	No	No
Cu	1[b]	0	ICP-OES	No	No
Hg	0	0	CV-AFS	No	No
Mn	0	0	ICP-OES	No	No
Mo	0	1[b]	ICP-OES	No	No
Ni	0	0	ICP-OES	No	No
Pb	0	0	ICP-SFMS	No	No
Sb	0	0	ICP-SFMS	No	No
Se	0	0	ICP-SFMS	No	No
Sn	0	1[b]	ICP-SFMS	No	No
Zn	0	0	ICP-OES	No	No

[a]: on a 99 % confidence level

[b]: on a 95 % confidence level

It was concluded that the material is stable at 18 ºC and 60 ºC for up to 4 weeks. The samples can be safely dispatched under conditions where the temperatures do not exceed 60 ºC for up to 4 weeks, i.e. at ambient temperature.

Because the potential degradation due to dispatch can be considered negligible, the uncertainty contribution from the short-term stability is not considered in the estimation of the total uncertainty of the material (see Section7.1).

5.2 Long-term stability study

For the long-term stability study, samples have been stored at 18 ºC for 0, 4, 8 and 12 months (1-year study) and for 0, 8, 16 and 24 months (2-year study). The reference temperature was set to -20 ºC. Two samples per each storage time were selected using a random stratified sampling scheme. From each vial, three samples were prepared by digestion in a microwave oven. As digestion reagents, 5 mL HNO_3 and 0.02 mL HF (5 mL HNO_3, 0.02 mL HF and 0.2 mL HCl for Sb and Sn) for the 1-year study samples were used. The 2-year study samples were digested with 6 mL HNO_3 and 2 mL HCl. The digests of 1-year study samples were analysed by means of ICP-SFMS (HR: As and Se; MR: Cr, Cu, Mn, Ni and Zn; LR: B, Cd, Hg, Mo, Pb, Sb and Sn). The digests of 2-year study samples were analysed by means of ICP-SFMS (HR: As and Se; MR: B, Cd, Mo, Pb, Sb, and Sn), ICP-OES (Cr, Cu, Mn, Ni and Zn) and CV-AFS (Hg). The measurements were performed under repeatability conditions, and in randomised manner to be able to separate a potential analytical drift from a trend over storage time. The results were corrected for the water content determined in each vial twice (Section 6.2).

The measurements of As, Hg and Se (1-year study) were performed close to the method LOD. Therefore, the results were not used.

The data were tested for outliers using the single and double Grubbs test (each time-scheme was evaluated separately). A few outliers were found in both 1-year and 2-year studies (see Table 4). Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Table 4: Outliers detected in the long-term stability measurements

Element	Number of individual outlying values	
	1-year study	2-year study
As	Not used	1[a]
B	0	0
Cd	1[a]	0
Cr	0	0
Cu	0	2[a]
Hg	Not used	0
Mn	0	0
Mo	0	1[a]
Ni	0	0
Pb	0	0
Sb	2[a]	1[b]
Se	Not used	0
Sn	0	0
Zn	0	0

[a]: on a 95 % confidence level

[b]: on a 99 % confidence level

Furthermore, the data were plotted against time and the regression lines were calculated (each time-scheme was evaluated separately). The slope of the regression lines was then tested for statistical significance (loss/increase due to storage conditions). For Cd and Cr in the 1-year study the slopes of the regression line were found to be significant on 95 % and 99 % confidence level, respectively. This is caused by the data of the samples stored at only reference temperature, for which one data point for Cd and five for Cr were lower in comparison to the other storage times. Since these findings were not confirmed by the 2-year stability study, it was concluded that the slope significance is rather a result of measurement error and does not reflect a real element distribution in the material. Therefore, it was decided to exclude these results and not to use them in the material stability evaluation.

Finally, the results of the both stability schemes were combined and evaluated together. Since the two datasets were obtained using different analytical techniques and in different time a correction had to be applied. The 1-year stability results were corrected by multiplying with a correction factor calculated from the ratio of the study averages. For most of the elements the correction factor was equal or less than 1.1 only for As and Hg higher factor had to be applied, i.e. 1.3 and 1.2, respectively. Therefore, for these elements only the 2-year study data were used to evaluate the material stability. Again, the data points were plotted against time and the regression lines were calculated. The slope of the regression lines was tested for statistical significance as well. Since all slopes were not significantly different from 0 on a both 95 % and 99% confidence level, the uncertainty contribution of the long-term stability, u_{lts} could be established as:

$$u_{\mathrm{lts}} = \frac{s}{\sqrt{\sum (x_{\mathrm{i}} - \overline{x})^2}} \cdot t_{\mathrm{sl}}, \tag{4}$$

where:

s:	standard deviation of all results of the stability study
x_{i}:	time point for each replicate
$\overline{x}$:	average of all time points
t_{sl}:	proposed shelf life (24 months at 18 ºC in this case)

When combining the stability data one degree of freedom was lost due to the correction applied. However, it was checked that this change has no impact on the uncertainty of stability and was therefore neglected.

The results of the evaluation of the material stability are summarised in Table 5. The results of the measurements are shown in Annex D.

Table 5: Results of the long-term stability tests

Element	Measurement technique	Slope significance	$u_{\text{lts, rel}}$[a] [%]	Source of data
As	ICP-SFMS	No	5.4	2-year stability study
B	ICP-SFMS	No	1.5	Combined 1-year and 2-year stability study
Cd	ICP-SFMS	No	1.9	2-year stability study
Cr	ICP-OES	No	0.9	2-year stability study
Cu	ICP-SFMS ICP-OES	No	1.2	Combined 1-year and 2-year stability study
Hg	CV-AFS	No	2.8	2-year stability study
Mn	ICP-SFMS ICP-OES	No	1.2	Combined 1-year and 2-year stability study
Mo	ICP-SFMS	No	1.3	Combined 1-year and 2-year stability study
Ni	ICP-SFMS ICP-OES	No	1.0	Combined 1-year and 2-year stability study
Pb	ICP-SFMS	No	1.2	Combined 1-year and 2-year stability study
Sb	ICP-SFMS	No	7.2	Combined 1-year and 2-year stability study
Se	ICP-SFMS	No	4.8	2-year stability study
Sn	ICP-SFMS	No	6.4	Combined 1-year and 2-year stability study
Zn	ICP-SFMS ICP-OES	No	1.1	Combined 1-year and 2-year stability study

[a]: established for a shelf life of 24 months at 18 ºC

Since the characterisation exercise took longer than planned, it was required to check the material stability beyond the established 24 months shelf life. This was done by comparative analysis of 2 vials of the CRM stored at the normal storage temperature (18 °C) and 2 references samples (placed at -20 °C directly after the material processing). Freezing of the reference samples is assumed to render the material degradation negligible. All the samples were analysed (five replicates per each vial) by means of ICP-SFMS (HR: As and Se; MR: Cr, Cu, Mn, Ni and Zn; LR: B, Cd, Hg, Mo, Pb, Sb and Sn), after digestion in a microwave oven using 5 mL HNO_3 and 0.02 mL HF (5 mL HNO_3, 0.2 mL HCL and 0.02 mL HF for Sb and Sn). Additionally, triplicate measurements of Cr, Mn, Sb and Zn using k_0-INAA were performed. The results were corrected for the water content determined in each vial twice (see Section 6.2).

The obtained results of the normal stock samples (stored at 18 °C) were compared with the certified value (see Section 7) taking into account their uncertainties. The uncertainty of the dedicated measurements was established as standard deviation divided by square root of number of measurements, i.e. 10 for ICP-SFMS and 6 for k_0-INAA. For the certified value its expanded standard uncertainty (k = 2) was used (see Section 7).

Additionally, a comparison of normalised results was performed to check the correctness of the measurement methods. The normalisation was done as described below:

- the normal stock results were divided by the results obtained from analysis of the reference samples,
- the certified value was set to 1,
- the uncertainty of the certified value was its expanded standard uncertainty (*k* = 2), see Section 7,
- the expanded standard uncertainty of the dedicated measurements was established as:

$$U_{\text{meas}} = 2 \cdot \frac{\overline{x_{\text{ns}}}}{\overline{x_{\text{ref}}}} \cdot \sqrt{\left(\frac{\frac{s_{\text{ns}}}{\sqrt{n_{\text{ns}}}}}{\overline{x_{\text{ns}}}} \right)^2 + \left(\frac{\frac{s_{\text{ref}}}{\sqrt{n_{\text{ref}}}}}{\overline{x_{\text{ref}}}} \right)^2} \quad , \qquad (5)$$

where:

U_{meas}: expanded standard measurement uncertainty with coverage factor, *k* = 2

s_{ns}, s_{ref}: standard deviations of results of normal stock samples and reference samples, respectively

n_{ns}, n_{ref}: number of results of normal stock samples and reference samples, respectively

$\overline{x_{\text{ns}}}$, $\overline{x_{\text{ref}}}$: average of all results of normal stock samples and reference samples, respectively

All the results obtained using k_0-INAA were in agreement with the certified values. The results obtained using ICP-SFMS were in agreement with the certified values with some exceptions: the reported data for Cd were below and for B, Cu, Mn above the uncertainty limit of the certified value. However, the values normalised to the reference samples were within the uncertainty of the certified value. This indicates a bias of the measurements or insufficient accuracy of the method used. Additional confirmation of this observation are the results of the k_0-INAA method, that showed the stability of the material in case of Mn (Cd, B and Cu were not measured). Therefore, it was concluded that the material is stable with respect to the content of all tested elements and its shelf life can be extended for the next 24 months at 18 °C. After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

The results of the stability control are summarised in Annex E.

6 Characterisation

6.1 Approach

The material characterisation was based on a laboratory intercomparison approach, i.e. the element content in the material was determined in different laboratories that applied different measurement procedures to avoid method bias.

Participants for the characterisation study were selected based on criteria that comprised both technical and quality management aspects. Fulfilment of the quality management requirements ensured the technical competence of the laboratory. 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. Having an accreditation was not mandatory. However, when applicable the accreditation scope is stated in the list of participants (see Section 1).

Sixteen laboratories participated in the characterisation exercise. Each laboratory received two vials of ERM-CD281 and was requested to provide 6 independent results, 3 per vial. The characterisation samples were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations (if necessary) and measurements had to be spread over two days and reported on dry mass basis. The water content had to be determined in each ERM-CD281 vial three times (Section 6.2).

As a quality control sample, each participant received a sample of BCR-281 Rye Grass as blind sample to perform a single analysis. The results for this sample have been used only to support the evaluation of the characterisation results (to confirm outliers, see Section 6.4), and therefore are not reported here.

6.2 Dry mass determination

For all measurements carried out during ERM-CD281 certification (homogeneity, stability and characterisation studies) the following protocol for dry mass determination was applied:

Dry mass determination should be carried out on a separate portion of at least 1 g, by drying in an oven at 105 °C ± 2 °C until constant mass (separate weighings should not differ by more than 5 mg) is attained.

The water content determined by the laboratories was in the range of 2 wt. % to 6 wt. %. However, results within each laboratory and over a longer time (up to one year) were consistent.

6.3 Methods used

Variety of acid digestion methods with different quantification steps (ICP-OES, ICP-QMS, ICP-SFMS, AAS, AFS) as well as methods without sample preparation (NAA, DMA) were used to characterise the material. Quantification was based on different principles: atomic emission, mass spectrometry, atomic absorption as well as neutron capture. It is rather unlikely that all these methods should be biased in the same way.

All methods used during the characterisation study are summarised in Annex F. 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-SFMS). Symbols 'a' and 'b' distinguish between measurements performed in one laboratory with different sample preparation and/or with different instrumentation, e.g. L01a ICP-SFMS and L01b ICP-SFMS.

6.4 Evaluation of results

The characterisation campaign resulted in 10 to 14 datasets per element. All individual results of the participants, grouped per element are displayed in tabular and/or graphical form in Annex G.

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:

- compliance with the analysis protocol: sample preparations and measurements performed on two days, analysis order and water content determination.
- correctness of the measurements based on common knowledge,
- measurement RSD for single dataset: acceptance value was 10 % and less (as obtained for the homogeneity measurements),
- absence of 'less than' and negative values,
- method performance, i.e. delivery of incorrect results for more then half of the analysed elements within one quantification method clearly indicates that the method is not under control. This was verified with the QC sample.

Based on the above some datasets were rejected as not technically valid (see Table 6).

Table 6: Datasets that showed non-compliances with the analysis protocol and technical specifications, and action taken

Element	Lab-method code	Description of problem	Action taken
Se	L01 AFS	RSD about 30 %	Results rejected as not technically valid
Pb	L01 ICP-OES	Lab reported 'less than' values	
Sn	L02 ICP-OES	Lab reported doubts about the results and negative value.	
As, Sb, Se	L02 AFS	Lab reported doubts about the results for Se and Sb. RSD about 40 % for As and 85 % (Sb and Se).	
Sn	L03 ICP-SFMS	RSD about 15 %	
Cr, Mn, Sb, Zn	L04 NAA	Samples were prepared the same day. Additionally, Mn was measured on one day. Cr, Sb and Zn were measured on three different days however each vial (3 subsamples) was analysed within one day (1st day: vial 1; 2nd day: vial 2 and 3rd day: QC samples). Mn was determined on one day (6 subsamples + QC sample). However, there was no significant difference among the results for ERM samples within and between days, and the results for QC samples were correct. Moreover, sample irradiation requires 10 days up to 1 month depending on the element.	Results accepted

Table 6: (continued)

Element	Lab-method code	Description of problem	Action taken
Se	L06 ICP-QMS	Lab reported unexpected problems caused by the DRC technology.	Results rejected as not technically valid
Se	L06 ICP-SFMS	RSD about 12 %	
As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Zn	L07 ICP-QMS	Lab reported 'less than' values for As, Hg and Sb. For 6 out of 9 remaining elements, RSD was above 10 % (B, Cd, Mn, Ni, Pb and Zn). Additionally, QC results differed from the reference value by 17 % – 87 % (B, Cd, Cr, Cu, Ni and Zn).	Results rejected as not technically valid
As, Cd, Cu, Hg, Ni, Se, Sn	L07 k_0-NAA	Lab reported 'less than' values.	
Se, Sn	L07 ET-AAS	Lab reported 'less than' values for Se. RSD for Sn about 40 %	
Cd, Cu, Ni, Pb, Zn	L08 ID ICP-QMS	Samples were prepared the same day but in two independent microwave runs, and additionally in the sequence as requested in the analysis protocol.	Results were accepted
Se	L08 ID ICP-SFMS	RSD about 17 %	Results rejected as not technically valid
As, Sb	L10 HG-AFS	Measurements below LOQ and with RSD about 30 %.	
B, Se	L10 ET-AAS	Measurements of B below LOQ with RSD about 55 %. RSD for Se about 14 %	
Hg	L10 CV-AAS	RSD about 30 %	
Hg	L11 CV-AAS	The sample weighing was performed the same day. However, the digestions and measurements were carried out on separated days.	Results were accepted
As, Se, Sn	L12 ICP-QMS	RSD for As above 15 %. For QC sample lab reported 'less than' values for Se and Sn, and for As significantly higher value.	Results rejected as not technically valid
As, Sn	L13 ICP-QMS	RSD about 30 % (As) and 50 % (Sn)	
Sn	L16 ID ICP-SFMS	Measurements performed under repeatability conditions. However, sample preparations (the largest source of result variations in IDMS analysis) were performed on two days. Water content was determined twice. However, the results within a vial were consistent.	Results were accepted

Further, the technically valid data were subjected to outlier tests (Dixon, Nalimov, Grubbs, Cochran). Based on these tests and visual inspection some outliers could be identified. No data was excluded from the evaluation based on outlier tests alone. The findings were verified by the QC sample. The data sets that were found to be outliers are listed, together with the action taken in Table 7.

Table 7: Results of the statistical evaluation of technically valid datasets

Element	Lab-method code	Description of problem	Action taken
Sb	L01a ICP-SFMS	Results were identified as outlier by all tests except Cochran test. However, measurement uncertainty was comparable to and overlapped with uncertainties from other labs.	Results were accepted
As	L14 ICP-QMS	Results were identified as outlier by all tests except Dixon test. Additionally, the QC sample value deviated significantly from the certified value.	Results were rejected
Cd, Mo, Pb, Sn	L10 ET-AAS	Results were identified as outlier by all tests for Cd, Pb, Sn and by three tests for Mo. Additionally, the QC sample values deviated significantly from the certified value or results of other labs (Sn). Moreover, the other elements measured with AAS were rejected after the technical evaluation (see Table 6).	Results were rejected
Cd, Cr, Cu, Mn, Mo, Pb, Zn	L02 ICP-OES	Labs reported large expanded uncertainties comparing to the uncertainties of the other labs. Both labs applied similar approach to asses the uncertainties: 2 x reproducibility standard deviation (from method validation/quality control charts/interlaboratory comparisons). It could be assumed that the uncertainty is overestimated.	Results were accepted
Cr, Cu, Mn, Mo, Ni, Zn	L05 ICP-QMS		

The certified value was calculated as the mean of means of the accepted datasets. The contribution of the material characterisation to the uncertainty of the certified value u_{char} was estimated as the standard error of the mean of means, and was calculated as the relative standard deviation divided by the square root of accepted datasets. The resulting data are summarised in Table 8.

Table 8: Summary of the characterisation study

Element	Number of independent, valid datasets	Mean of laboratory means[a] [mg/kg]	$u_{\text{char, rel}}$ [%]
As	7	0.0419	3.9
B	7	5.50	3.4
Cd	7	0.1199	1.9
Cr	12	24.77	2.3
Cu	10	10.15	1.7
Hg	9	0.01635	5.1
Mn	12	81.6	1.7
Mo	9	2.219	1.8
Ni	11	15.22	1.5
Pb	8	1.669	1.9
Sb	7	0.0423	3.0
Se	6	0.0225	3.5
Sn	6	0.0619	4.3
Zn	13	30.47	1.4

[a]: reported on dry mass basis (see Section 6.2)

7 Assigned values

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 a certified value for the elements.

The certified uncertainty consists of uncertainties related to characterisation, u_{char} (see Section 6.4), between-bottle heterogeneity, u_{bb} (see Section 4.1) and degradation during long-term storage, u_{ltsl} (see Section 5.2). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{\mathrm{CRM,\,rel}}$) as given by:

$$U_{\mathrm{CRM,\,rel}} = k \cdot \sqrt{u^2_{\mathrm{char,\,rel}} + u^2_{\mathrm{bb,\,rel}} + u^2_{\mathrm{lts,\,rel}}}\ , \tag{6}$$

where:

k: coverage factor equalling 2, representing a level of confidence of about 95 %.

The certified values and their uncertainties are summarised in Table 9.

Table 9: Certified values and their uncertainties for ERM-CD281

Element	Certified value[a] [mg/kg]	$u_{\mathrm{char,\,rel}}$ [%]	$u_{\mathrm{bb,\,rel}}$ [%]	$u_{\mathrm{lts,\,rel}}$ [%]	$U_{\mathrm{CRM,\,rel}}$ [%]	U_{CRM} [mg/kg]
As	0.042	3.9	9.4	5.4	23.0	0.010
B	5.5	3.4	0.8	1.5	7.6	0.5
Cd	0.120	1.9	0.8	1.9	5.6	0.007
Cr	24.8	2.3	0.6	0.9	5.1	1.3
Cu	10.2	1.7	0.6	1.2	4.3	0.5
Hg	0.0164	5.1	3.3	2.8	13.4	0.0022
Mn	82	1.7	0.5	1.2	4.3	4
Mo	2.22	1.8	1.4	1.3	5.2	0.12
Ni	15.2	1.5	0.7	1.0	3.9	0.6
Pb	1.67	1.9	2.3	1.2	6.4	0.11
Sb	0.042	3.0	1.5	7.2	15.9	0.007
Se	0.023	3.5	3.4	4.8	13.7	0.004
Sn	0.062	4.3	2.9	6.4	16.5	0.011
Zn	30.5	1.4	0.3	1.1	3.6	1.1

[a]: reported on dry mass basis (see Section 6.2)

7.2 Additional material information

The results of semi-quantitative screening analysis using ICP-SFMS is given as additional material information (see Table 10). The elements were determined using 18 scans over the mass range, resulting in a total measurement time of 300 s. The results are an average of triplicate measurements.

Table 10: Additional material information

Element	Mass fraction[a] [g/kg]
Ca	6.3
Fe	0.18
K	34
Mg	1.6
Na	4.0
P	2.8
S	3.4
Si	1.3

[a]: average of triplicate measurements reported on dry mass basis

8 Metrological traceability and commutability

8.1 Metrological traceability

Traceability of the certified values to the International System of Units (SI) is ensured through the set-up of the characterisation. The participating laboratories used a number of different methods for the sample preparation as well as for the final determination, thus eliminating any possibility of method dependent results. Only validated methods were used. Different calibrants were employed, including commercial standard solutions and CRMs. Most of the laboratories also used matrix CRMs for quality control (see Annex F). The values of the calibrants and QC samples are traceable to the SI, as stated on the respective certificates. In addition, the agreement between the results confirms absence of any significant method bias and demonstrates the identity of the analytes.

8.2 Commutability

Commutable CRMs should exhibit a similar analytical behaviour for given methods as a real laboratory sample. The laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding sample preparation, calibration and detection. The good agreement between the results obtained indicates commutability of the material. However, it has to be kept in mind that the certified reference materials might show behaviour different from that of real samples, in particular during digestion, due to their small particle sizes in contrast to the possibility larger particle sizes encountered for real laboratory samples, and the intensive processing that these materials have undergone.

9 Instructions for use

9.1 Storage conditions

The materials shall be stored at 18 °C ± 5 °C and in the dark. Care shall be taken to avoid moisture pickup once the vials are open, as the material is hygroscopic. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.2 Safety and protection for the environment

The usual laboratory safety measures apply.

9.3 Use of the material

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

9.4 Minimum sample intake

The minimum sample intake representative for all elements is 200 mg. However, lower sample intakes can be also applied, i.e. 100 mg for all elements As, B, Cr, Hg, Mn, Mo, Ni, Pb, Se, Sn and Zn and 50 mg for As, Cr, Hg, Pb and Sn.

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 105 °C ± 2 °C until constant mass (separate weighings 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 the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

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 [9].

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.

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Annexes

Annex A: Results of the homogeneity measurements

ERM-CD281, B: mass fractions reported on dry mass basis [mg/kg]

Vial #	Replicate 1	Replicate 2	Replicate 3
2	5.41	5.49	5.47
172	5.55	5.36	5.52
301	5.41	5.48	5.48
458	5.55	5.66	5.68
636	5.52	5.51	5.80
749	5.60	5.37	5.18[a]
900	5.50	5.80	5.46
1027	5.61	5.75	5.39
1190	5.46	5.75	5.09[a]
1364	5.40	5.64	5.72
1519	5.39	5.46	5.45
1714	5.49	5.73	5.51
1940	5.51	5.78	5.59
2146	5.74	5.79	5.54
2385	5.58	5.60	5.54

[a]: Outlier on a 95 % confidence level

ERM-CD281, Cd: mass fractions reported on dry mass basis [mg/kg]

Vial #	Replicate 1	Replicate 2	Replicate 3
2	0.133	0.131	0.126
172	0.130	0.129	0.127
301	0.135	0.130	0.126
458	0.130	0.126	0.122
636	0.127	0.129	0.121
749	0.132	0.130	0.127
900	0.126	0.130	0.136
1027	0.130	0.129	0.129
1190	0.132	0.131	0.128
1364	0.131	0.130	0.124
1519	0.127	0.130	0.125
1714	0.136	0.133	0.123
1940	0.129	0.131	0.123
2146	0.130	0.131	0.125
2385	0.133	0.130	0.127

Annex B: Results of the minimum sample intake measurements

ERM-CD281, As: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	0.0354	0.0465	0.0272
2	0.0347	0.0361	0.0284
3	0.0329	0.0324	0.0301
4	0.0347	0.0308	0.0359
5	0.0474	0.0279	0.0258
6	0.0334	0.0336	0.0346

ERM-CD281, B: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	4.35	4.26	4.07
2	4.22	4.27	4.00
3	4.32	4.12	4.17
4	4.45	4.43	3.85
5	4.39	4.44	4.42
6	4.42	4.31	3.90

ERM-CD281, Cd: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	0.122	0.118	0.119
2	0.122	0.121	0.107
3	0.120	0.118	0.108
4	0.121	0.112	0.122
5	0.121	0.113	0.117
6	0.119	0.114	0.118

ERM-CD281, Cr: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	21.1	20.5	21.0
2	21.2	20.5	20.8
3	21.0	20.6	21.0
4	20.9	20.5	20.7
5	20.8	20.7	20.9
6	21.1	20.7	20.3

ERM-CD281, Cu: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	11.9	12.6[a]	12.3
2	11.7	11.9	11.8
3	11.8	11.8	12.4
4	11.9	11.8	12.0
5	11.8	11.9	12.1
6	12.0	11.9	11.7

[a]: Outlier on a 95 % confidence level

ERM-CD281, Hg: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	0.0128	0.0114	0.0109
2	0.0128	0.0116	0.0108
3	0.0130	0.0117	0.0114
4	0.0135	0.0120	0.0125
5	0.0136	0.0120	0.0121
6	0.0130	0.0121	0.0113

ERM-CD281, Mn: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	80.8	79.9	81.1
2	79.3	78.0	76.3
3	78.9	78.1	80.9
4	79.9	79.1	80.0
5	79.5	78.3	81.2
6	80.1	78.9	77.0

ERM-CD281, Mo: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	1.98	1.91	1.93
2	1.99	1.93	1.84
3	2.00	1.93	1.89
4	1.98	1.93	1.92
5	1.96	1.92	1.90
6	1.97	1.94	1.85

ERM-CD281, Ni: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	14.7	14.3	14.9
2	14.5	14.1	14.6
3	14.6	14.6	14.6
4	14.5	14.3	14.6
5	14.6	14.2	14.9
6	14.5	14.5	14.1

ERM-CD281, Pb: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	1.53	1.45	1.50
2	1.51	1.46	1.42
3	1.51	1.48	1.49
4	1.56	1.47	1.50
5	1.53	1.47	1.44
6	1.52	1.49	1.43

ERM-CD281, Sb: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	0.0296	0.0309	0.0295
2	0.0294	0.0266	0.0294
3	0.0293	0.0278	0.0301
4	0.0298	0.0292	0.0280
5	0.0301	0.0272	0.0309
6	0.0307	0.0286	0.0281

ERM-CD281, Se: mass fractions reported on dry mass basis [mg/kg]

Replicate #	200 mg	100 mg	50 mg
1	0.0259	0.0189	0.0213
2	0.0193	0.0247	0.0211
3	0.0227	0.0206	0.0242
4	0.0211	0.0171	0.0198
5	0.0240	0.0252	0.0144
6	0.0237	0.0172	0.0305

ERM-CD281, Sn: mass fractions reported on dry mass basis [mg/kg]

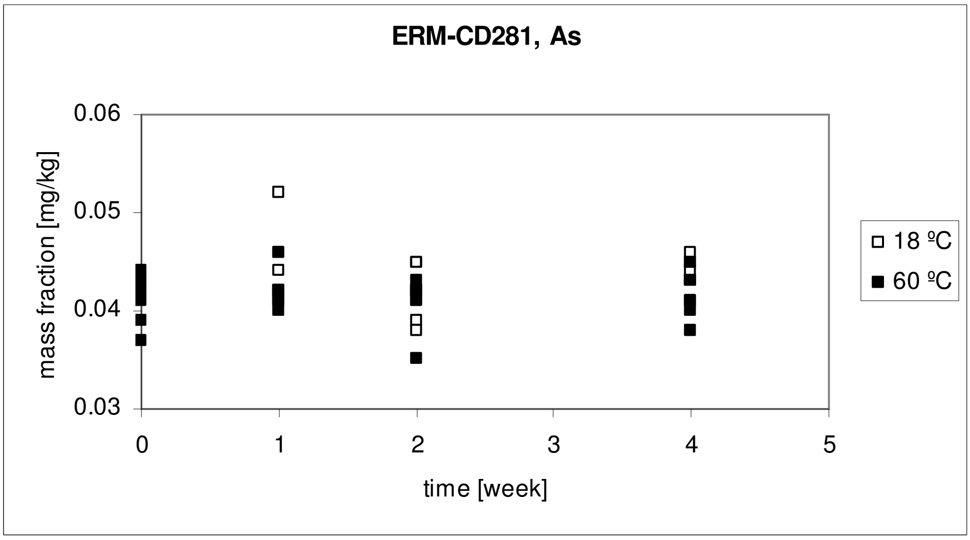
Replicate #	200 mg	100 mg	50 mg
1	0.0482	0.0494	0.0430
2	0.0462	0.0393	0.0439
3	0.0424	0.0511	0.0445
4	0.0490	0.0441	0.0506
5	0.0487	0.0475	0.0462
6	0.0470	0.0464	0.0415

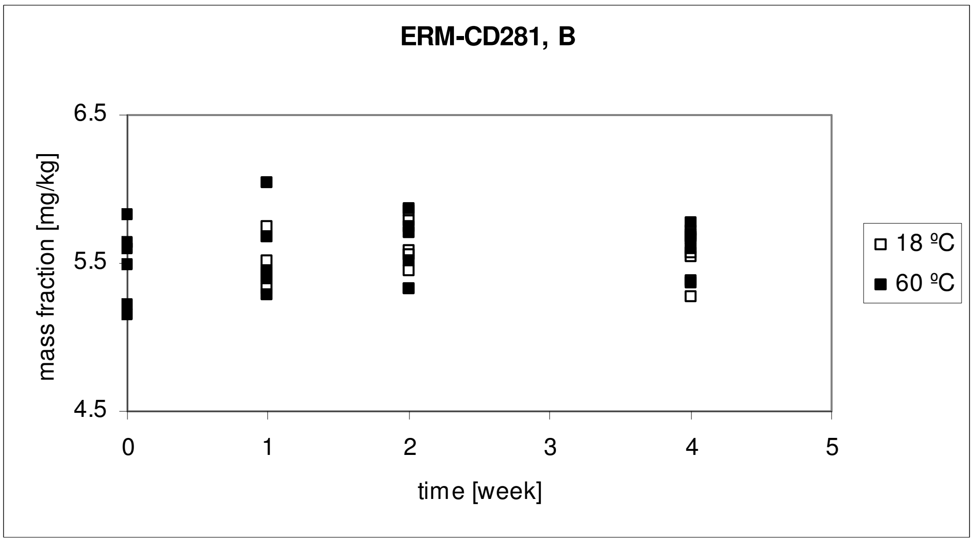
ERM-CD281, Zn: mass fractions reported on dry mass basis [mg/kg]

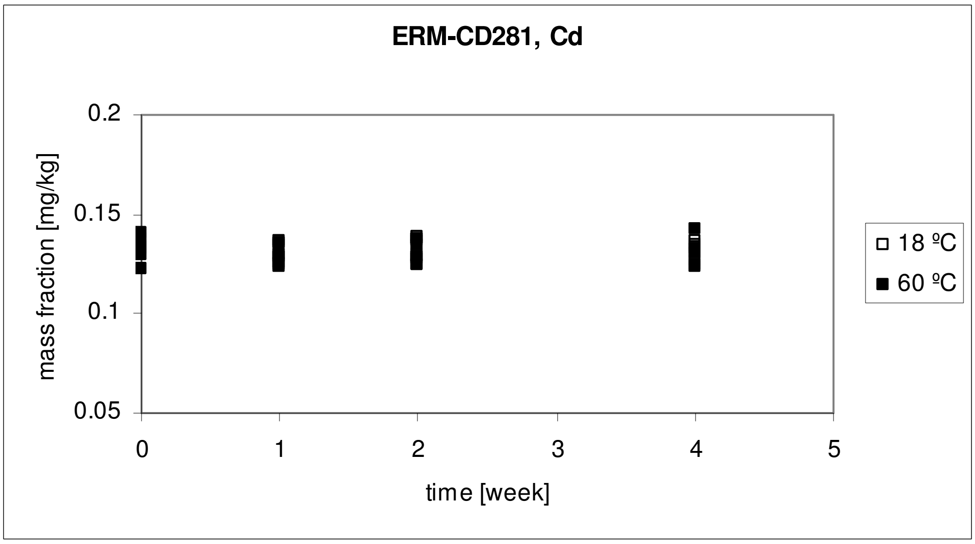
Replicate #	200 mg	100 mg	50 mg
1	27.6	26.6	26.8
2	27.3	26.6	25.2
3	27.4	26.6	26.5
4	27.2	27.1	26.3
5	27.1	26.7	26.4
6	27.5	26.6	25.4

Annex C: Results of the short-term stability measurements

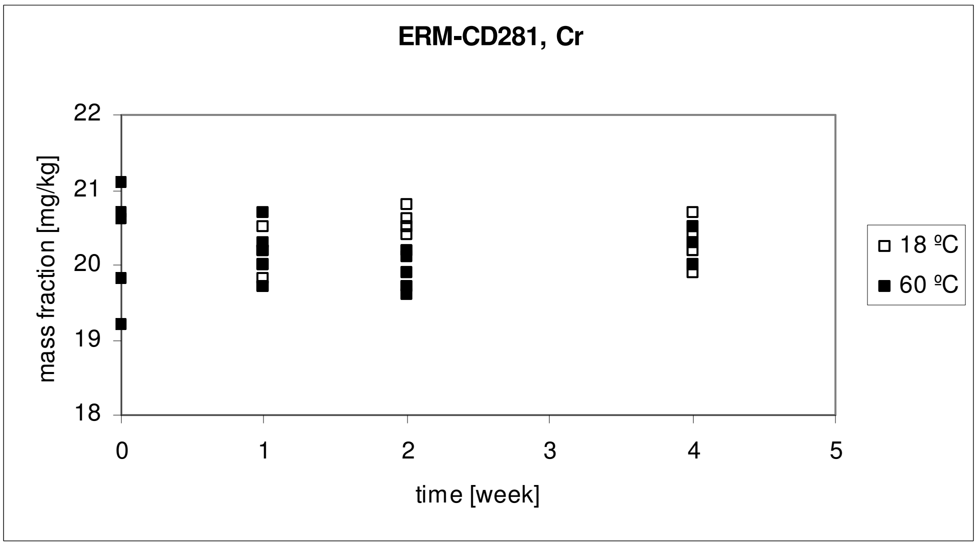
Results reported on dry mass basis

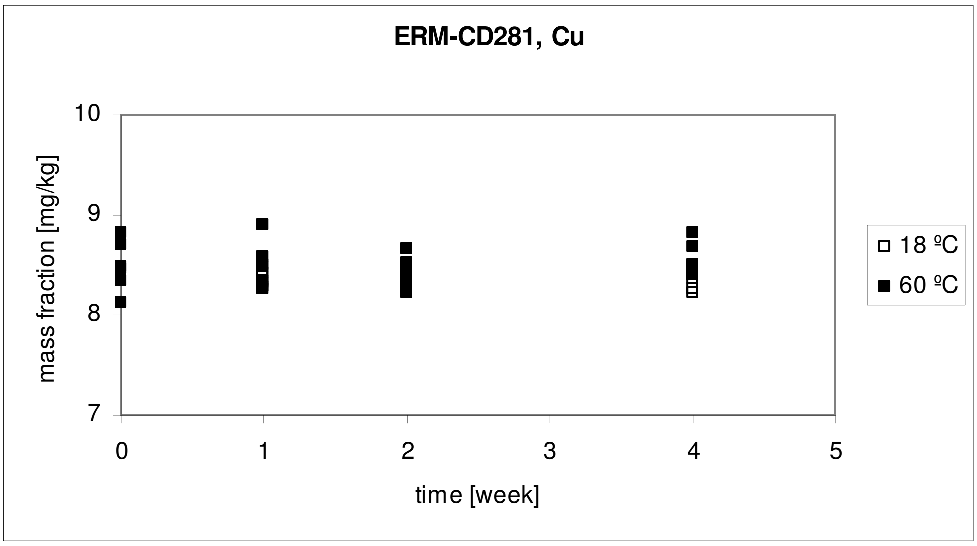


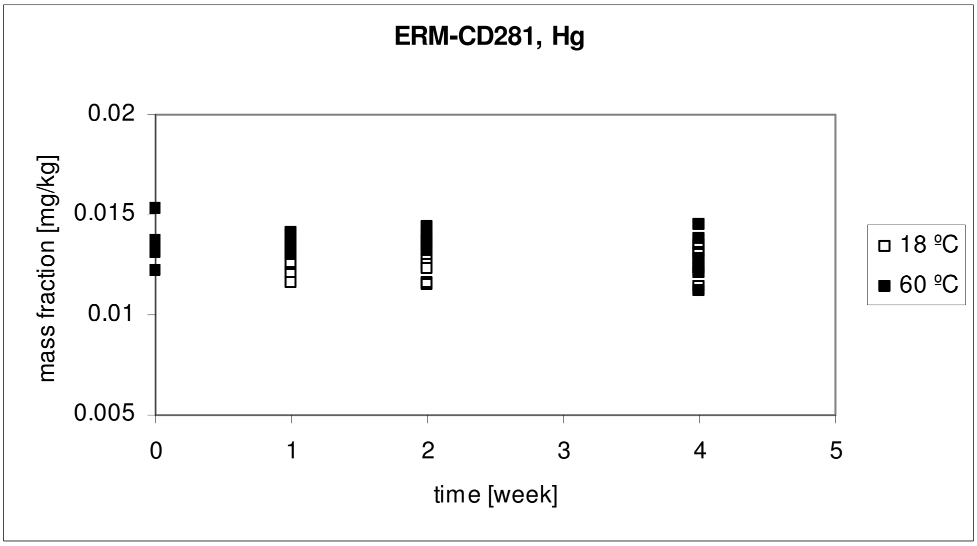




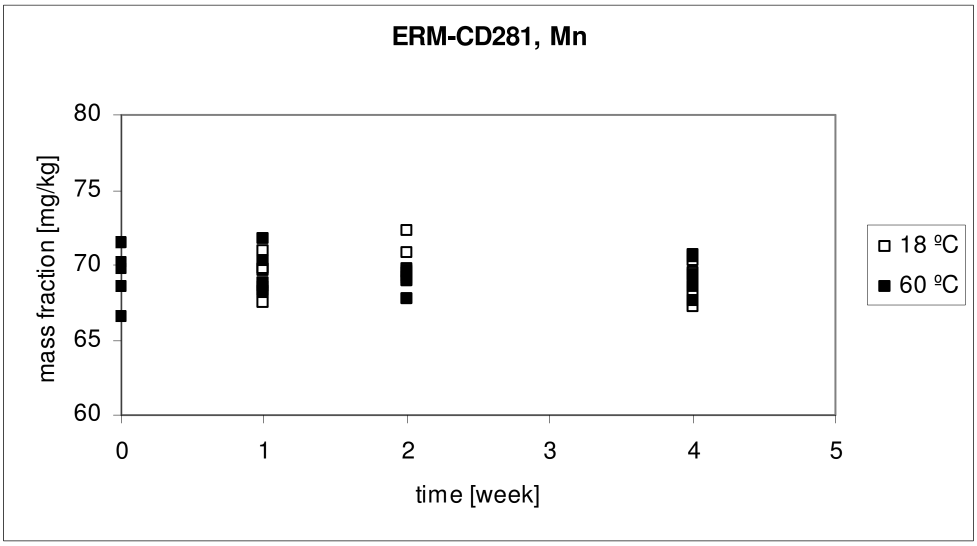
Results reported on dry mass basis

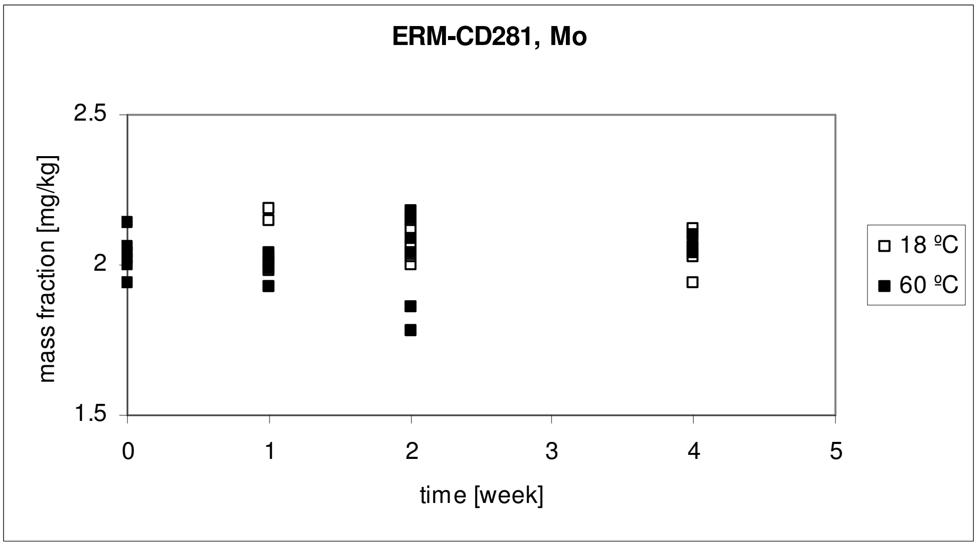


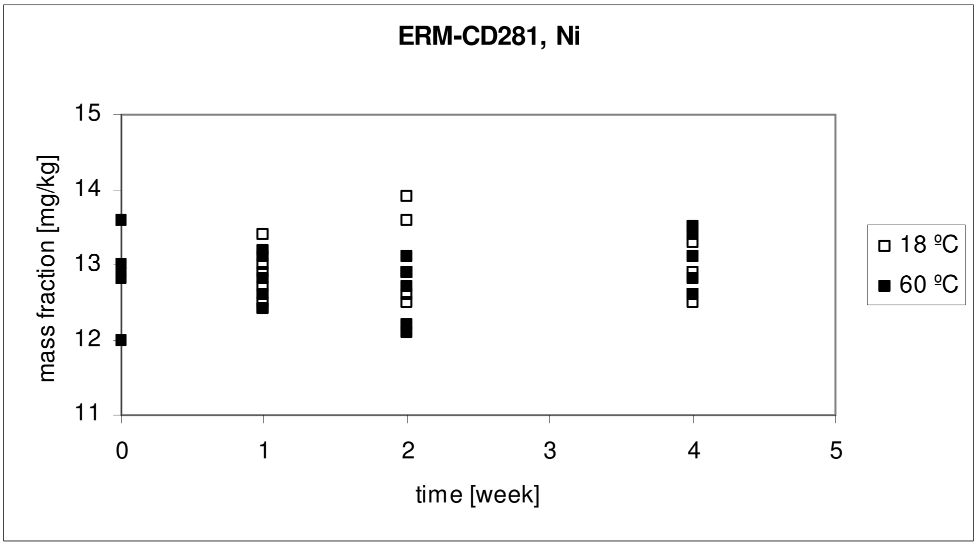




Results reported on dry mass basis







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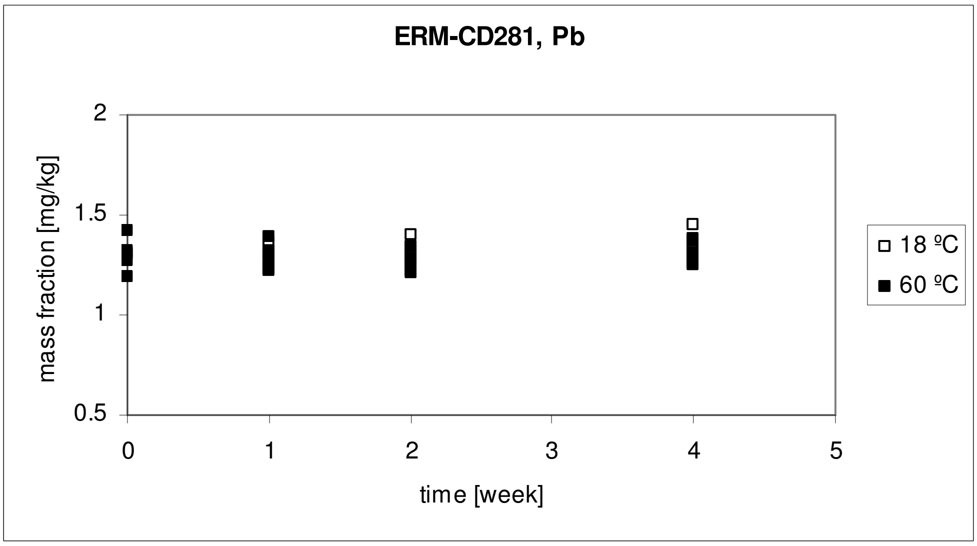
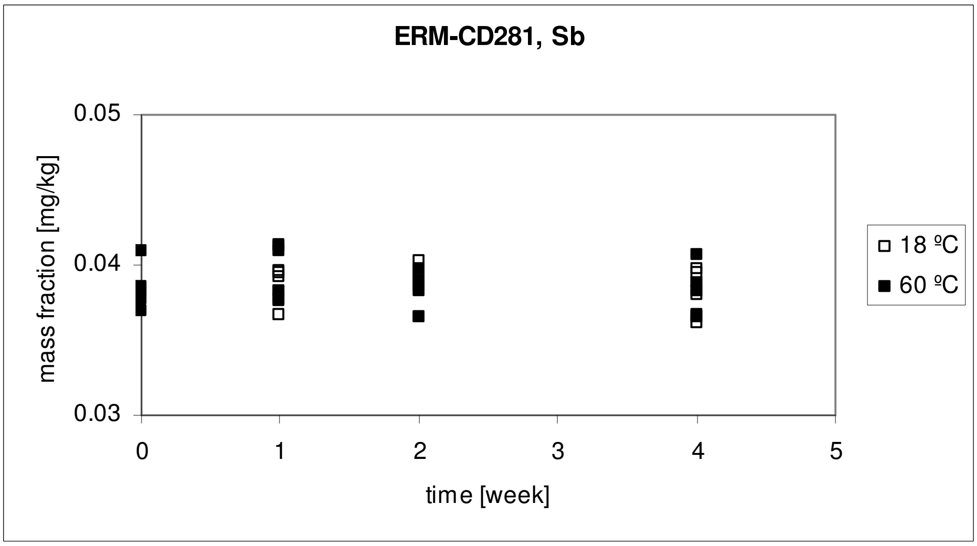
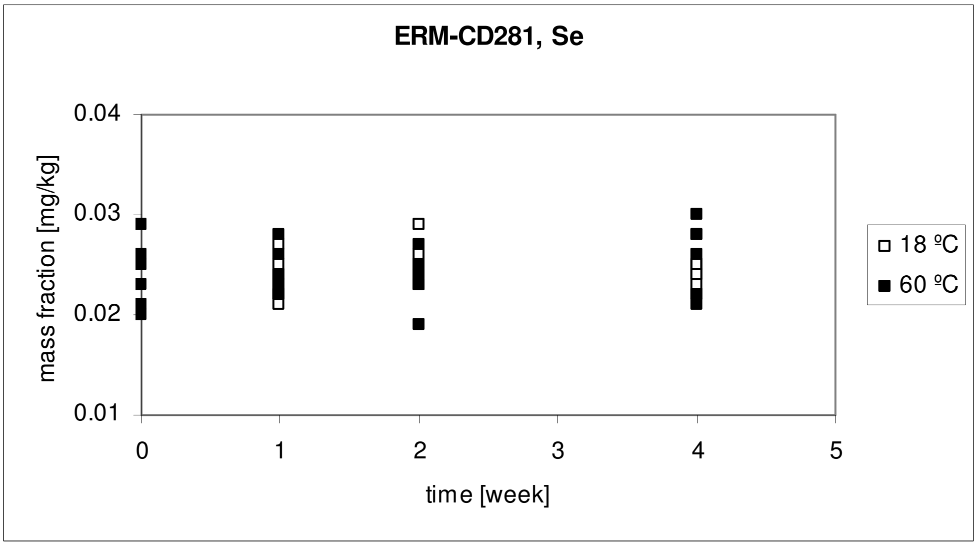
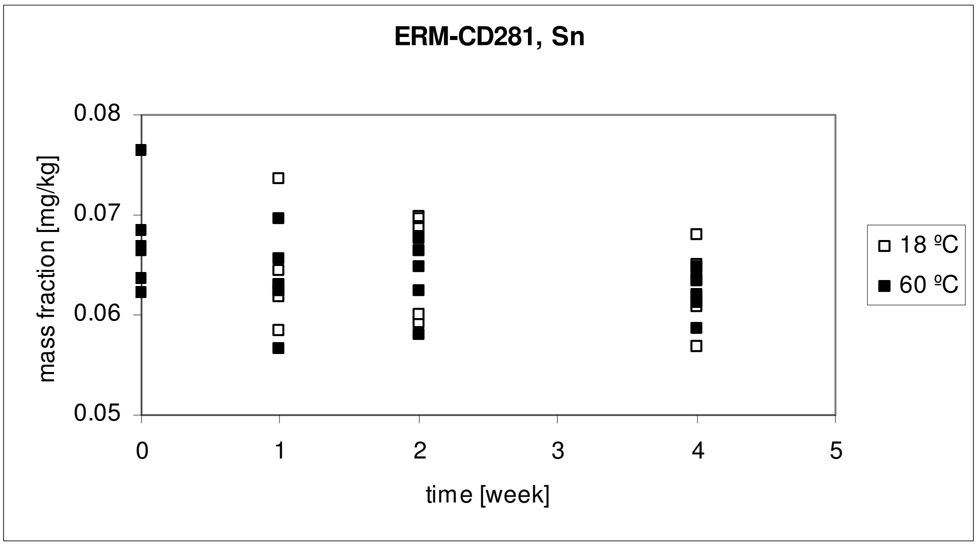
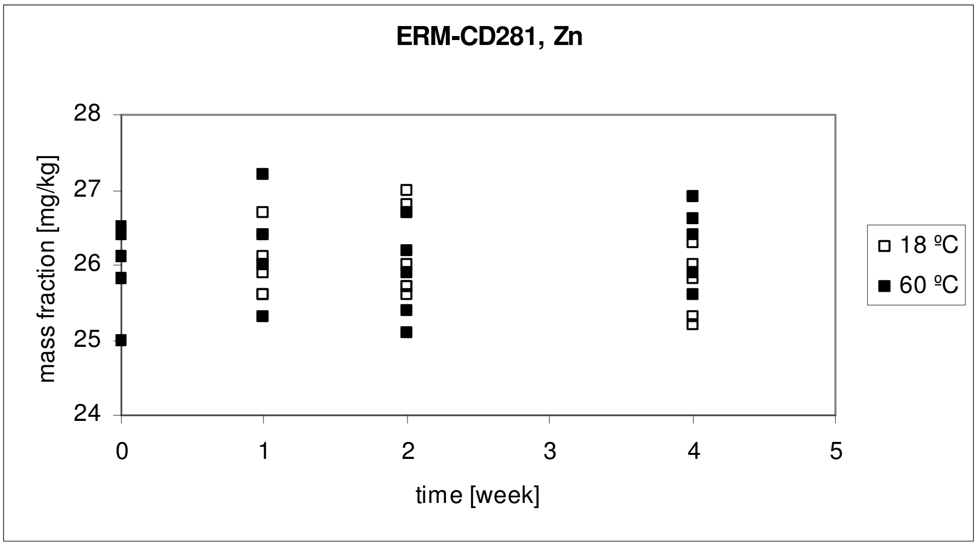






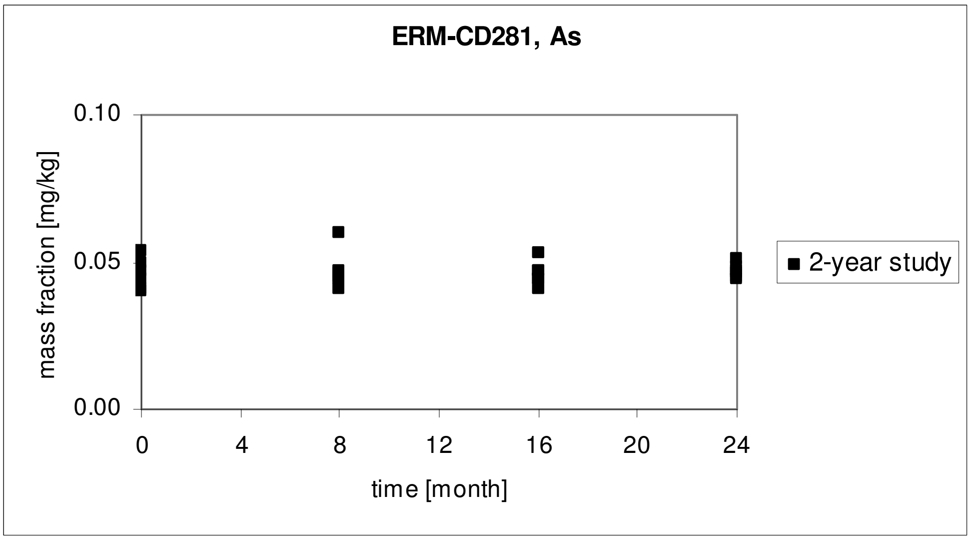
Results reported on dry mass basis

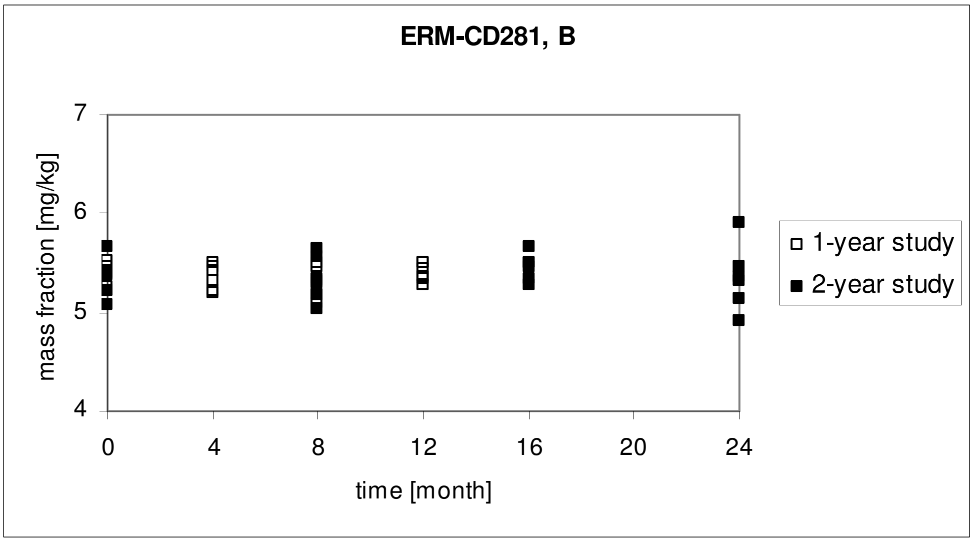


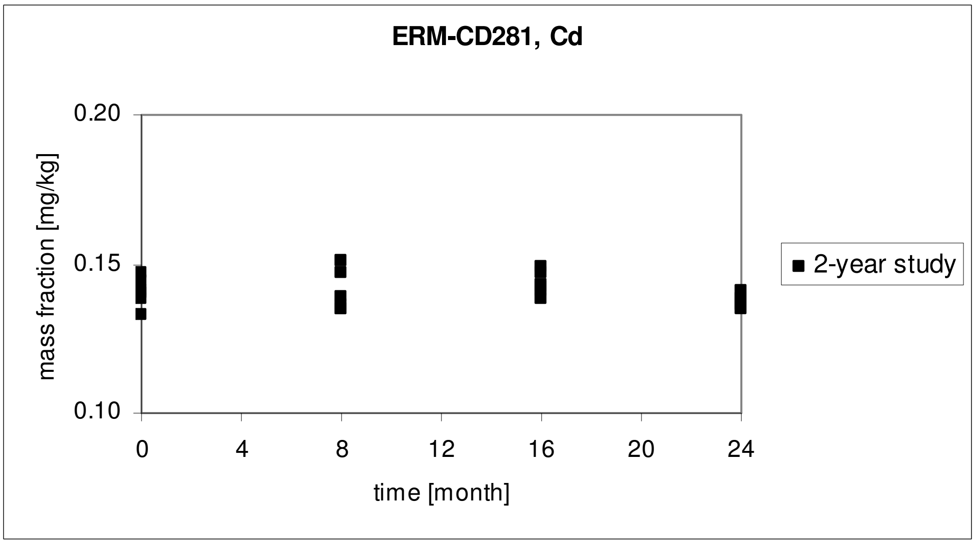


Annex D: Results of the long-term stability measurements

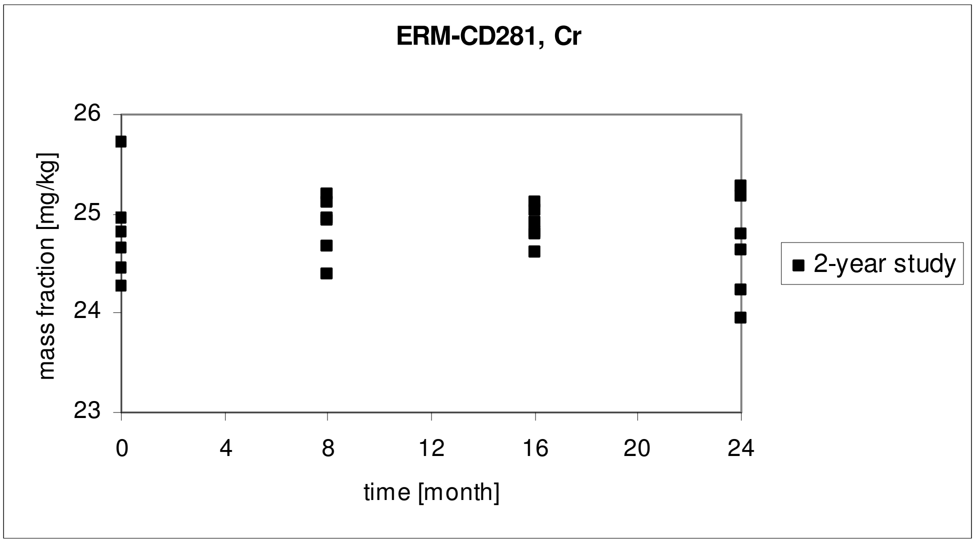
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

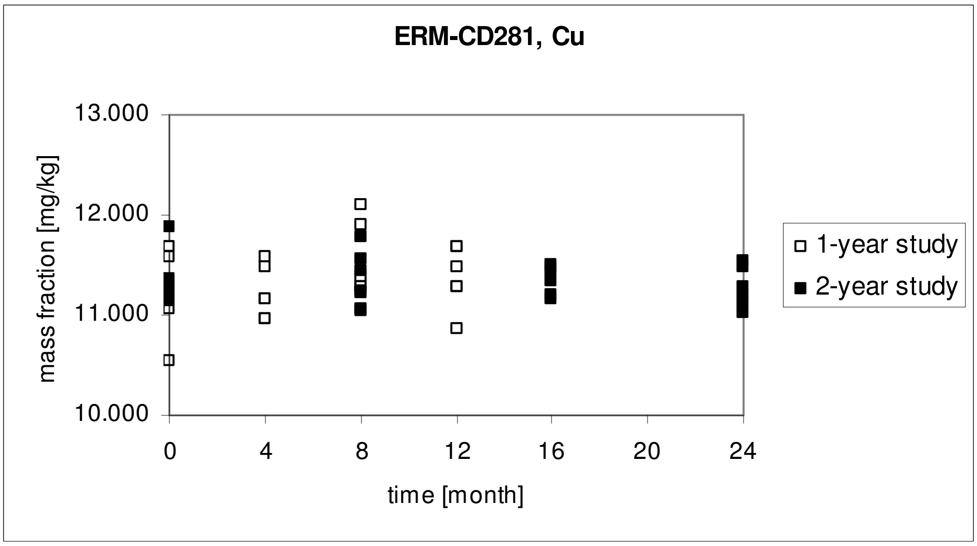


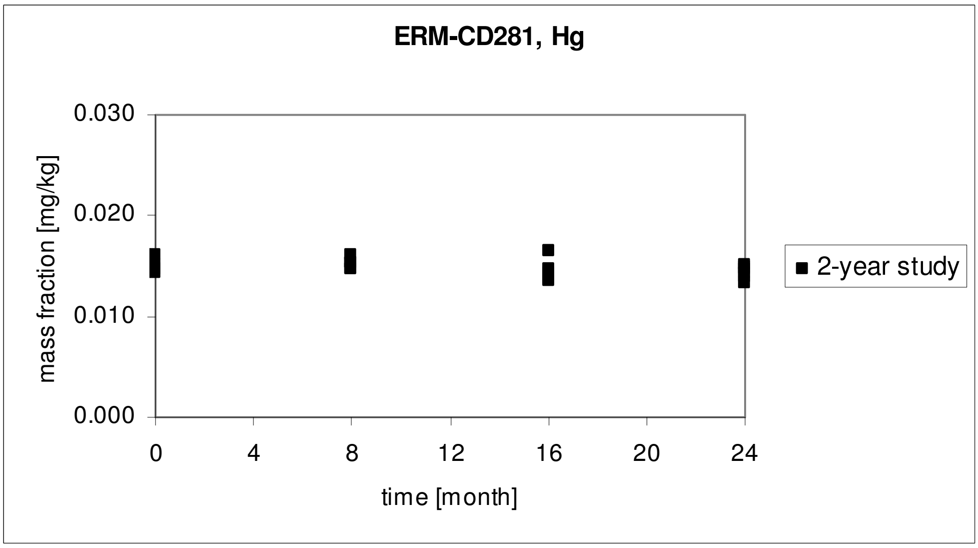




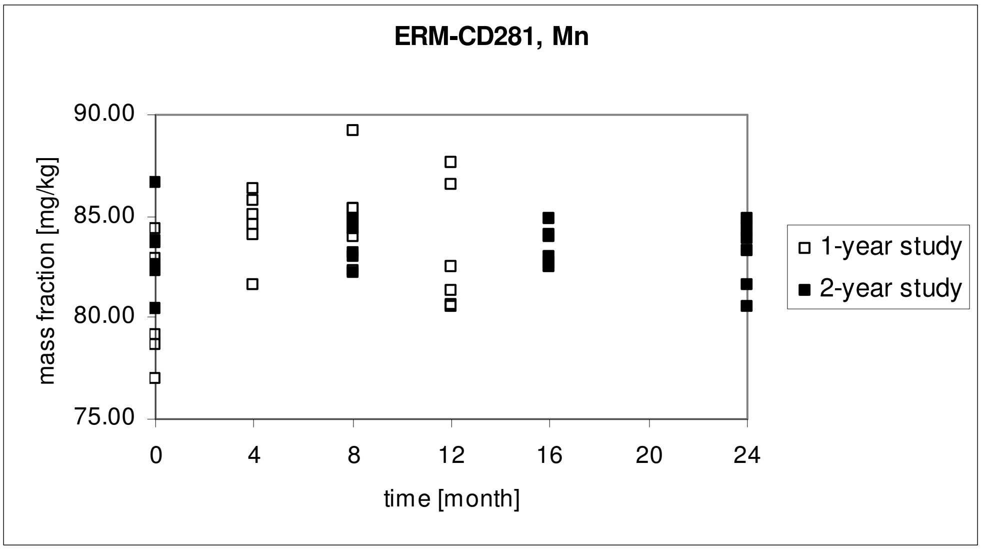
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

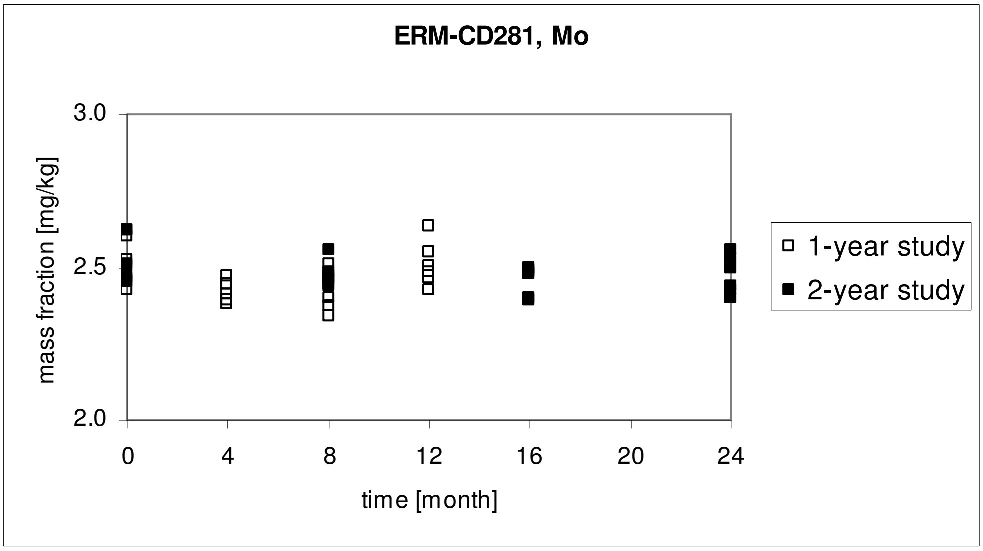


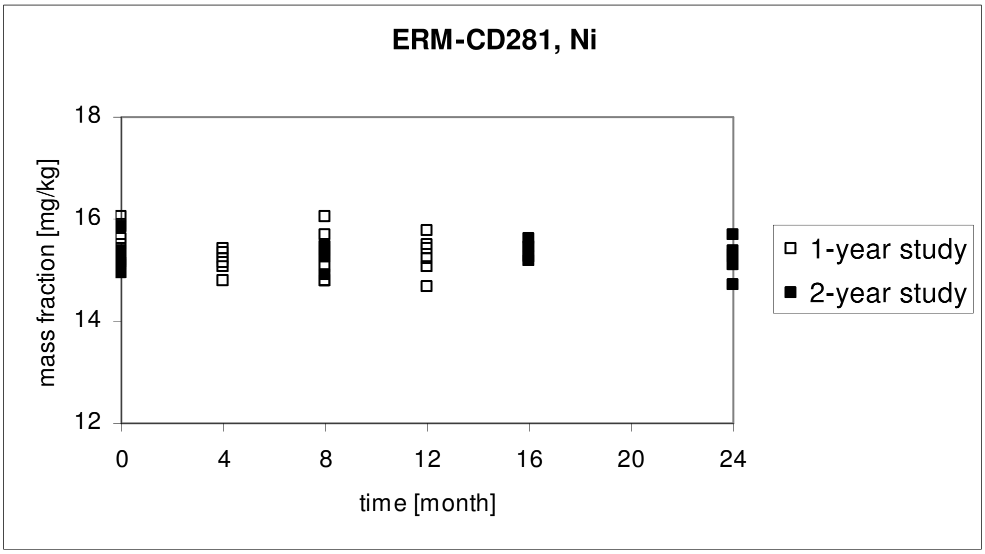




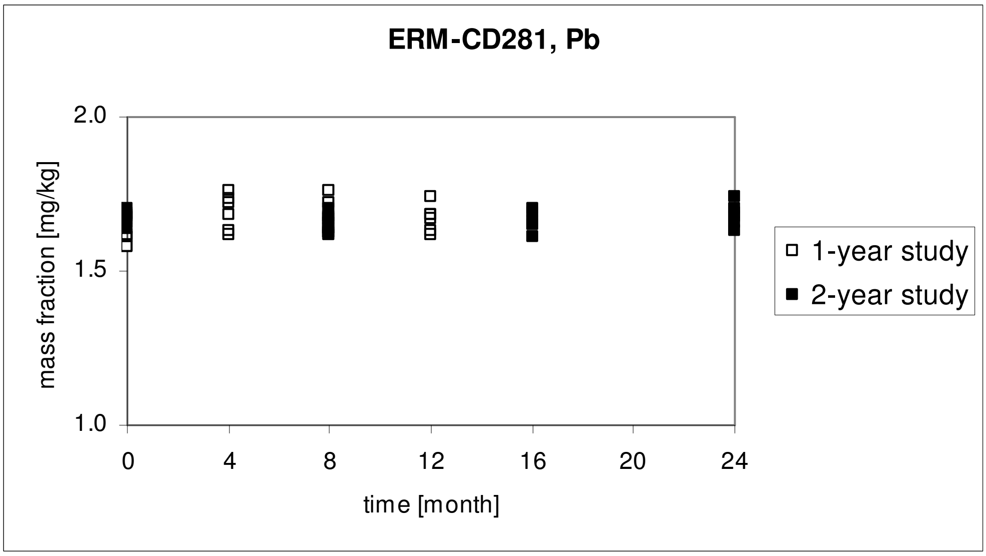
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

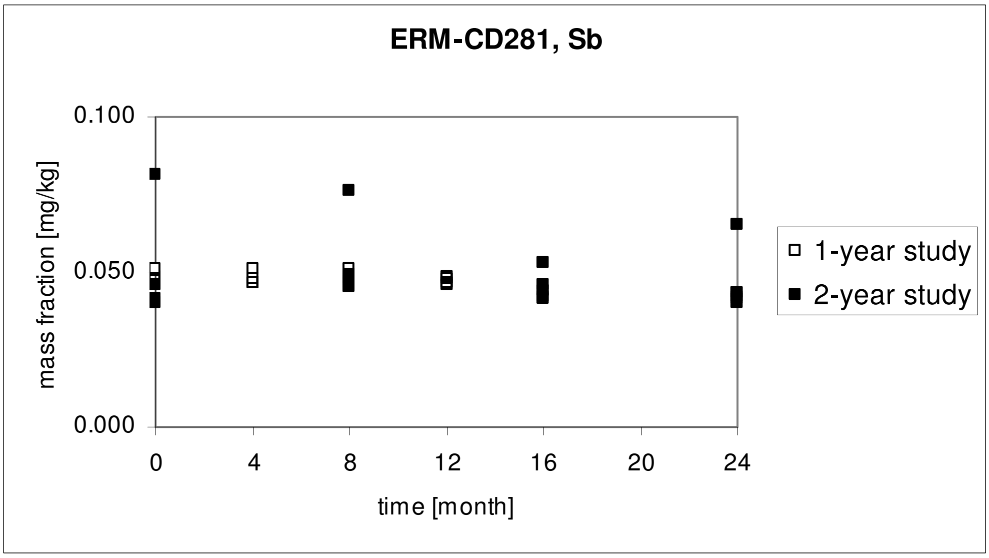


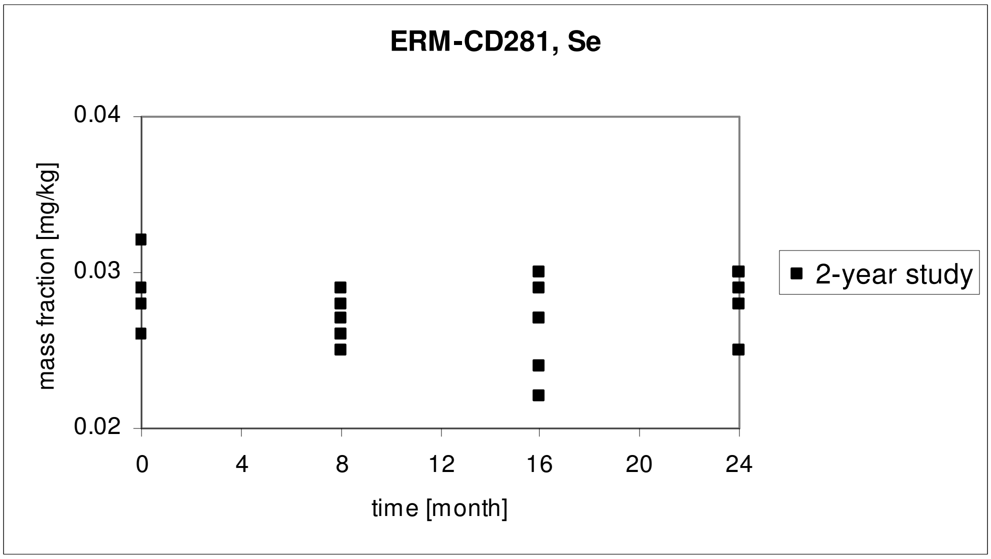




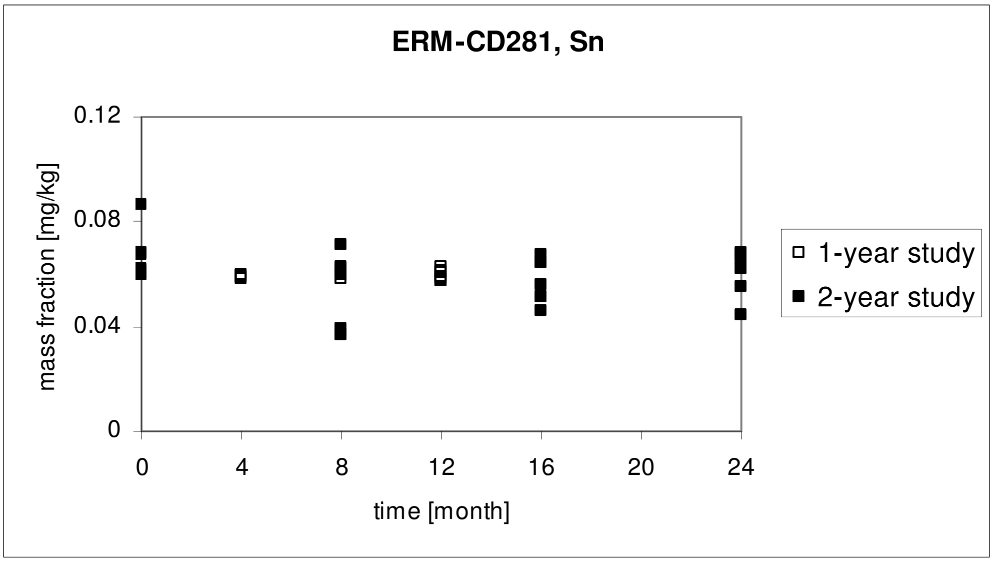
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

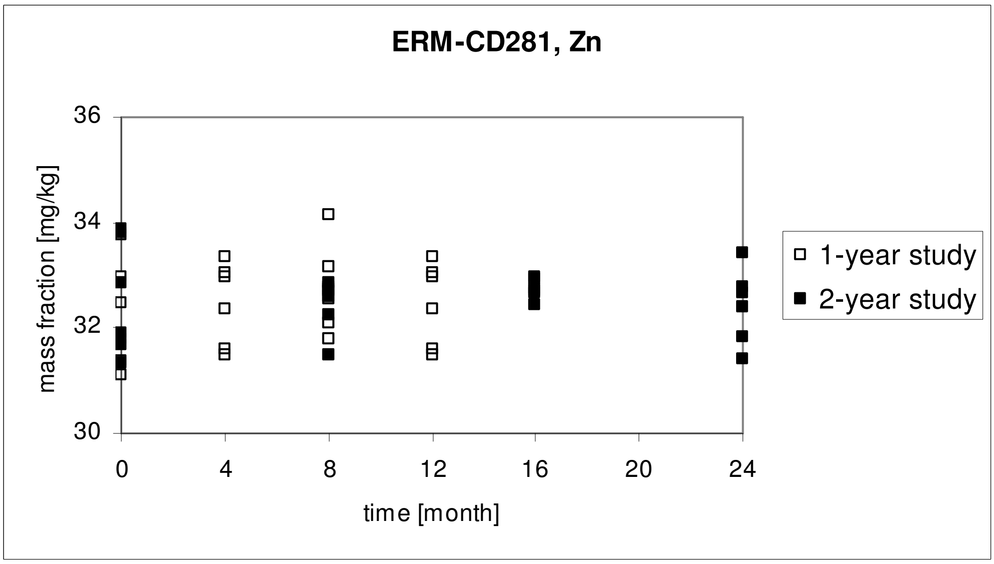






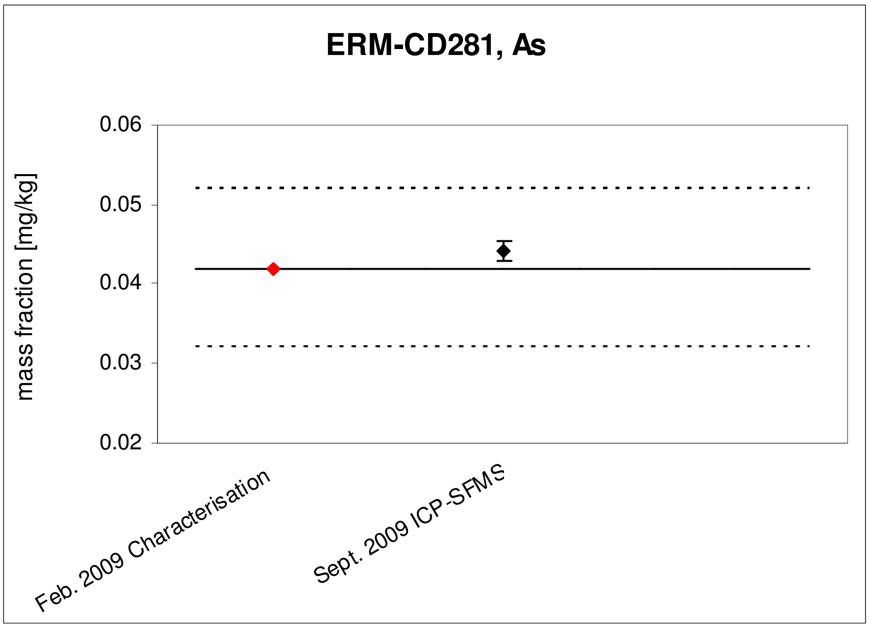
Results reported on dry mass basis. Correction applied when 1-year study is combined with 2-year study.

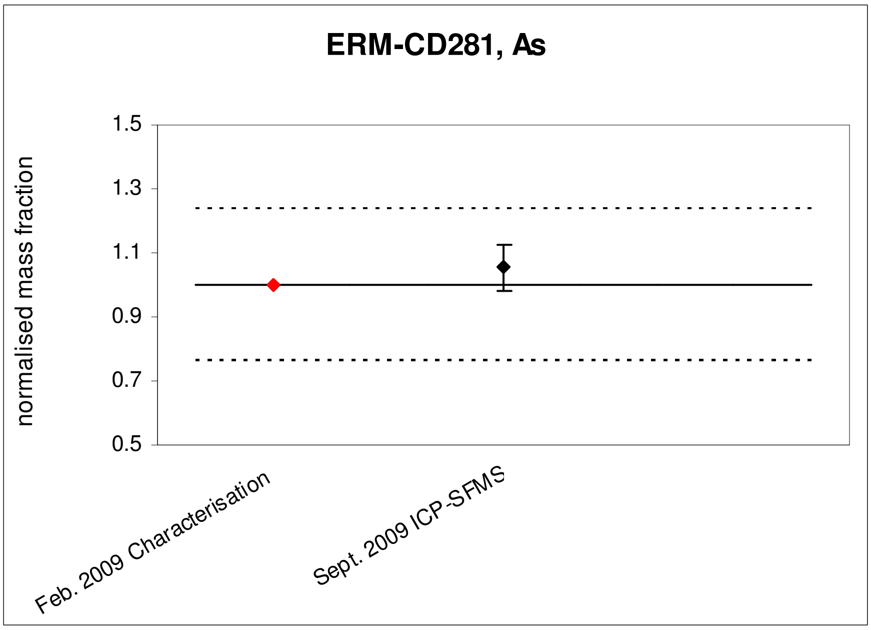




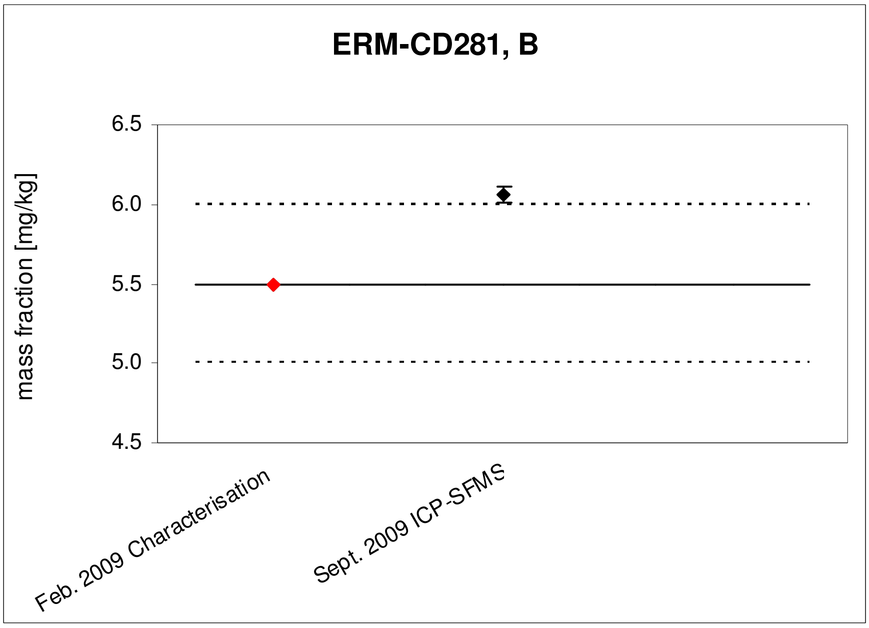
Annex E: Results of the stability control measurements

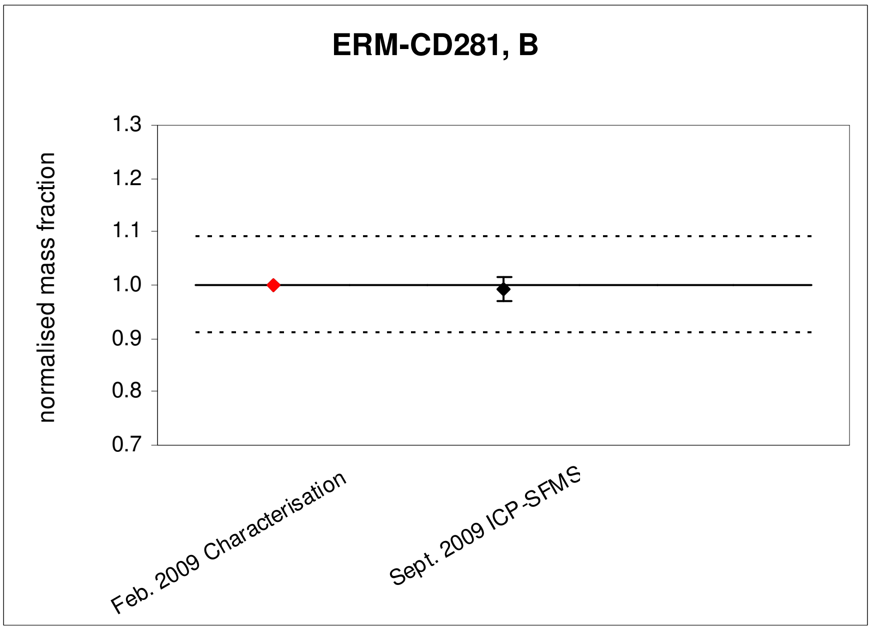
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



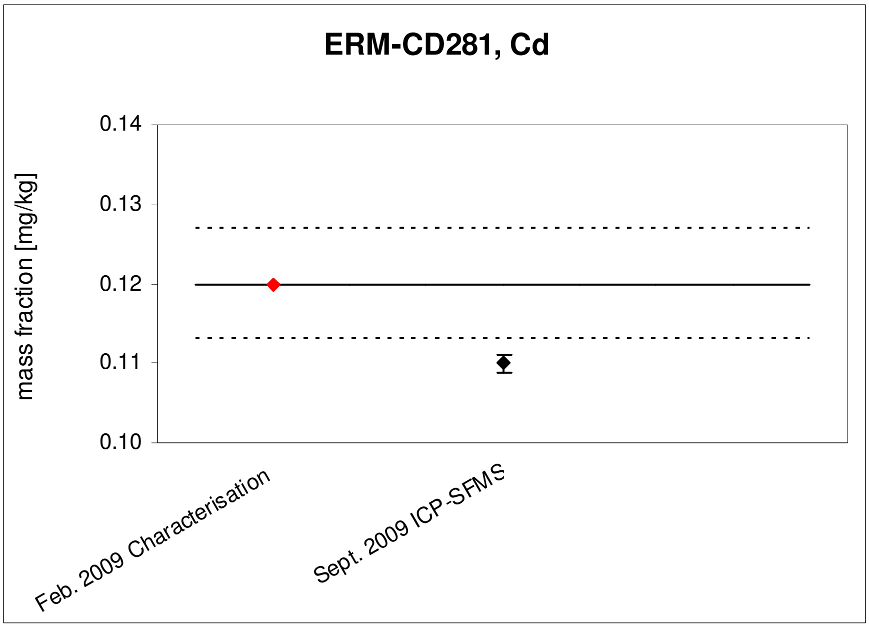


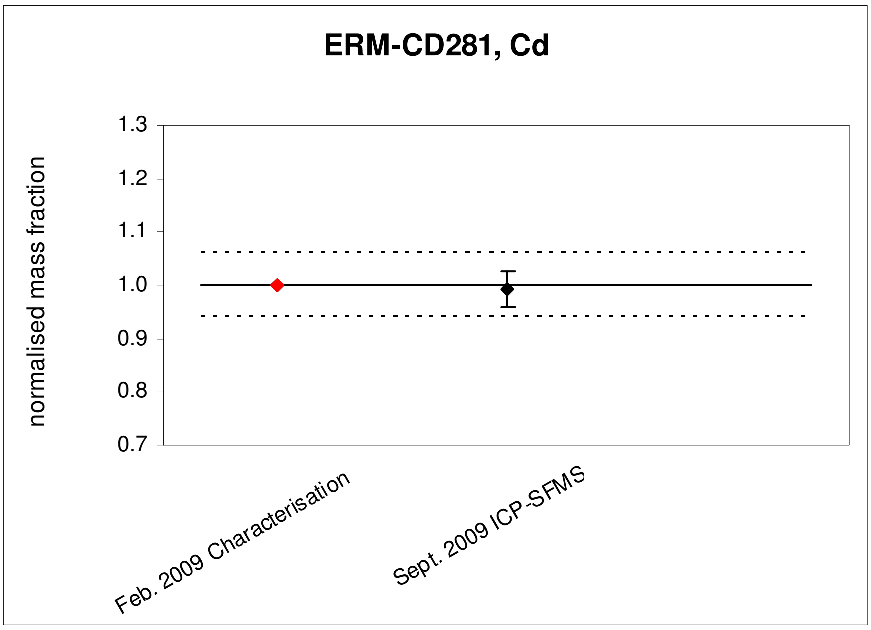
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



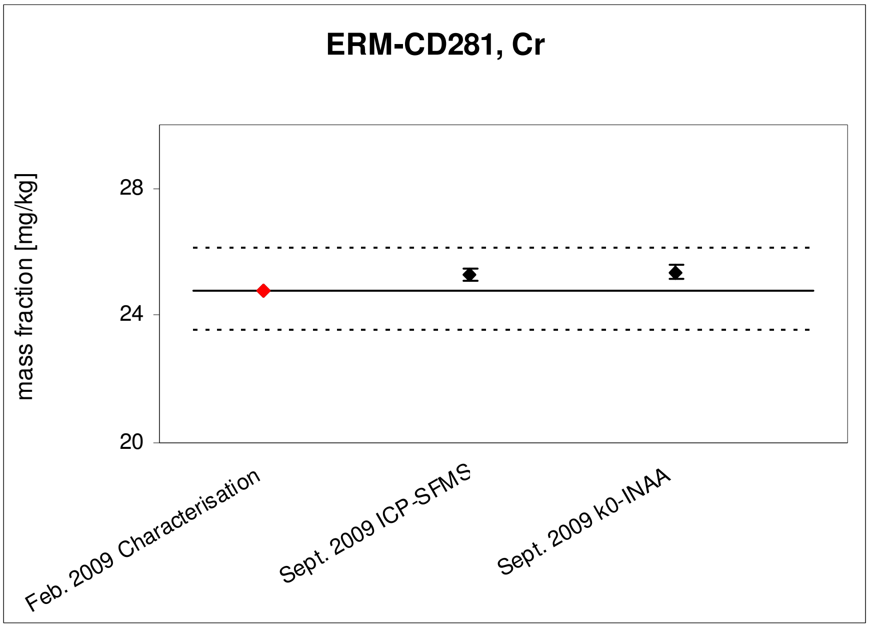


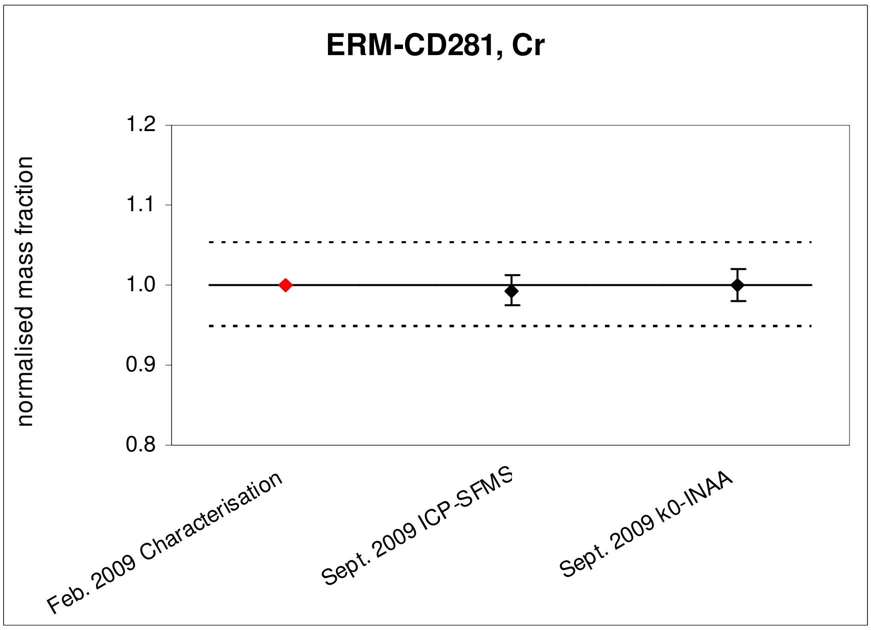
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



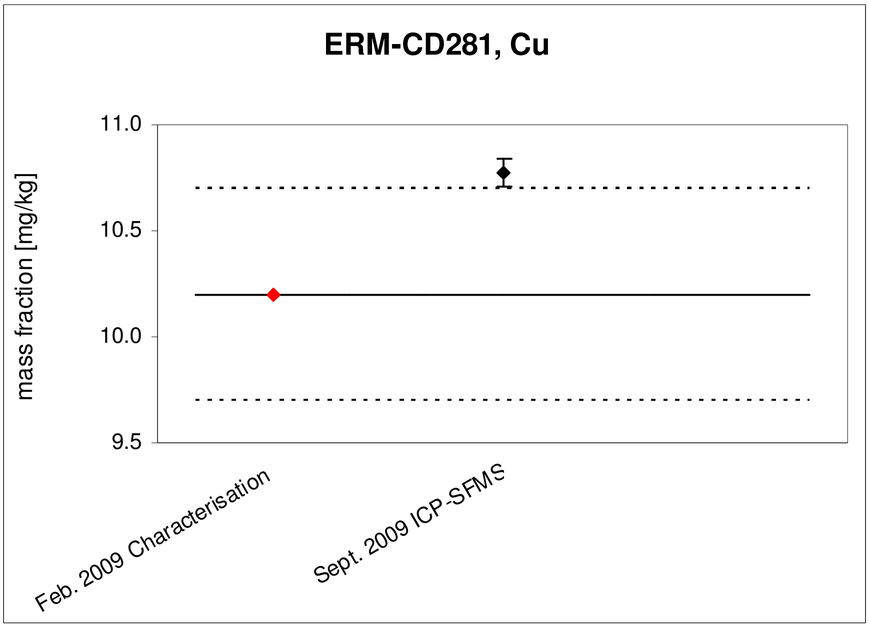


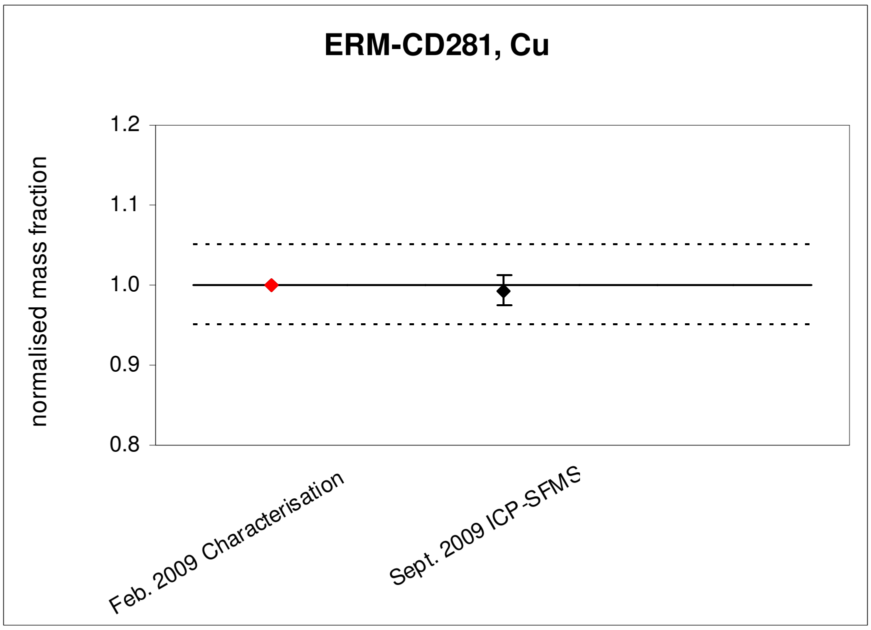
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



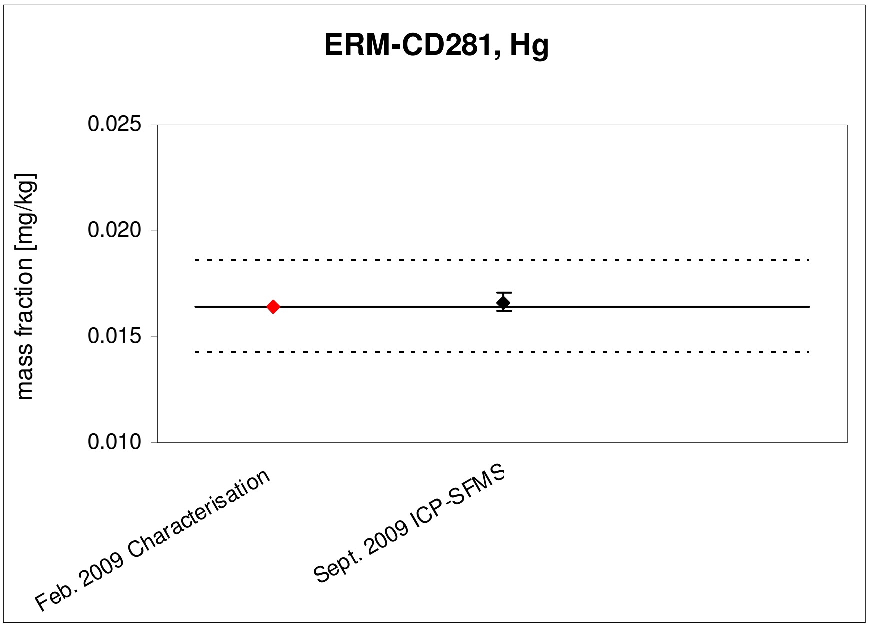


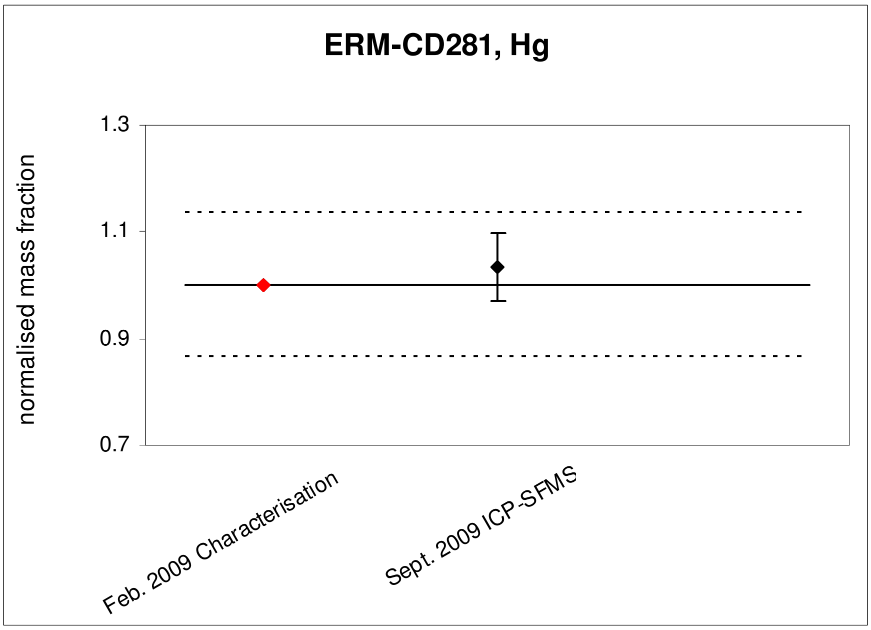
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



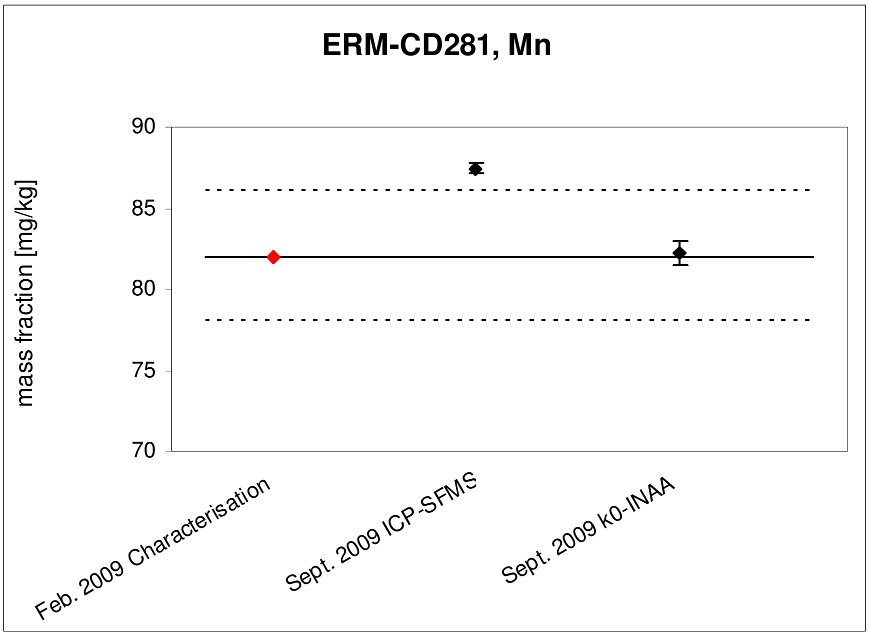


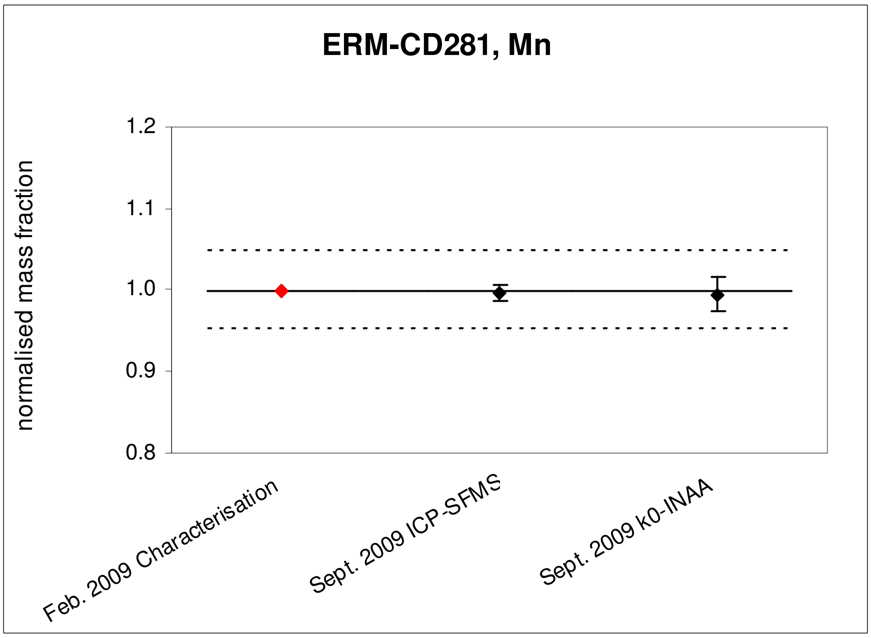
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



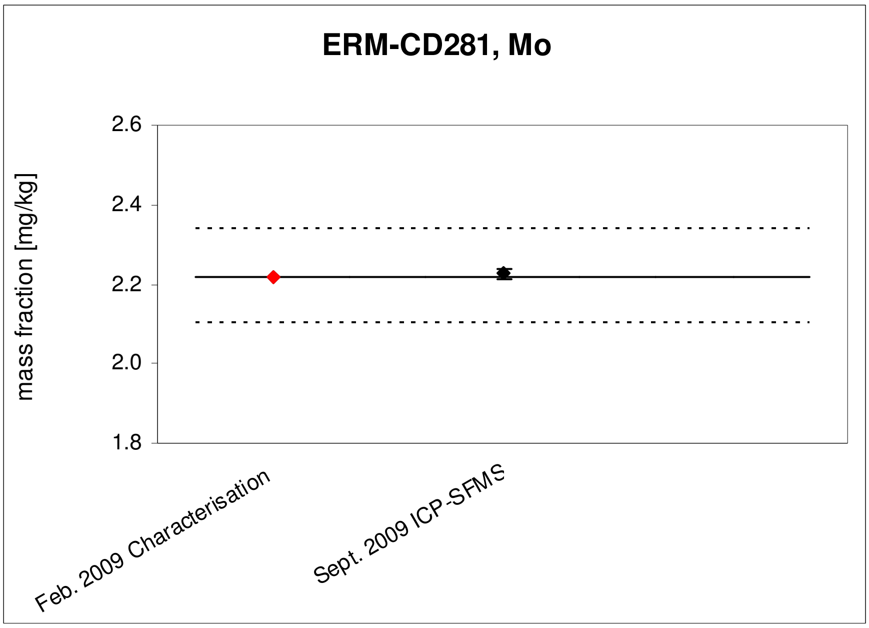


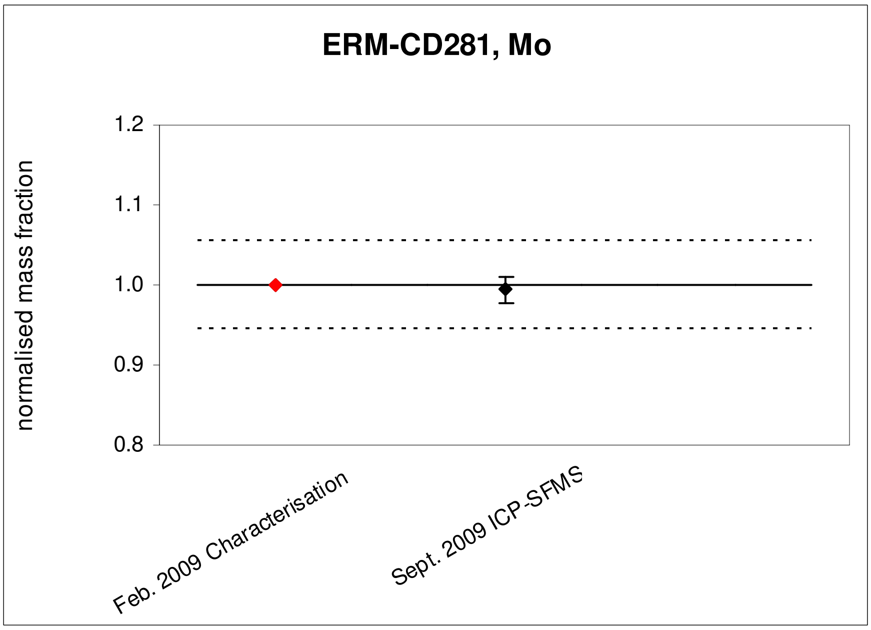
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.





Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.





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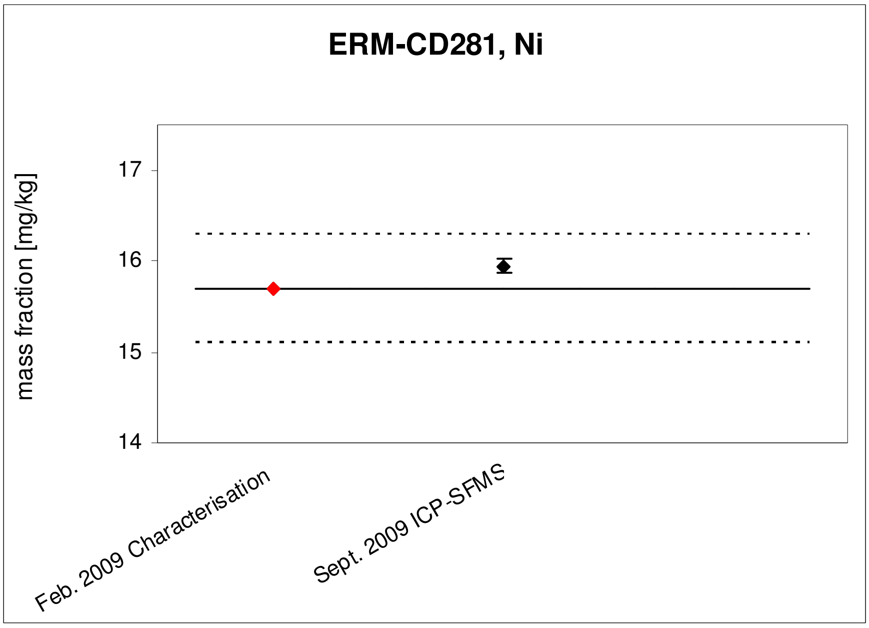
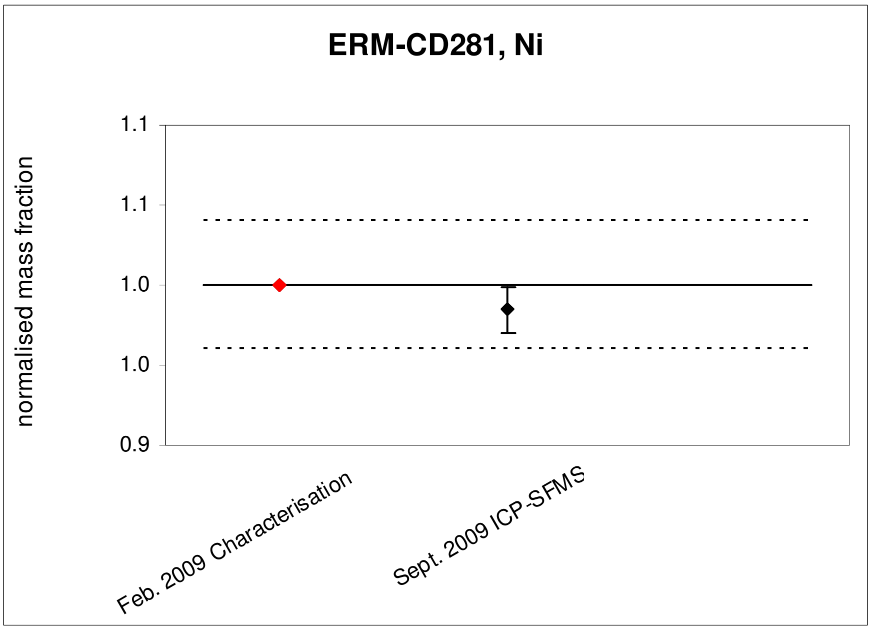
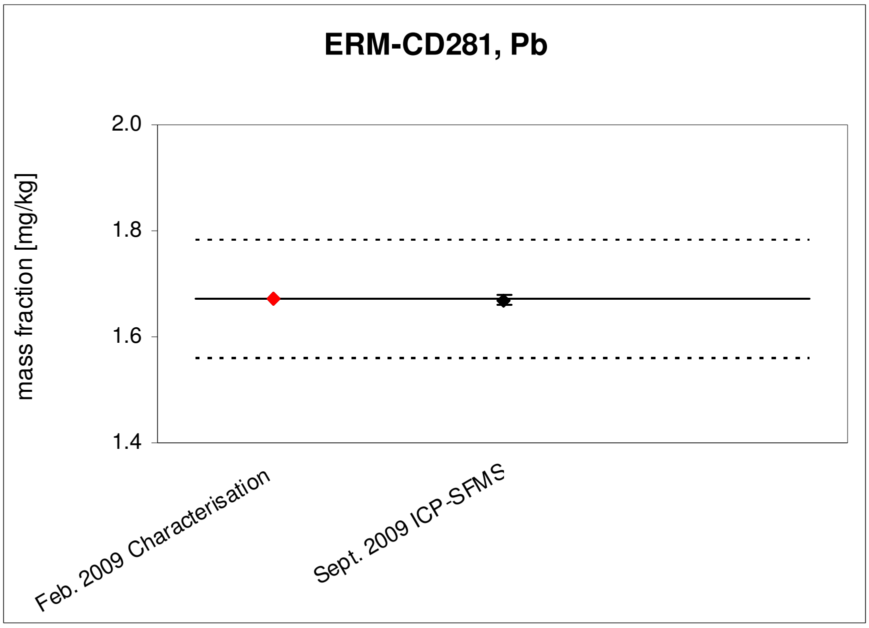
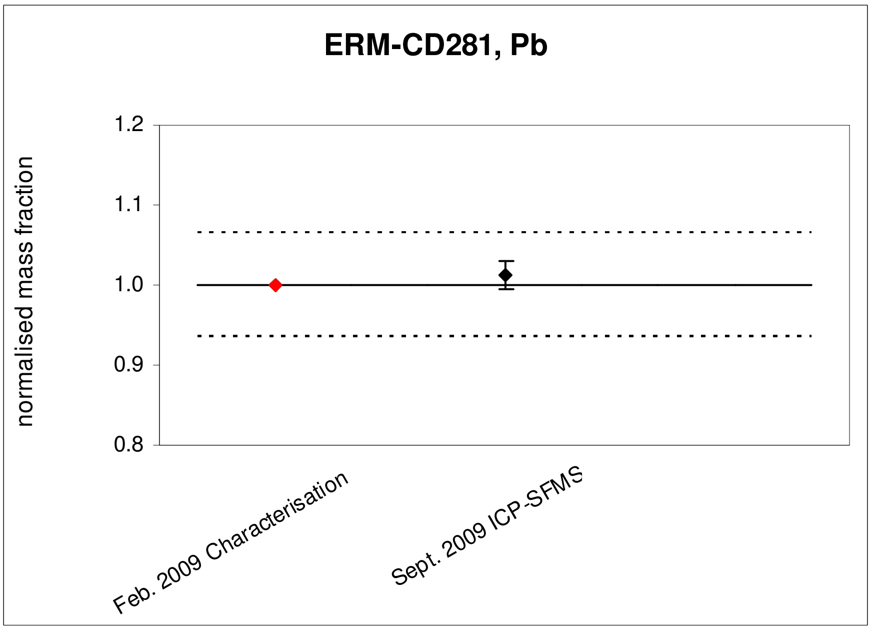


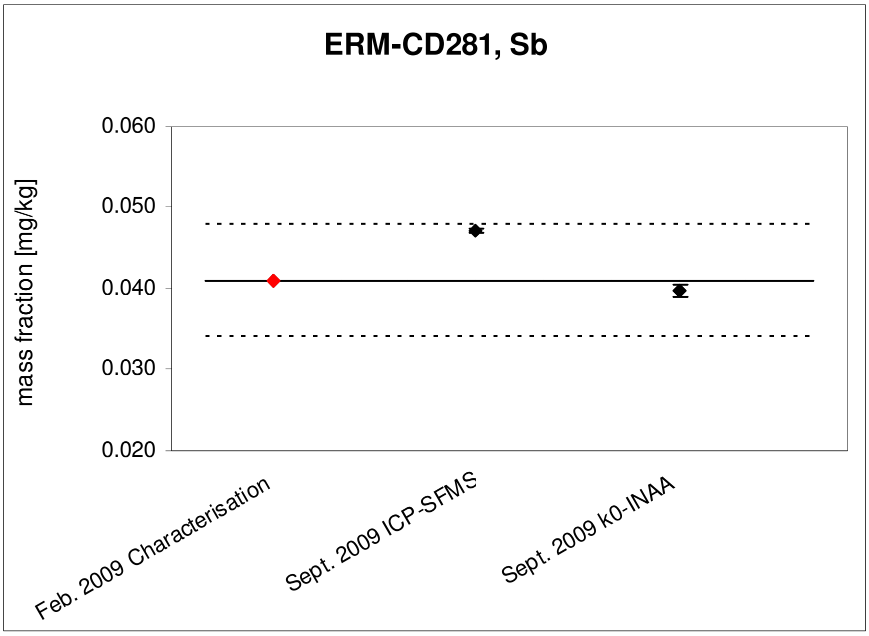


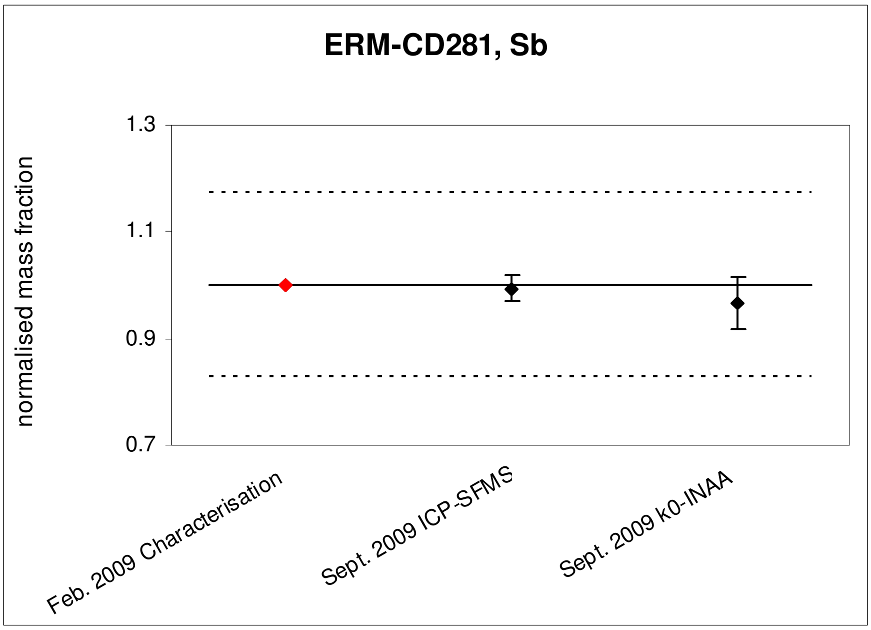
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



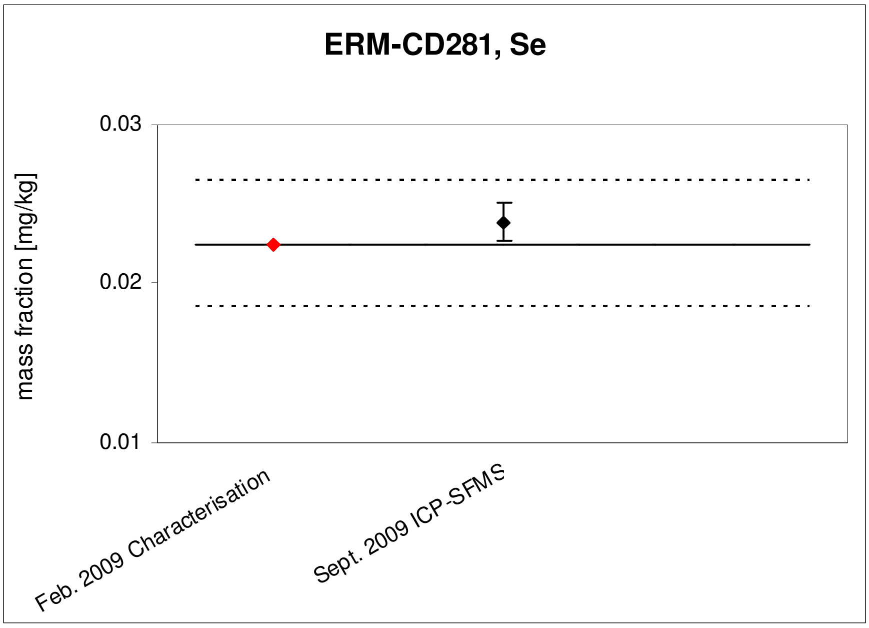


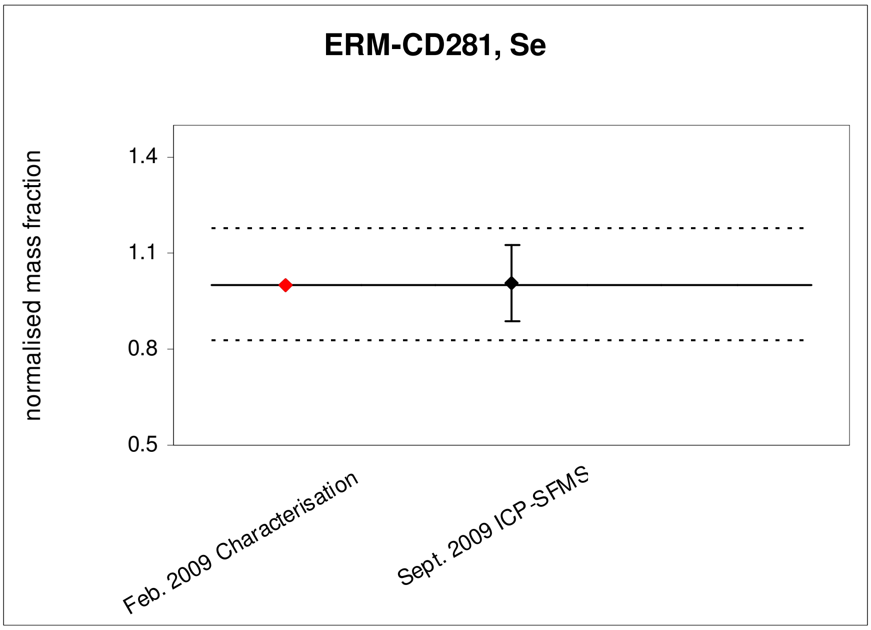
Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.





Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.





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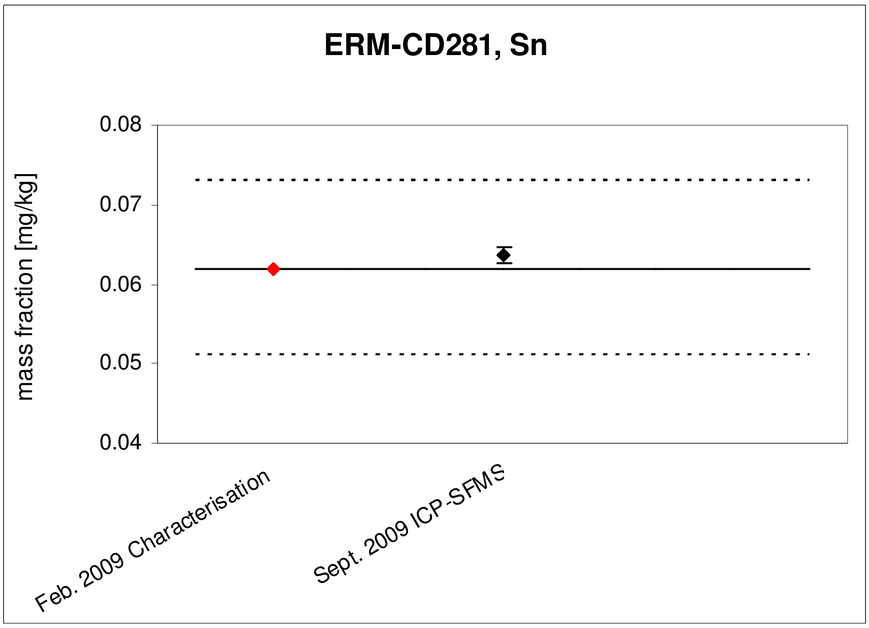
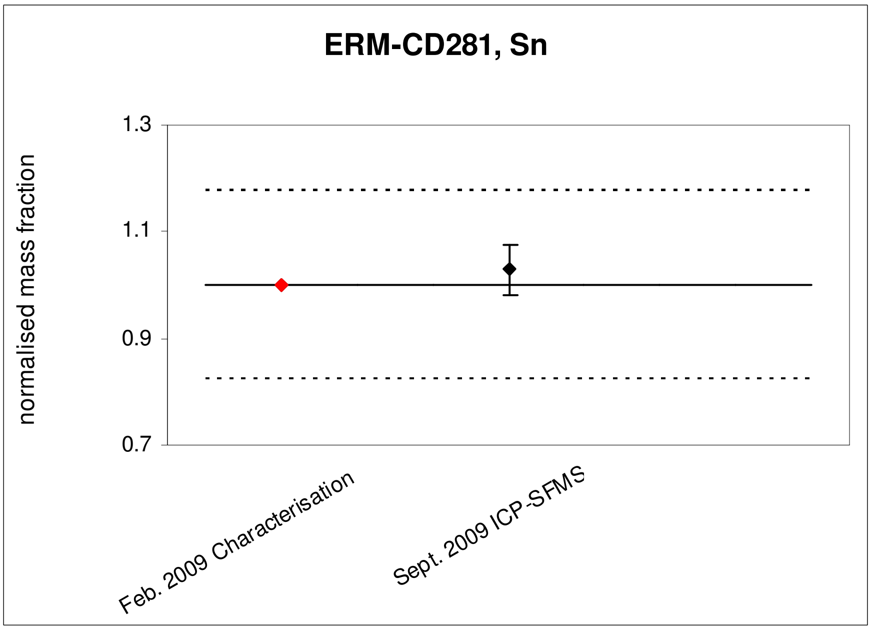
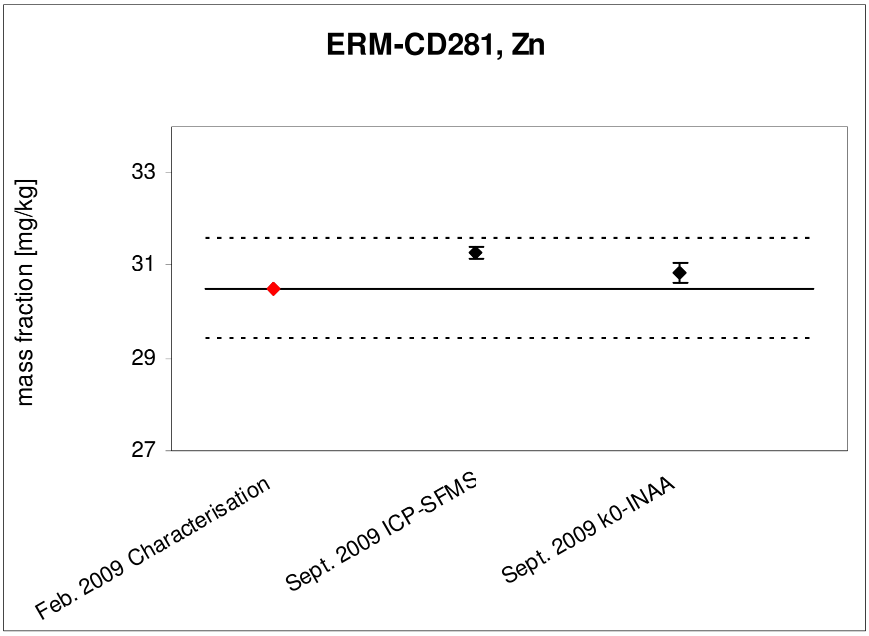
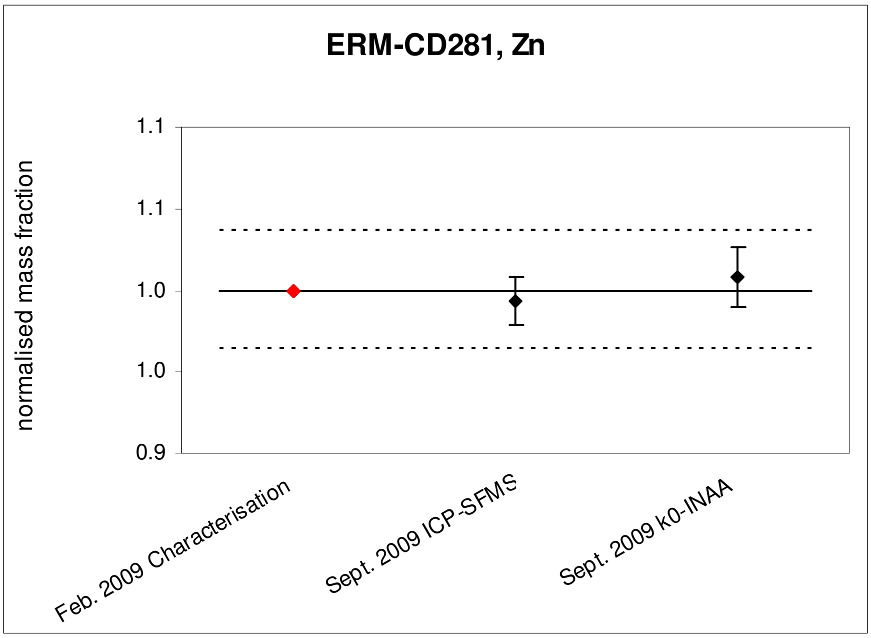




Results reported on dry mass basis. The normalisation of the shown data was done as described in Section 5.2. Error bars in the graphs represent expanded uncertainties as described in Section 5.2. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.





Annex F: Summary of methods used in the characterisation

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L01a ICP-SFMS	All	0.3	Microwave assisted closed digestion using 5 mL HNO_3 and 0.02 mL HF plus 0.2 mL HCl (Sb, Sn), heating at 170 °C for 60 min	Ultra Scientific (US) single element ICP standards QC: NIST 1547	ICP- SFMS (Finnigan MAT, ELEMENT 2), two-points external calibration checked against synthetic QC sample at ½ max concentration, internal standard In or Lu, isotopes monitored: ^{75}As, ^{9}B, ^{10}B, ^{111}Cd, ^{114}Cd, ^{52}Cr, ^{53}Cr, ^{63}Cu, ^{65}Cu, ^{201}Hg, ^{202}Hg, ^{55}Mn, ^{95}Mo, ^{98}Mo, ^{60}Ni, $^{206-208}$Pb, ^{123}Sb, ^{78}Se, ^{120}Sn, ^{64}Zn and ^{66}Zn, mass resolution: HR (As, Se), MR (Cr, Cu, Mn, Ni, Zn), LR (B, Cd, Hg, Mo, Pb, Sb, Sn), blank correction
L01b ICP-SFMS	As, Hg, Se		Microwave assisted closed digestion using 5 mL HNO_3, 0.02 mL HF and 0.2 mL HCl, heating at 170 °C for 60 min		ICP-SFMS (Finnigan MAT, ELEMENT 2), home made steady-state hydride generation (sodium borohydride), two-points external calibration checked against synthetic QC sample at ½ max concentration, internal standard In or Lu, isotopes monitored: ^{75}As (HR), $^{201,\ 202}$Hg (LR), ^{78}Se (HR), blank correction
L01 ICP-OES	B, Cr, Cu, Mn, Ni, Pb, Zn		Microwave assisted closed digestion using 5 mL HNO_3 and 0.02 mL HF, heating at 170 °C for 60 min		P-E Optima 4300DV (ICP-OES), two-points external calibration checked against synthetic QC sample at ½ max concentration, wavelengths [nm]: 249.677 (B), 205.56 (Cr), 324.752 (Cu), 257.61 (Mn), 231.604 (Ni), 220.353 (Pb), 213.857 (Zn), blank correction
L01 AFS	Hg, Se		Microwave assisted closed digestion using 5 mL HNO_3, 0.02 mL HF and 0.2 mL HCl, heating at 170 °C for 60 min		PSAnalytical M055B002 (AFS), two-points external calibration checked against synthetic QC sample at ½ max concentration, blank correction

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L02 AFS	As, Sb, Se	0.5	Oven (Berghof DAB-3) digestion using 10 g of acid mixture (9.5 g HNO_3 and 0.5 g $HClO_4$), heating at 190 °C for 10 h, 0.5 mL HF added for resolving the possible residue	Single element standards CPI international or Inorganic Ventures QC: CRM281, NBS1572	AFS with hydride generator (PSA), external calibration, wavelengths [nm]: 193.7 (As), 217.6 (Sb), 196 (Se)
L02 ICP-OES	B, Cd, Cr, Cu, Mn, Mo. Ni, Pb, Sn, Zn				Varian Vista AX CCD simultaneous ICP-OES, external calibration with internal standard Ge or Lu, wavelengths [nm]: 249.678 (B), 214.439 (Cd), 267.716 (Cr), 327.395 (Cu), 257.61 (Mn), 202.032 (Mo), 231.604 (Ni), 220.353 (Pb), 189.927 (Sn), 206.2 (Zn)
L02 CV-AFS	Hg				CV-AFS (PSA 10.025 Millennium Merlin), external calibration
L03 ICP-SFMS	As, B, Cd, Mo, Ni, Pb, Sb, Se, Sn	1	Closed microwave oven digestion using 6 mL HNO_3 Suprapur and 2 mL HCl Suprapur, microwave oven program: 10 min ramp to 500 W, hold for 5 min at 500 W, 5 min ramp to 1000 W, hold 10 min at 1000 W, cool until < 50 °C, no residue left after digestion	Spex multielement solutions Merck single element solution (B)	ICP-SFMS (Thermo Finnigan Element 2), linear calibration with internal standard ^{103}Rh, isotopes monitored: ^{75}As, ^{9}B, ^{11}B, ^{114}Cd (corrected for ^{118}Sn), ^{98}Mo, ^{60}Ni, $^{206\text{-}208}$Pb, ^{121}Sb, ^{78}Se, ^{118}Sn, mass resolution: HR (As, Se), MR (B, Cd, Mo, Ni, Pb, Sb, Sn), procedure blank
L03 CV-AFS	Hg			Merck single element solution	CV-A-AFS (Leeman Labs Inc. – Hydra AF Gold Plus), external linear calibration, wavelength 254 nm, procedure blank, measurements according to EPA Method 1631
L04 k_0-NAA	Cr, Mn, Sb, Zn	0.3	No preparation	BCR 530 (Al 99,9%-Au 0,1%) flux monitor QC: NIST1633b; NIST1464a	429 min irradiation with flux 3.0 x 10^{11} neutrons/(cm^2 s), decay time 14 days (Cr, Sb, Zn), 1 h (Mn), lines (keV): 320 (Cr), 847,1810 (Mn), 603,1691 (Sb), 1115 (Zn), isotope used: ^{51}Cr, ^{56}Mn, ^{124}Sb, ^{65}Zn

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L05a ICP-QMS	As, Cr, Hg, Se	0.5	Closed vessel microwave digestion using 5 mL of mixture HNO_3 and HCl (4:1), about 180 ℃, 30 min, digests made up to 10 mL with deionised water, then 1 mL sample diluted 5-fold with HNO_3 (1 % v/v) containing Rh as internal standard (12 µg/L), the same procedure for reagent blanks, CRMs, spiked samples and a spiked blank	SpectrosoL standard solutions QC: NIST 1515, NIST 1547, NIST 1548a	ICP-QMS (Agilent 7500ce ICP-MS), external calibration, isotopes monitored: ^{75}As, ^{52}Cr, ^{202}Hg, ^{78}Se, CC mode: He (As, Cr), standard (Hg), H_2 (Se), data correction for reagent blank and recovery of spike
L05b ICP-QMS	B, Cd, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Zn			Standard solutions (SpectrosoL, CertiPUR, ARISTAR) QC: NIST 1515, NIST 1547, NIST 1548a	ICP-QMS (Perkin Elmer Elan 6000 ICP-MS), external calibration, isotopes monitored: ^{11}B, ^{111}Cd, ^{65}Cu, ^{55}Mn, ^{95}Mo, ^{62}Ni, ^{208}Pb, ^{121}Sb, ^{118}Sn, ^{66}Zn, data correction for reagent blank and recovery of spike
L06 ICP-OES	B, Cr, Cu, Mn, Mo, Ni, Zn	0.2	Microwave digestion using 0.5 mL HCl suprapure and 5 mL HNO_3 subboiled distilled, power ramp from 0 – 1440 W within 10 min, hold 1440 W for 10 min, then 0 W and cooling for 20 min	Spex multielement standards Traceability: check against certified single standard	ICP-OES (Spectro Ciros Vision), wavelengths (nm): 249.773 (B), 267.716 (Cr), 324.754 (Cu), 257.611 (Mn), 202.03 (Mo), 231.604 (Ni), 213.856 (Zn)
L06 ICP-QMS	As, Se, Sn		Closed microwave digestion using 6 mL HNO_3 + 1 mL HF, power: ramp 0-10 min: 0-1400 W; 10-20 min: 1400 W, pressure at 60 bar, temp at 200 ^{o}C, addition of 6 mL saturated boric acid solution, additional blank digestion for contamination control	Certified single element standard (Spex, CPI) BCR281 (QC) Traceability: check against assurance multi-element standard	ICP-QMS (ELAN DRC II, Perkin-Elmer – LAS), standard addition calibration with internal standard (Rh), isotopes monitored: ^{91}AsO, ^{80}Se, ^{118}Sn, ^{120}Sn, DRC mode: O_2 (As), CH_4 (Se, Sn), blank correction
L06 ICP-SFMS					ICP-SFMS (Element 1, Finnigan MAT), 7 point calibration curve with internal standard (Rh), isotopes monitored: ^{75}As, ^{77}Se, ^{82}Se, ^{120}Sn, mass resolution: HR (As, Se) and LR (Sn) blank correction

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L07 ICP-QMS	As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Zn	0.2 0.5 (Sn)	EPA method 3052: *Microwave assisted acid digestion of siliceous and organically based matrices* using 9 mL HNO_3 and 1 mL HF, 180 °C, 20 min Sn: 10 mL H_2SO_4 (9 N) and 5 mL HNO_3, heating at 275 °C for 2 h	Single standards (Merck, Alfa Aesar, CPI) Traceability: NIST SRMs	ICP-QMS (Elan 6000, Perkin Elmer), external calibration with internal standard (Rn or Lu) for matrix-correction and spiking, isotopes monitored: ^{75}As, $^{10\text{-}11}$B, $^{111\text{-}113}$Cd, ^{53}Cr, $^{63\text{-}65}$Cu, $^{200\text{-}202}$Hg, ^{55}Mn, $^{96\text{-}98}$Mo, $^{60\text{-}62}$Ni, $^{206\text{-}208}$Pb, $^{121\text{-}123}$Sb, $^{66\text{-}68}$Zn, blank correction
L07 ET-AAS	Se, Sn				AAS (Aanalyst 200, Perkin Elmer), standard addition calibration, wavelengths [nm]: 196,0 (Se), 286.3 (Sn), slit 0.5 nm, blank correction
L07 k_0-NAA	As, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Sb, Se, Sn, Zn	0.5	No preparation	Au (IRMM-530) flux monitor	240 min irradiation with flux 3.49 x 10^{11} neutrons/(cm^2 s), decay time: +/- 150 min to +/- 41 days, measuring time: 3600 s to +/- 95000 s, lines: 559.8 (As), 527.9 (Cd), 320.1 (Cr), 1345.8 (Cu), 279.2 (Hg), 846.8 (Mn), 140.5 (Mo), 1481.9 (Ni), 602.3/1691 (Sb), 136/264.7 (Se), 158.6 (Sn),1115.5 (Zn), isotope used: ^{76}As, ^{115}Cd, ^{51}Cr, ^{64}Cu, ^{203}Hg, ^{56}Mn, ^{99m}Tc, ^{65}Ni, ^{124}Sb, ^{75}Se, ^{117m}Se, ^{65}Zn
L08 ID ICP-QMS	Cd, Cu, Ni, Pb, Zn	0.2	Closed microwave oven digestion using 5 mL HNO_3, 1 mL H_2O_2 and 0.15 mL HF, heating: 10 min (280 W), 5 min (0 W), 10 min (550 W), 5 min (0 W), 6 min (720 W), 7 min (0 W) and 10 min (280 W), blends between sample and spike prepared gravimetrically, before digestion sample spiking	Spike: ^{111}Cd, ^{65}Cu, ^{61}Ni, ^{206}Pb, ^{82}Se, ^{67}Zn, concentrations by reverse ID	ICP-QMS (VG PQ Excell, Thermo Electron), double ID, isotopes monitored: $^{112/111}$Cd, $^{63/65}$Cu, $^{61/60}$Ni, $^{208/206}$Pb, $^{68/67}$Zn, ratio measurements on two working isotopes, correction for: Mo interference (Cd), for matrix background (Cu, Ni, Zn), for blank (Pb)
L08 ID ICP-SFMS	Se	0.4			ICP- SFMS (VG Axiom, Thermo Electron), double ID, isotopes monitored: $^{82/80}$Se (LR), ratio measurements on two working isotopes, CCT mode: mixture of He and H_2, correction for blank

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L09 ICP-QMS	B, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn	0.2	Microwave assisted digestion using 8 mL HNO_3, 1 mL HCl and 2 mL HF, 200 °C, 45 min B, Hg: 8 mL HNO_3 and 1 mL HCl	Baker Instra Analyzed ICP Standards CRM 281 No 743 (QC)	ICP-QMS (Perkin Elmer Elan DRC II), external calibration with internal standards (Be, Ge, Y, In, Re) and matrix matched standards, isotopes monitored: ^{11}B, ^{114}Cd, ^{52}Cr, ^{65}Cu, ^{55}Mn, ^{98}Mo, ^{60}Ni, ^{208}Pb, ^{64}Zn
L09 CV-AAS	Hg				CV-AAS (Perkin Elmer FIMS 400), external calibration and matrix matched standards, reductant for cold vapour generation 0.2 % $NaBH_4$ and 3 % HCl, wavelength 253.7 nm, slit 0.7 nm
L10 HG-AFS	As, Sb	0.4	Microwave assisted digestion using 2 mL ultrapure water (Milli-Q, 18.2 Mohm cm), 4 mL HNO_3 (69 % m/m) and 2 mL H_2O_2 (33 % m/m), heating to 90 ℃ in 1 min and 30 s, to 200 ℃ in 12 min, at 200 ℃ for 15 min	As_2O_5, $Hg(NO_3)_2$, $Mn(NO_3)_2$ (Panreac) H_3BO_3, $CdCl_2$, $Cr(NO_3)_3$, $(NH_4)_6Mo_7O_{24}$, $SnCl_4$, $Zn(NO_3)_2$ SeO_2 (Merck) $Cu(NO_3)_2$, $Ni(NO_3)_2$ $Pb(NO_3)_2$ (Scharlau) $K[Sb(OH)_6]$ (Aldrich)	HG-AFS (Millenium 10055 PS Analytical), external calibration, wavelengths [nm]: 193.7 (As), 217.6 (Sb), blank correction
L10 ET-AAS	B, Cd, Mo, Pb, Se, Sn				1100 ET-AAS coupled with HGA 700 and AS70 autosampler Perkin Elmer), deuterium background correction, external calibration, wavelengths (nm): 249.7 (B), 228.8 (Cd), 313.3 (Mo), 283.3 (Pb), 224.6 (Sn), slit 0.7 nm, blank correction Se: 4110ZL ET-AAS coupled with TGHA and AS 71 autosampler, Perkin Elmer, Zeeman background correction, external calibration, wavelength 196 nm, slit 0.7 nm, blank correction
L10 ICP-OES	Cr, Cu, Mn, Ni, Zn				ICP-OES (Optima 3300 DV Perkin Elmer), background correction, external calibration, wavelengths (nm): 267.716 (Cr), 324.752 (Cu), 257.61 (Mn), 231.604 (Ni), 213.857 (Zn), blank correction
L10 CV-AAS	Hg				CV-AAS (FIAS 400 coupled with 4110ZL spectrometer and AS 71 autosampler, Perkin Elmer), external calibration, wavelength 253.7 nm, slit 0.7 nm, blank correction

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L11 DMA	Hg	0.05	No preparation	JSI standard solution	DMA (Milestone Srl.), decomposition tempereture 650 °C, wavelength 254 nm
L11 CV-AAS		0.2	Closed Teflon vessels digestion using 4 mL HNO_3, heating at 100 °C for 12 h		CV-AAS (LDC Milton Roy), wavelength 253.7 nm, blank correction
L11 ET-AAS	Cd, Cr, Cu, Ni, Pb	0.35	Closed vessel microwave digestion using 4 mL HNO_3 (s.p.) and 0.1 mL HF (s.p.), heating to 180 °C in 20 min, hold 20 min, the same procedure applied for blanks	Merck standard solutions	ET-AAS (Hitachi Z-8270 polarized Zeeman AAS), external calibration, Zeeman background correction, wavelengths [nm]: 228.8 (Cd), 359.3 (Cr), 324.8 (Cu), 323 (Ni), 283.3 (Pb), slit 1.3 nm and 0.2 nm (Ni)
L11 FAAS	Mn, Zn				FAAS (Varian, Spectra AA110), external calibration, deuterium background correction, wavelengths [nm]: 324.8 (Mn), 324.8 (Zn), nitrous oxide-acetylene flame (Mn) and air-acetylene flame (Zn)
L11 ICP-QMS	Cr, Cu, Mn, Mo, Ni, Pb, Sb, Zn,				ICP-QMS (Agillent, ICP-MS 7500ce), external calibration, CC mode: He (Cr, Mo), H_2 (Sb), isotopes monitored: ^{52}Cr, ^{63}Cu, ^{55}Mn, ^{95}Mo, ^{60}Ni, $^{206-208}$Pb, ^{121}Sb, ^{66}Zn
L11 RNAA	As, Se	0.2, 0.2 - 0.4 (Se)	No sample preparation before irradiation. Digestion and separation of the sample was done after irradiation	Merck ICP single standards	20 h (As) and 40 h (Se) irradiation, with flux 1.10 x 10^{12} neutrons/(cm^2 s), decay time (days): 2 - 3 (As), 14 - 20 (Se), measuring time (h): 1 - 2 (As), 14 -20 (Se), lines (keV): 559.1 (As), 400.7 (Se), isotope used: : ^{76}As, ^{75}Se

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L11 k_0-INAA	Cr, Mn, Mo, Sb, Zn	0.2	No preparation	flux monitors: Al-Au (0.1 %), Zn (99.99 %), Zr (99.8 %) NIST 1547 Peach Leaves (QC) Validated using BCR CRMs (different matrices)	7 and 1200 min irradiation with flux 1.10 x 10^{12} neutrons/(cm^2 s), decay time: 30 - 36 days (Cr, Sb, Zn), 2 h (Mn), 8 - 12 days (Mo), measuring time: 16 h (Cr, Sb, Zn), 25 min (Mn), 15 h (Mo), lines (keV): 320.1 (Cr), 846.8 (Mn), 140.5 (Mo), 602.7 (Sb), 1115.5 (Zn), isotope used: ^{51}Cr, ^{56}Mn, ^{99m}Tc, ^{124}Sb, ^{65}Zn
L12 ICP-QMS	As, Se, Sn	2	Closed microwave digestion using 2 mL HF and 4.5 mL HNO_3, 240 °C, 50 min, centrifugation	Metal salts in acids (VWR)	ICP-QMS (Perkin Elmer Elan DRC II), external calibration (linear regression through zero) with internal standard (Rh), isotopes monitored: ^{75}As, ^{78}Se, ^{118}Sn, LR (all elements), DRC mode: standard (As, Se), NH_3 (Se)
L13 ICP-QMS	As, Sn	0.5	Digestion according to SS-EN ISO 15587-2, closed microwave digestion using 15 mL HNO_3 and 1 mL H_2O_2, 170 °C, 10 min, predigestion open system 100 °C	Multi 3 ICP-MS, Multi 4 ICP-MS (PerkinElmer)	ICP-QMS (Perkin Elmer ELAN DRC-e), internal calibration (linear through zero), Internal standards ^{103}Rh (As) and ^{115}In (Sn), isotopes monitored: ^{75}As, ^{118}Sn, ^{120}Sn, DRC mode: NH_4, blank correction (Sn)
L14 ICP-QMS	As	0.5	Microwave digestion using 10 mL HNO_3 (7 M), 180 °C, 37 min, filtration	ICP multielement standard VI for MS (AccuStandard Inc.) NIST 1568a Rice flour (QC)	ICP-QMS (Elan 6000 Perkin Elmer), isotope monitored ^{75}As,standard addition calibration, blank correction

Lab-method code	Elements	Sample mass [g]	Sample preparation	Calibrants	Instrumentation and measurement method
L15 ID ICP-SFMS	Se, Sn	0.5	Sample weighing, spiking (^{77}Se or ^{117}Sn), microwave digestion using 3 mL HNO_3, 2 mL H_2O_2 and 1mL HCl, 185 °C, 35 min	NIST SRM3149 (Se), NIST SRM3161a (Sn)	ICP-SFMS (ThermoFisher Scientific), acid matrix of calibration standards, isotopes monitored: $^{77, 78, 82}$Se (HR) and $^{117, 118, 120}$Sn (MR)
L16 ID ICP-SFMS	Sn	0.5	High pressure asher digestion using 3 mL HCl and 2 mL HNO_3, 320 °C, 240 min (150 min at 320 °C), trace-matrix separation with Truspec resin	Sn metal (BAM)	ICP-QMS (Element XR, Thermo Fisher Scientific), isotope monitored ^{117}Sn, blank correction

Annex G: Results of the characterisation measurements

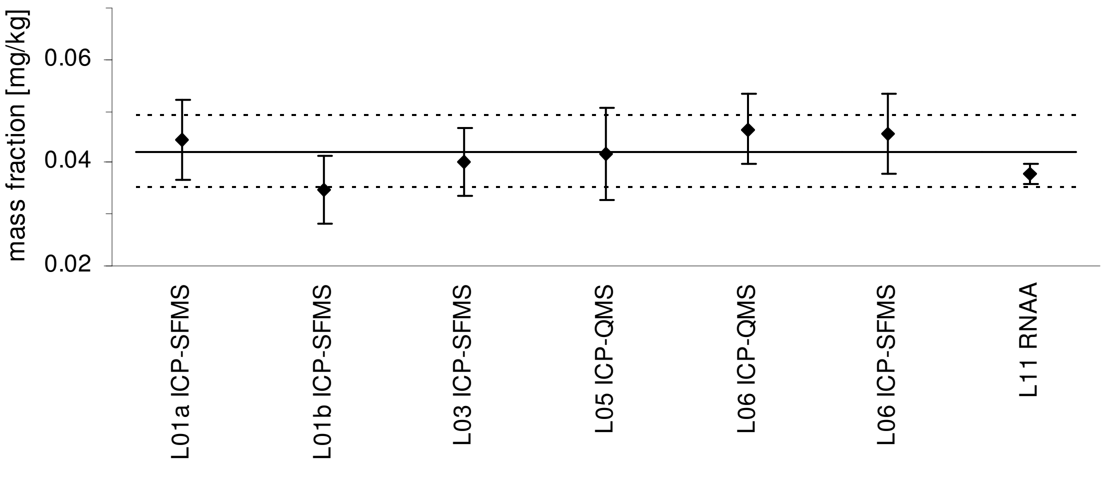
ERM-CD281, As

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	0.0522	0.0497	0.0496	0.0514	0.0593	0.0478	0.0443	0.0081
	0.0358	0.038	0.0372	0.0359	0.0373	0.0379		
L01b ICP-SFMS	0.0348	0.0362	0.034	0.0339	0.0327	0.0366	0.0347	0.0015
L03 ICP-SFMS	0.0423	0.0402	0.0389	0.0410	0.0394	0.0395	0.0402	0.0013
L05 ICP-QMS	0.039	0.048	0.039	0.039	0.041	0.044	0.0417	0.0037
L06 ICP-QMS	0.05236	0.04658	0.04474	0.04474	0.04546	0.04519	0.04651	0.00294
L06 ICP-SFMS	0.05390	0.04298	0.04364	0.04406	0.04454	0.04399	0.04552	0.00414
L11 RNAA	0.0344	0.0344	0.0425	0.0361	0.0365	0.0427	0.0378	0.0038

	Excluded results[a]							
L02 AFS	0.060	0.037	0.033	0.060	0.018	0.060	0.045	0.018
L07 ICP-QMS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
L07 k_0-NAA	< 0.2	< 0.2	< 0.2	< 0.3	< 0.2	< 0.2		
L10 HG-AFS	0.21	0.16	0.10	0.21	0.15	0.12	0.16	0.05
L12 ICP-QMS	0.17	0.20	0.17	0.14	0.13	0.15	0.16	0.03
L13 ICP-QMS	0.072	0.121	0.059	0.063	0.089	0.056	0.077	0.025
L14 ICP-QMS	0.056	0.055	0.064	0.052	0.064	0.063	0.059	0.005

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



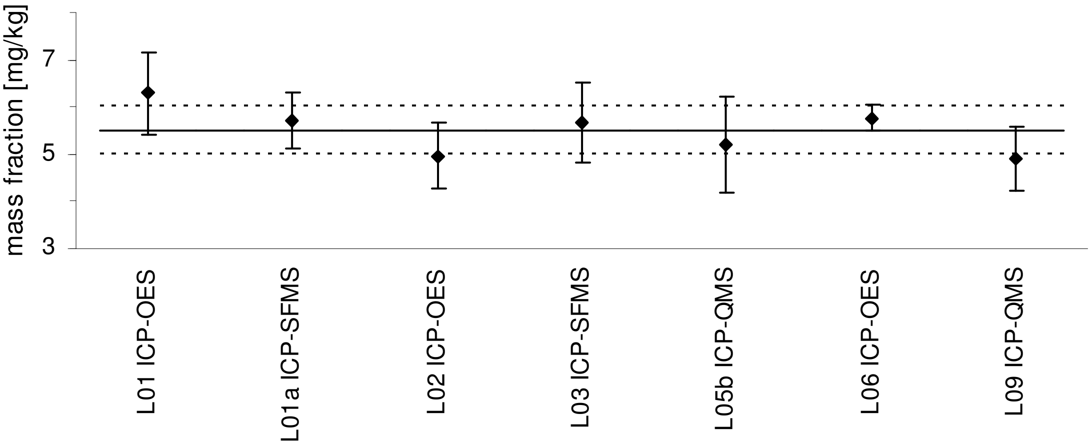
ERM-CD281, B

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	*s* [mg/kg]
L01 ICP-OES	6.33	6.44	6.14	6.31	6.44	6.05	6.29	0.16
L01a ICP-SFMS	5.82	5.58	5.77	5.82	5.65	5.59	5.71	0.11
L02 ICP-OES	4.931	4.947	5.000	4.939	4.986	4.982	4.964	0.029
L03 ICP-SFMS	5.643	5.539	5.568	5.549	5.563	6.099	5.660	0.218
L05b ICP-QMS	5.1	5.4	5.2	5.3	5.1	5.1	5.2	0.1
L06 ICP-OES	5.69	5.81	5.80	5.78	5.86	5.69	5.77	0.07
L09 ICP-QMS	5.02	4.84	4.84	5.16	4.69	4.97	4.92	0.16

	Excluded results[a]							
L07 ICP-QMS	7.55	6.22	5.11	8.72	5.22	7.61	6.74	1.45
L10 ET-AAS	5.2	12.5	5.1	4.7	16.0	7.7	8.5	4.7

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

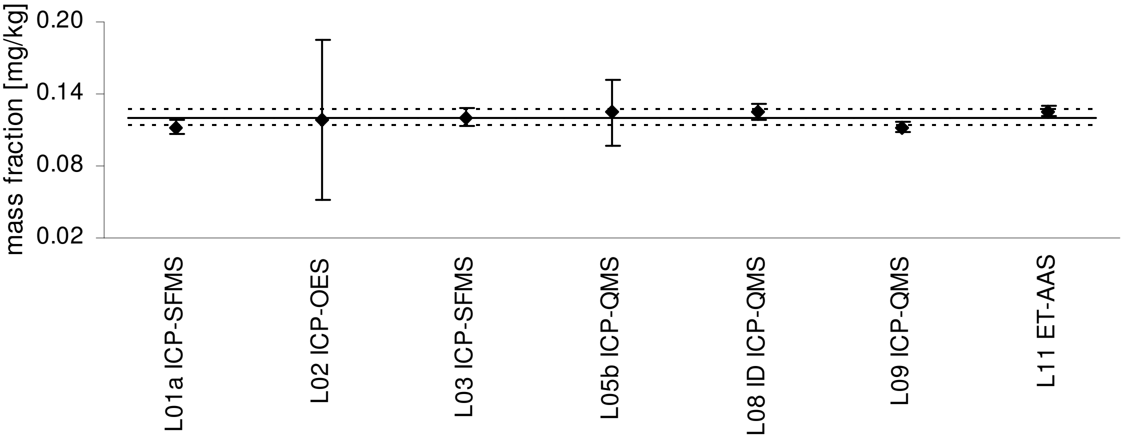


ERM-CD281, Cd

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	0.113	0.11	0.113	0.113	0.113	0.112	0.112	0.001
L02 ICP-OES	0.115	0.122	0.112	0.120	0.122	0.120	0.119	0.004
L03 ICP-SFMS	0.116	0.125	0.118	0.123	0.121	0.122	0.121	0.003
L05b ICP-QMS	0.128	0.126	0.121	0.127	0.123	0.121	0.124	0.003
L08 ID ICP-QMS	0.134	0.129	0.125	0.126	0.125	0.113	0.125	0.007
L09 ICP-QMS	0.121	0.111	0.108	0.11	0.108	0.114	0.112	0.005
L11 ET-AAS	0.127	0.127	0.123	0.130	0.125	0.123	0.126	0.003
	Excluded results[a]							
L07 k_0-NAA	< 1	< 1.5	< 1.5	< 1.5	< 1	< 1.5		
L07 ICP-QMS	0.15	0.12	0.13	0.16	0.13	0.15	0.14	0.02
L10 ET-AAS	0.165	0.156	0.149	0.171	0.152	0.157	0.158	0.008

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

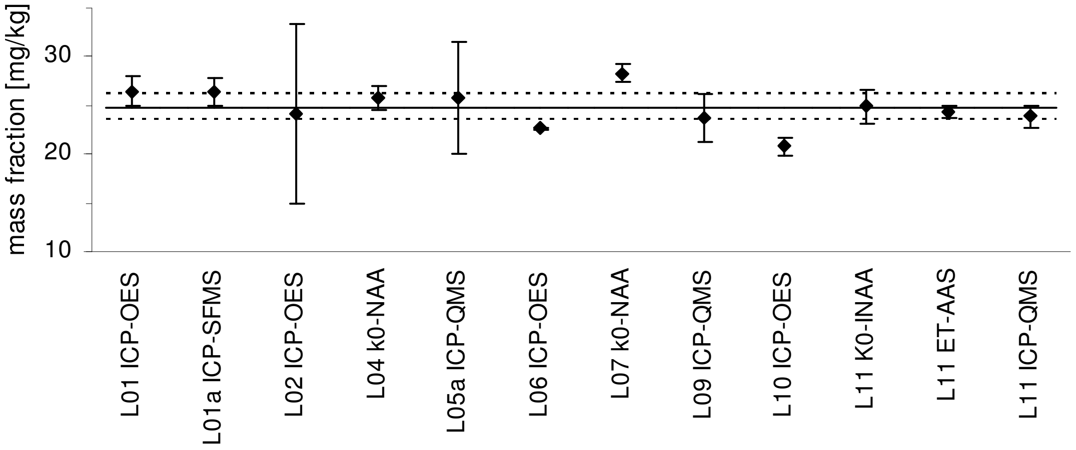


ERM-CD281, Cr

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01 ICP-OES	26.2	26.2	26.1	27.0	26.5	26.8	26.5	0.4
L01a ICP-SFMS	26.6	26.1	25.9	26.7	27.0	26.4	26.5	0.404
L02 ICP-OES	24.117	24.005	24.208	24.212	24.302	24.258	24.184	0.107
L04 k$_0$-NAA	26.11	25.14	26.17	25.85	25.61	25.86	25.79	0.38
L05a ICP-QMS	24.9	25.4	25.9	25.4	26.2	27.0	25.8	0.7
L06 ICP-OES	22.4	22.8	22.6	22.9	22.4	22.7	22.6	0.2
L07 k$_0$-NAA	29	28	28	29	28	28	28	1
L09 ICP-QMS	24.24	25.01	24.06	23.07	22.94	22.74	23.68	0.90
L10 ICP-OES	21.08	20.15	21.13	20.13	19.95	22.22	20.78	0.87
L11 K$_0$-INAA	25.4	24.8	24.8	24.6	24.8	24.8	24.9	0.3
L11 ET-AAS	25.1	24.2	23.9	25.2	24.1	24.0	24.4	0.6
L11 ICP-QMS	24.6	23.3	24.3	23.3	23.9	23.6	23.8	0.5
	Excluded results[a]							
L07 ICP-QMS	32.3	26.8	27.1	31.9	27.0	31.0	29.4	2.6

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

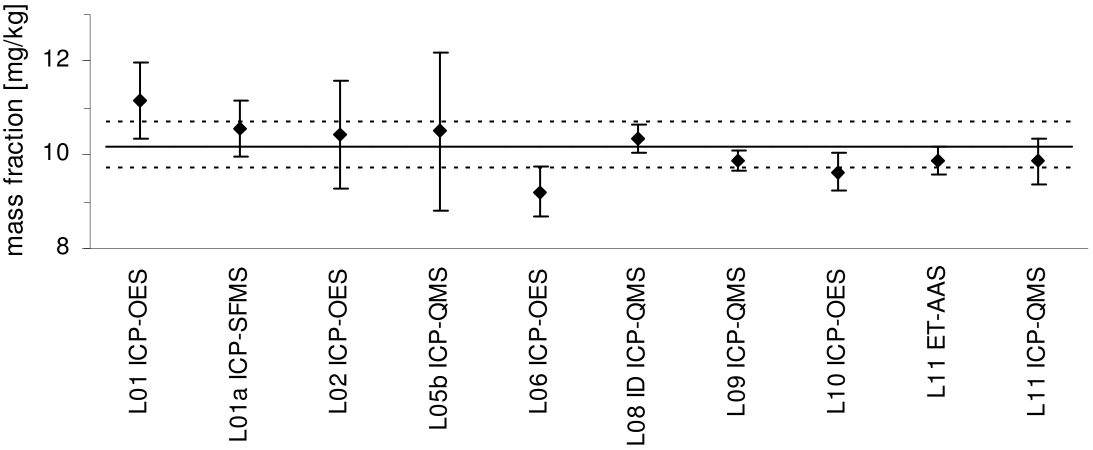


ERM-CD281, Cu

Lab-method code	Individual results[a]						$\overline{x}$	*s*
	[mg/kg]						[mg/kg]	[mg/kg]
L01 ICP-OES	11.1	11.1	11.2	11.2	11.2	11.2	11.2	0.1
L01a ICP-SFMS	10.8	10.5	10.4	10.7	10.6	10.4	10.6	0.2
L02 ICP-OES	10.190	10.238	10.568	10.364	10.580	10.658	10.433	0.196
L05b ICP-QMS	10.51	10.77	10.54	10.36	10.56	10.27	10.50	0.17
L06 ICP-OES	9.05	9.56	9.27	9.25	9.06	9.11	9.22	0.19
L08 ID ICP-QMS	10.483	10.412	10.615	10.143	10.605	9.934	10.365	0.272
L09 ICP-QMS	9.84	10.19	10.00	9.83	9.85	9.63	9.89	0.19
L10 ICP-OES	10.3	9.61	9.57	9.75	9.03	9.57	9.64	0.41
L11 ET-AAS	10.10	9.86	9.62	10.10	9.67	9.86	9.87	0.20
L11 ICP-QMS	9.74	9.94	9.74	9.97	9.87	9.97	9.87	0.11
	Excluded results[a]							
L07 k_0-NAA	< 150	< 200	< 100	< 100	< 200	< 150		
L07 ICP-QMS	13.3	11.0	11.4	11.6	11.4	13.5	12.0	1.1

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

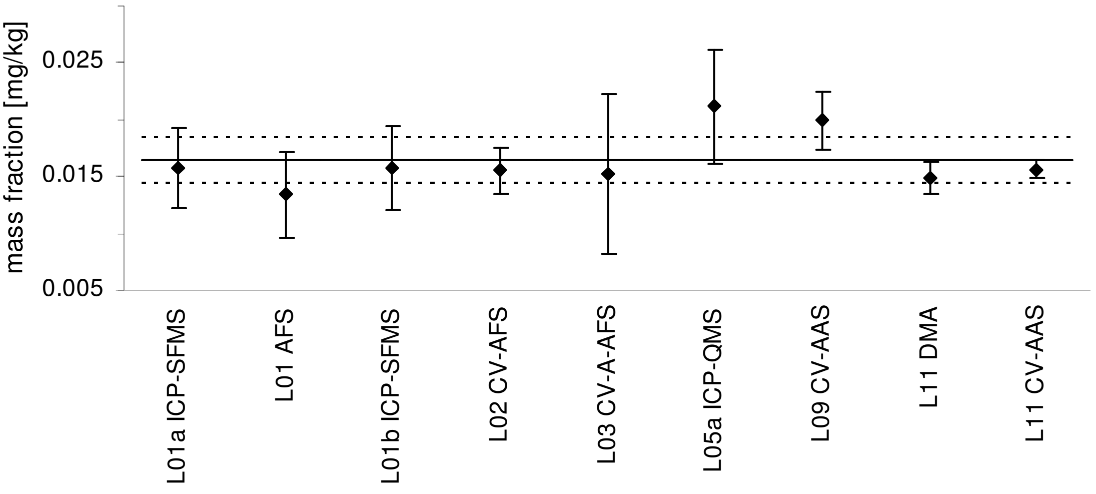


ERM-CD281, Hg

Lab-method code	Individual results^{a} [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	0.0173	0.0174	0.0169	0.0180	0.0174	0.0180	0.0158	0.0019
	0.0133	0.0131	0.0140	0.0145	0.0145	0.0146		
L01 AFS	0.0138	0.0124	0.0130	0.0145	0.0126	0.0139	0.0134	0.0008
L01b ICP-SFMS	0.0149	0.0156	0.0159	0.0159	0.0160	0.0162	0.0158	0.0005
L02 CV-AFS	0.016	0.016	0.016	0.016	0.015	0.014	0.016	0.001
L03 CV-A-AFS	0.0158	0.0158	0.0150	0.0149	0.0157	0.0141	0.0152	0.0007
L05a ICP-QMS	0.023	0.022	0.019	0.022	0.021	0.020	0.021	0.001
L09 CV-AAS	0.0215	0.0191	0.0197	0.0190	0.0195	0.0206	0.0199	0.0010
L11 DMA	0.0143	0.0132	0.0174	0.0143	0.0150	0.0146	0.0148	0.0014
L11 CV-AAS	0.0162	0.0160	0.0152	0.0155	0.0156	0.0154	0.0157	0.0004
	Excluded results^{a}							
L07 k_0-NAA	< 0.07	< 0.07	< 0.09	< 0.09	< 0.07	< 0.08		
L07 ICP-QMS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
L10 CV-AAS	0.0398	0.0249	0.0401	0.0616	0.046	0.0289	0.0205	0.0402

^{a}: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

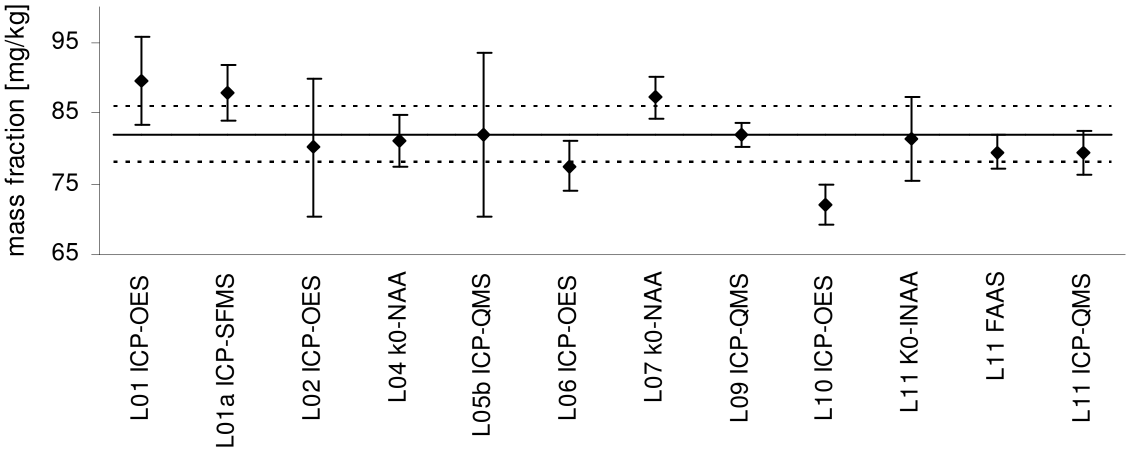


ERM-CD281, Mn

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01 ICP-OES	88.4	89.4	89.3	90.2	90.4	89.7	89.6	0.7
L01a ICP-SFMS	88.8	86.4	88.2	89.5	88.6	86.3	88.0	1.3
L02 ICP-OES	80.181	79.585	80.283	79.680	80.237	80.697	80.111	0.414
L04 k_0-NAA	81.08	81.07	80.12	82.14	79.7	82.37	81.08	1.06
L05b ICP-QMS	82.27	83.24	82.33	80.76	82.52	80.66	81.96	1.03
L06 ICP-OES	77.4	78.1	77.2	77.3	76.9	77.8	77.5	0.4
L07 k_0-NAA	89.0	87.0	85.0	88.0	88.0	86.0	87.2	1.5
L09 ICP-QMS	81.87	84.72	82.58	81.85	81.14	79.55	81.95	1.70
L10 ICP-OES	73.9	68.6	75.1	68.9	72.6	73.3	72.1	2.7
L11 K_0-INAA	81.4	80.8	82.5	81.0	81.8	80.8	81.4	0.7
L11 FAAS	80.2	80.2	78.7	79.0	79.4	79.4	79.5	0.6
L11 ICP-QMS	78.5	79.5	78.4	80.8	78.7	80.4	79.4	1.0
	Excluded results[a]							
L07 ICP-QMS	88.9	83.7	133.0	82.2	135.5	130.3	108.9	26.4

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

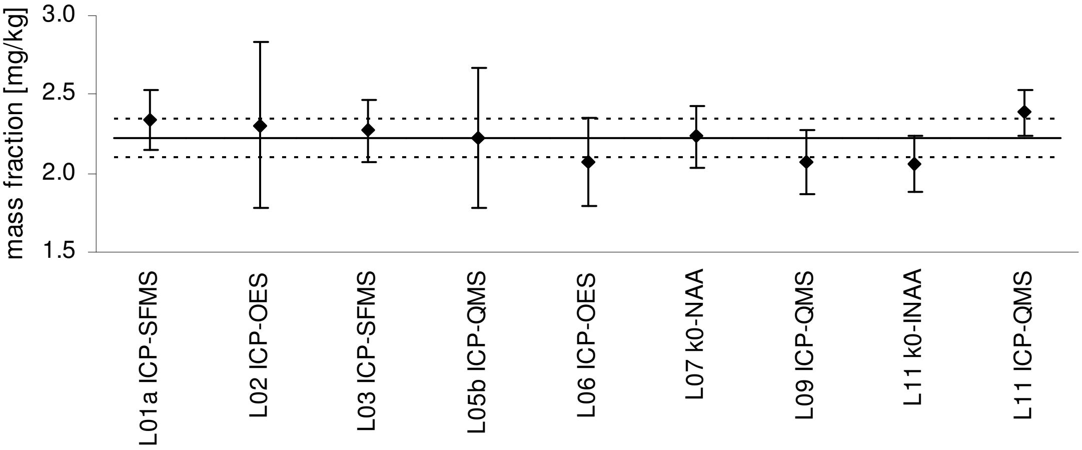


ERM-CD281, Mo

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	2.34	2.29	2.33	2.44	2.34	2.28	2.34	0.06
L02 ICP-OES	2.424	2.324	2.300	2.423	2.256	2.107	2.306	0.118
L03 ICP-SFMS	2.258	2.269	2.240	2.239	2.301	2.320	2.271	0.033
L05b ICP-QMS	2.219	2.240	2.209	2.245	2.196	2.270	2.230	0.027
L06 ICP-OES	2.15	2.17	2.01	2.04	2.03	2.04	2.07	0.07
L07 k_0-NAA	2.2	2.2	2.2	2.2	2.3	2.3	2.2	0.1
L09 ICP-QMS	2.03	2.11	2.10	2.07	2.10	2.02	2.07	0.04
L11 k_0-INAA	2.15	2.04	2.17	2.04	2.00	1.97	2.06	0.08
L11 ICP-QMS	2.43	2.37	2.31	2.45	2.47	2.30	2.39	0.07
	Excluded results[a]							
L07 ICP-QMS	2.62	2.24	2.38	2.70	2.38	2.79	2.52	0.22
L10 ET-AAS	1.80	1.60	1.60	1.78	1.67	1.74	1.70	0.09

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

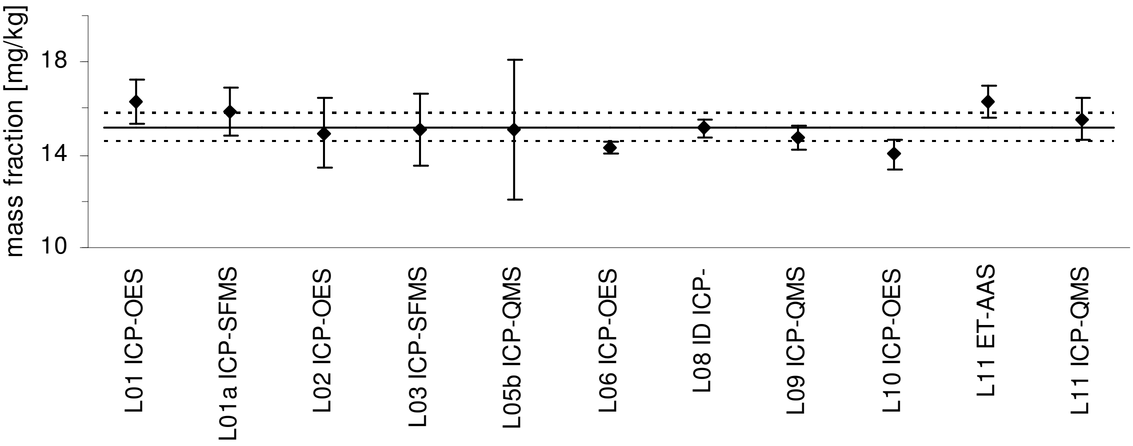


ERM-CD281, Ni

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	*s* [mg/kg]
L01 ICP-OES	15.9	16.2	16.0	16.8	16.4	16.5	16.3	0.3
L01a ICP-SFMS	16.0	15.5	15.8	16.4	16.0	15.6	15.9	0.3
L02 ICP-OES	14.926	14.873	15.049	15.103	14.934	14.838	14.954	0.102
L03 ICP-SFMS	14.91	15.15	14.72	14.80	15.46	15.56	15.10	0.35
L05b ICP-QMS	15.24	15.22	14.98	15.02	15.17	15.07	15.12	0.11
L06 ICP-OES	13.9	14.8	14.3	14.5	14.4	13.9	14.3	0.4
L08 ID ICP-QMS	15.219	15.126	15.662	14.714	15.293	14.809	15.137	0.344
L09 ICP-QMS	15.22	15.54	14.94	14.49	14.28	13.97	14.74	0.60
L10 ICP-OES	12.99	13.96	14.46	14.03	14.93	13.81	14.03	0.65
L11 ET-AAS	16.9	16.4	15.7	16.9	16.2	15.7	16.3	0.5
L11 ICP-QMS	15.6	15.4	16.0	15.0	15.7	15.6	15.6	0.3
	Excluded results[a]							
L07 k_0-NAA	< 950	< 950	< 700	< 700	< 600	< 600		
L07 ICP-QMS	20.1	17.2	16	20.3	15.8	19	18.1	2.0

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

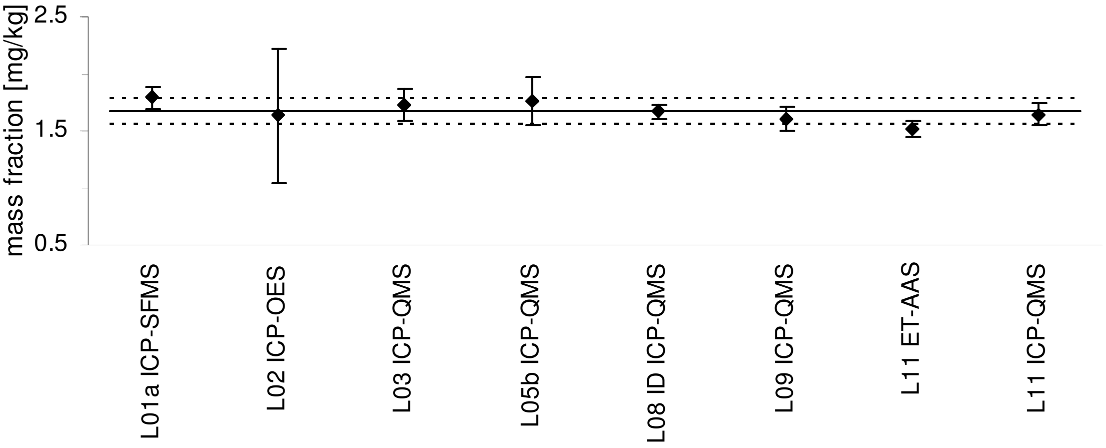


ERM-CD281, Pb

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	1.79	1.76	1.80	1.83	1.79	1.78	1.79	0.02
L02 ICP-OES	1.639	1.566	1.624	1.699	1.698	1.577	1.634	0.057
L03 ICP-QMS	1.665	1.738	1.653	1.745	1.811	1.736	1.725	0.058
L05b ICP-QMS	1.734	1.802	1.754	1.764	1.777	1.720	1.759	0.030
L08 ID ICP-QMS	1.720	1.656	1.719	1.617	1.591	1.723	1.671	0.058
L09 ICP-QMS	1.658	1.645	1.636	1.636	1.533	1.533	1.607	0.058
L11 ET-AAS	1.66	1.54	1.45	1.62	1.38	1.46	1.52	0.11
L11 ICP-QMS	1.78	1.62	1.59	1.65	1.61	1.64	1.65	0.07
	Excluded results[a]							
L01 ICP-OES	< 20	< 20	< 20	< 20	< 20	< 20		
L07 ICP-QMS	2.02	1.72	1.78	3.50	1.76	2.16	2.16	0.68
L10 ET-AAS	2.164	2.365	1.795	2.227	1.919	2.047	2.086	0.209

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

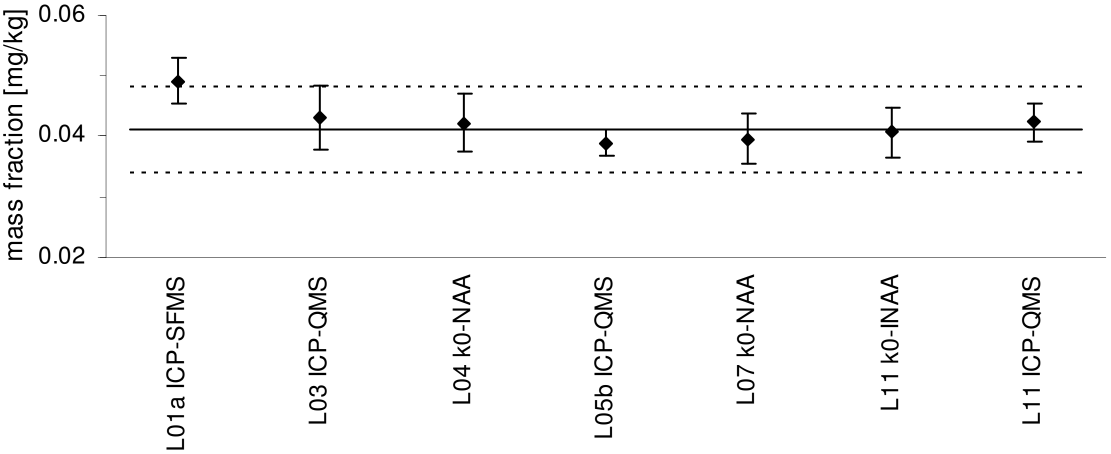


ERM-CD281, Sb

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	0.0497	0.0486	0.0505	0.0510	0.0466	0.0485	0.0492	0.0016
L03 ICP-QMS	0.0445	0.0421	0.0443	0.0427	0.0414	0.0442	0.0432	0.0013
L04 k_0-NAA	0.0424	0.0450	0.0358	0.0419	0.0443	0.0444	0.0423	0.0034
L05b ICP-QMS	0.038	0.040	0.040	0.037	0.040	0.039	0.039	0.001
L07 k_0-NAA	0.042	0.037	0.037	0.042	0.039	0.041	0.040	0.002
L11 k_0-INAA	0.044	0.041	0.037	0.042	0.039	0.041	0.041	0.002
L11 ICP-QMS	0.043	0.043	0.042	0.042	0.042	0.042	0.042	0.001
	Excluded results[a]							
L02 AFS	0.025	0.124	0.151	0.017	0.264	0.358	0.157	0.134
L07 ICP-QMS	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		
L10 HG-AFS	0.70	0.85	0.91	1.03	1.02	0.36	0.81	0.25

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



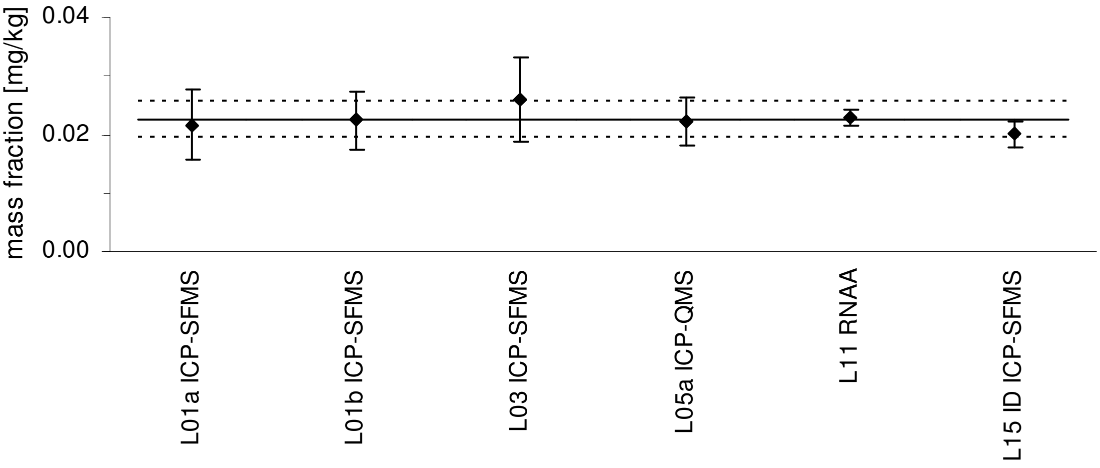
ERM-CD281, Se

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	0.0225	0.0205	0.0219	0.0208	0.0208	0.0236	0.0217	0.0012
L01b ICP-SFMS	0.0232	0.0246	0.0214	0.0223	0.0224	0.0205	0.0224	0.0014
L03 ICP-SFMS	0.0302	0.0258	0.0246	0.0260	0.0250	0.0241	0.0260	0.0022
L05a ICP-QMS	0.022	0.022	0.022	0.025	0.022	0.020	0.022	0.002
L11 RNAA	0.0223	0.0220	0.0223	0.0235	0.0232	0.0243	0.0229	0.0009
L15 ID ICP-SFMS	0.0200	0.0195	0.0202	0.0204	0.0198	0.0203	0.0200	0.0003

	Excluded results[a]							
L01 AFS	0.166	0.154	0.206	0.121	0.091	0.155	0.149	0.039
L02 AFS	0.108	0.154	0.011	0.154	0.018	0.026	0.079	0.068
L06 ICP-SFMS	0.02734	0.02661	0.02735	0.03610	0.03001	0.03042	0.02964	0.00353
L07 k_0-NAA	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2		
L07 ET-AAS	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		
L08 ID ICP-SFMS	0.037	0.034	0.034	0.040	0.027	0.025	0.033	0.006
L10 ET-AAS	0.17	0.19	0.19	0.17	0.16	0.23	0.19	0.03
L12 ICP-QMS	0.63	0.65	0.71	0.66	0.64	0.73	0.67	0.04

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.

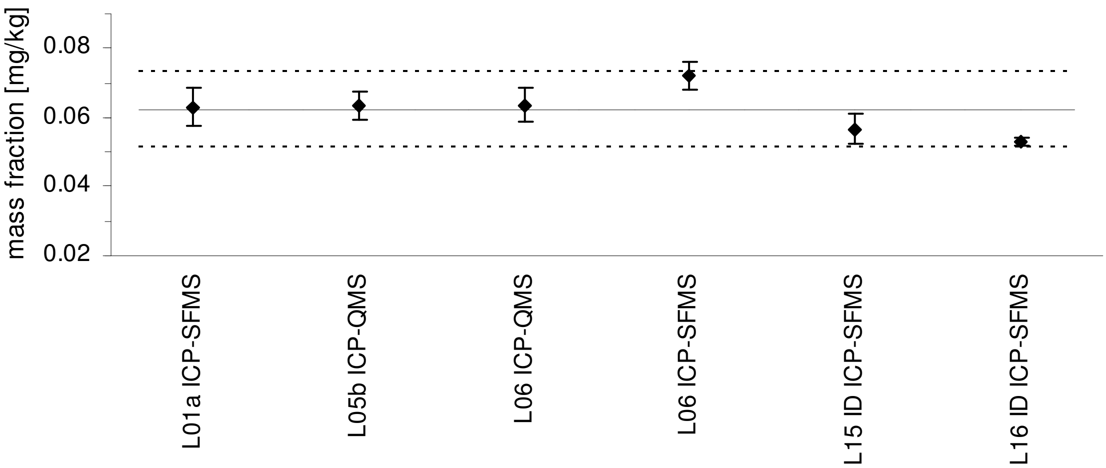


ERM-CD281, Sn

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	s [mg/kg]
L01a ICP-SFMS	0.0629	0.0631	0.0649	0.0633	0.0624	0.0617	0.0631	0.0011
L05b ICP-QMS	0.064	0.063	0.060	0.066	0.065	0.061	0.063	0.002
L06 ICP-QMS	0.06095	0.06194	0.06402	0.06825	0.06362	0.06304	0.06364	0.00253
L06 ICP-SFMS	0.07485	0.07047	0.07371	0.07151	0.07056	0.07083	0.07199	0.00185
L15 ID ICP-SFMS	0.0523	0.0625	0.0598	0.0565	0.049	0.0602	0.0567	0.0052
L16 ID ICP-SFMS	0.05610	-	0.05582	0.04946	0.05118	0.05289	0.05309	0.00289
	Excluded results[a]							
L02 ICP-OES	0.066	0.102	0.013	0.104	0.223	-0.058		
L03 ICP-SFMS	0.0505	0.0437	0.0591	0.0524	0.0612	0.0688	0.0560	0.0089
L07 k_0-NAA	< 10	< 10	< 15	< 16	< 11	< 11		
L07 ET-AAS	0.23	0.16	0.27	0.30	0.11	0.12	0.20	0.08
L10 ET-AAS	8.415	7.879	6.822	8.049	8.273	9.122	8.093	0.756
L12 ICP-QMS	0.10	0.09	0.08	0.07	0.08	0.08	0.08	0.01
L13 ICP-QMS	0.215	0.116	0.077	0.078	0.090	0.200	0.129	0.062

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



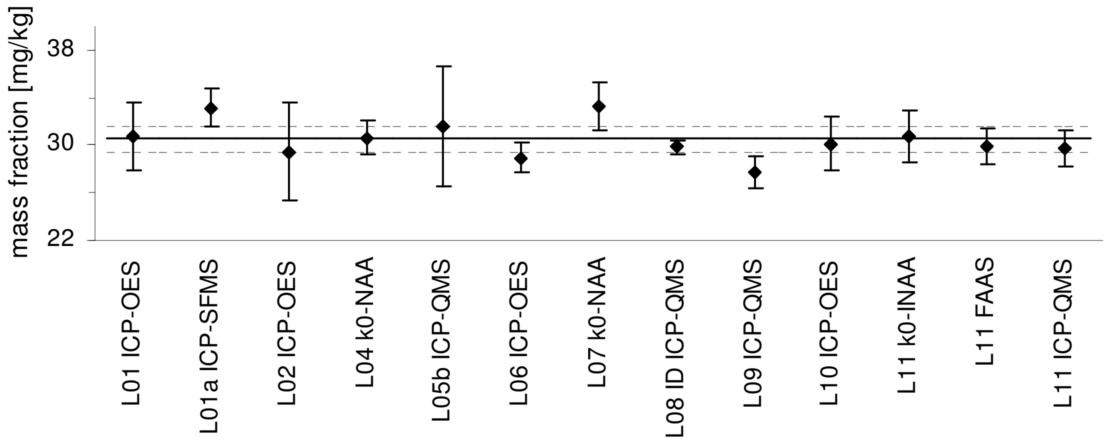
ERM-CD281, Zn

Lab-method code	Individual results[a] [mg/kg]						$\overline{x}$ [mg/kg]	*s* [mg/kg]
L01 ICP-OES	30.3	30.6	30.8	31.3	30.9	30.8	30.8	0.3
L01a ICP-SFMS	33.2	32.1	33.2	33.5	33.7	33.3	33.2	0.6
L02 ICP-OES	29.699	29.484	29.627	29.207	29.601	29.047	29.444	0.260
L04 k_0-NAA	30.502	30.088	31.128	30.522	30.957	30.452	30.608	0.376
L05b ICP-QMS	31.8	32.0	31.8	31.4	31.6	31.1	31.6	0.3
L06 ICP-OES	28.8	29.7	29.1	28.9	28.6	28.7	29.0	0.4
L07 k_0-NAA	34.0	34.0	32.0	34.0	33.0	33.0	33.3	0.8
L08 ID ICP-QMS	30.47	30.26	30.69	29.23	29.78	28.55	29.83	0.82
L09 ICP-QMS	29.64	29.77	26.78	29.20	25.94	25.24	27.76	2.01
L10 ICP-OES	29.5	27.9	31.3	28.5	29.8	33.8	30.1	2.1
L11 k_0-INAA	30.7	30.9	30.3	30.9	30.7	30.9	30.7	0.2
L11 FAAS	30.6	29.0	30.4	30.3	29.5	30.0	30.0	0.6
L11 ICP-QMS	29.3	29.9	29.4	30.7	29.3	29.8	29.7	0.5

	Excluded results[a]							
L07 ICP-QMS	69.6	44.6	69.1	43.7	70.9	67.3	60.9	13.0

[a]: reported on dry mass basis

Excluded results were not used for the calculation of the certified value. Error bars in the graph represent expanded uncertainties as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



European Commission

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Abstract

This report describes the preparation and certification of the rye grass Certified Reference Material (CRM) ERM-CD281. This CRM replaces the exhausted predecessor BCR-281. ERM-CD281 was processed and certified by the European Commission, Directorate General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

ERM-CD281 has been certified for its content of As, B, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn.

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

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