Certification Report

Certified Reference Material ERM®-CD100

Trace elements and pentachlorophenol in wood

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Summary

This report describes the preparation and the certification of a reference material for the determination of six trace elements (As, Cd, Cr, Cu, Hg and Pb) and pentachlorophenol (PCP) in wood.

The certified reference material ERM - CD100 is intended for the verification of a correct implementation of standardised analytical methods for waste wood characterisation. Furthermore it can be used for the validation of modified or new analytical procedures.

The following mass fractions and corresponding uncertainties were certified:

Analyte	Certified value [1)]	Uncertainty [2)]
	Mass fraction in mg/kg [3)]	
Arsenic	3.1	± 0.5
Cadmium	3.02	± 0.24
Chromium	36.4	± 2.6
Copper	22.9	± 1.7
Mercury	0.60	± 0.14
Lead	39	± 4
Pentachlorophenol	7.9	± 0.6

1) For the trace elements, the certified value is the mean of 7 - 10 laboratory means obtained using different AAS and ICP techniques. For PCP, the certified value is the mean of 8 laboratory means obtained using GC-ECD, GC-MS including IDMS and HPLC-MS/MS. The values are traceable to the SI (Système International d'Unités) via calibration using substances with certified purity.

2) Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the expression of uncertainty in measurement, ISO, 1993.

3) All results are corrected to the dry mass content of the wood material determined after drying to constant mass at (103 ± 2) °C.

ERM-CD100 is provided in 250 ml amber glass bottles each containing (74 ± 1) g of ground wood material that passed a sieve of 1 mm mesh size. The minimum sample intake for one determination is 0.5 g for trace elements and 4 g for pentachlorophenol.

The certified values are valid for a period of 12 months beginning with the dispatch of the reference material from BAM.

List of abbreviations

(if not explained elsewhere)

CV AAS	cold vapour atomic absorption spectrometry
CV AFS	cold vapour atomic fluorescence spectrometry
ET AAS	electrothermal atomic absorption spectrometry
GC-ECD	gas chromatography with electron capture detector
GC-MS	gas chromatography - mass spectrometry
HG AAS	hydride generation atomic absorption spectrometry
HG ICP OES	hydride generation inductively coupled plasma optical emission spectrometry
HPLC-MS/MS	high performance liquid chromatography - tandem mass spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP OES	inductively coupled plasma optical emission spectrometry
KF	Karl Fischer
M	arithmetic mean of means
MA 30	Sartorius Moisture Analyzer
N	number of accepted data sets
SD	standard deviation of an individual data set
SD_M	standard deviation of the mean of means

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1 Introduction

In view of an efficient and sustainable use of natural resources, the recycling of waste materials is a matter of growing economic and public concern. In this context increasing attention is paid to the utilisation of recovered waste wood originating in large amounts from construction and demolition activities. As industrially treated waste wood often contains meanwhile restricted hazardous substances, in several European countries the utilisation of waste wood (recycling or combustion) is regulated by legislation defining permissible limits for the content of several elements and organic compounds which are classified as priority environmental pollutants. The corresponding values laid down in the German *Ordinance on the Management of Waste Wood* [1] are given in Table 1.

Tab. 1: Limiting values for wood chips used in the manufacture of derived timber products [1]

Analyte	Permissible content (mg/kg)
Arsenic	2
Cadmium	2
Chlorine	600
Chromium	30
Copper	20
Fluorine	100
Lead	30
Mercury	0.4
Pentachlorophenol	3
Polychlorinated biphenyls	5

Thus, for decision-making with respect to waste wood management reliable analytical data are needed and – due to their great economic and environmental impact – must be assured by appropriate quality control.

A very useful tool for quality assurance of analytical results is the application of suitable certified reference materials (CRM). However, to our knowledge up to now there is only one CRM commercially available for the analysis of impregnated wood (BCR-683), which moreover only covers pentachlorophenol and some polycyclic aromatic hydrocarbons. No material is available for the determination of heavy metals which were (and partly are) in use as wood preservatives.

To fill this gap a project to certify a new wood material for its mass fractions of arsenic, cadmium, chromium, copper, lead, mercury, and pentachlorophenol was initiated by BAM.

2 Candidate material

The material was prepared at BAM using three different raw materials:

(1) waste wood (North American pine) industrially treated with PCP,
(2) German pine wood, industrially impregnated with wood preservatives containing As, Cr and Cu,
(3) untreated German beech wood.

The raw materials were separately subjected to the following processing:

- chopping with a commercial shredder,

- milling of the wood chips embrittled with liquid nitrogen by means of a cutting mill with a bottom sieve of 2 mm mesh size,
- additional milling of the ground stock under continuous cooling (liquid nitrogen) with a centrifugal mill using a 1 mm mesh ring sieve.

A certain amount of mill charge (3) was immersed in an aqueous solution of Cd, Hg and Pb salts and thereafter slowly dried over several weeks to constant weight to yield fraction (4).

To fit the mass fractions of the relevant analytes to legal threshold values, stepwise blending of the wood materials (1) to (4) was performed by means of a 120 litre drum hoop mixer. Final homogenisation and bottling were carried out with a spinning riffler.
A total of 200 units containing (74 ± 1) g of homogenized wood material each were bottled in 250 ml amber glass containers with screw caps equipped with PTFE insert and sealed with shrinking foil. The bottles were stored at -(20 ± 2) °C in the dark.

3 Homogeneity study

Twelve bottles were selected equidistantly from the whole batch of 200 units following the sequence of bottling. The selected units were analysed three times each using sample intakes of 0.5 g and also of 2 g for the determination of trace elements and of 4 g for the determination of PCP.
For trace element determination the wood material was digested with aqua regia following the procedures given in EN 13657 [2]:

(1) boiling in an open reaction vessel under reflux for 2 h using a sample intake of 2 g,
(2) microwave digestion for 20 min in a closed vessel using a sample intake of 0.5 g.

The extraction of PCP was performed according to CEN/TR 14823 [3]. All prepared solutions were analysed under repeatability conditions after randomisation in one run with one calibration. Results and used analytical methods are given in Annex 2.
The estimates of inhomogeneity contributions u_{bb} potentially hidden by the measurement uncertainty and to be included into the total uncertainty budget were estimated according to ISO Guide 35 [4] as the maximum of the values obtained from Eq. (1) and (2).

$$u_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \qquad (1)$$

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \times \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

where:

MS_{among}	mean of squared deviations between bottles (from 1-way ANOVA)
MS_{within}	mean of squared deviations within bottles (from 1-way ANOVA)
n	number of replicate sub-samples per bottle
N	number of bottles selected for homogeneity study

4 Stability study

Stability testing was carried out according to the so-called isochronous design [5]. Selected units of the candidate material were subjected to accelerated ageing at temperatures between 4 °C and 60 °C over periods of 4 weeks to 12 months (see Annex 3). After the respective periods of time the individual units were stored at -20 °C. All units were analysed in triplicate for trace elements and PCP after digestion/extraction using the same procedures as for homogeneity testing and the analytical methods given in Annex 3.

A total of six digests/extracts obtained from two reference samples which had been kept at -20 °C since bottling and being evenly distributed over the whole measurement sequence were analysed together with the exposed samples in one run under repeatability conditions.
All measurement results from the stability study are given in Annex 3. They were evaluated using software SoftCRM version 1.2.2 [6]. Significant impact of storage conditions on the stability of the certified properties could not be detected, neither of storage time nor of temperature (up to +60 °C). In all cases the slope of the linear regression did not significantly differ from zero.
Furthermore, published literature data and previous experience collated over substantial periods of time with similar materials used in large proficiency testing schemes provide evidence of an extreme stability of all analytes under consideration. Although under these conditions an expansion of the total uncertainty of the certified value is generally not encouraged, in this specific case the approach of ISO Guide 35 was followed, mainly due to the lack of sound alternatives. A long-term uncertainty contribution $u_{lts,r}$ was estimated representing the product of the relative standard uncertainty of the slope of the regression line for the recommended storage temperature +4 °C, multiplied by a factor of 3 (taking into account a minimum shelf life of three years).
Stability testing will be continued by further measurements of units stored at 4 °C, 23 °C and 40 °C over the period of availability of the material. That way, information on the long term stability of units of ERM-CD100 having been opened at least once for withdrawal of material is expected in the course of the post certification monitoring.

5 Certification study

5.1 Design of the study

The certification study was organised as an interlaboratory comparison. Laboratories invited to participate were selected on the basis of their expertise demonstrated in the course of a preceding proficiency test where a similar wood material was requested to be analysed for trace elements and PCP.
Up to ten independent equipment/operator combinations including three from BAM, Division I.1 (in case of trace elements) and two from BAM, Division I.2 (in case of PCP) participated in the certification of the mass fractions of the analytes under investigation. Each participant received one unit of bottled wood material and was asked to analyse six independent sub-samples for their contents of trace elements and/or PCP. The moisture content of the bottled wood material had to be determined in triplicate using separate sub-samples. Additionally, information on details of the applied analytical procedures as well as on the uncertainties of used calibration standards was requested.

5.2 Participants

BAM Bundesanstalt für Materialforschung und –prüfung, Division I.1, Berlin (DE)
BAM Bundesanstalt für Materialforschung und –prüfung, Division I.2, Berlin (DE)
EUKOS Umweltanalytik Nord GmbH, Plön (DE)
Fraunhofer-Institut für Holzforschung, Wilhelm-Klauditz-Institut (WKI), Braunschweig (DE)
Holzforschung Austria, Wien (AT)
Institut für Hygiene und Umwelt, Hamburg (DE)
Johann Heinrich von Thünen-Institut, Hamburg (DE)
Materialprüfungsanstalt Eberswalde GmbH, Eberswalde (DE)
Pfleiderer AG, DUROPAL GmbH, Arnsberg (DE)
SGS Institut Fresenius GmbH, Berlin (DE)

5.3 Analytical methods

For the determination of trace elements open and closed vessel digestion procedures and different detection methods (AAS, AFS, ICP OES and ICP-MS) were applied.
The determination of PCP was performed by all participants following the analytical protocol given in CEN/TR 14823 using GC-ECD or GC-MS as detection methods.
Methods used by the participants in the course of the certification study for the determination of trace elements, PCP and moisture content of the candidate material are indicated in the tables of Annex 1, respectively. Details of sample pre-treatment prior to analysis are compiled in the following Tables 2 and 3.

Tab. 2: Sample digestion for the determination of trace elements

Lab code	Sample intake (g)	Acid mixture	Apparatus
03	2.003 – 2.028	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)
04	0.50 – 0.55	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)
05	0.502 – 0.510	HNO_3 + H_2O_2	Closed vessel (microwave)
06	0.490 – 0.604	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)
08	0.396 – 1.396	HNO_3 + H_2O_2	Closed vessel (microwave)
09	0.259 – 0.570	HNO_3 + H_2O_2	Closed vessel (microwave)
10	5.0	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)
11	0.592 – 0.790	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)
12	0.503 – 0.508	HNO_3	Closed vessel (microwave)
13	0.512 – 0.593	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)

Tab. 3: Sample pre-treatment for the determination of PCP

Lab code	Sample intake (g)	Extraction method	Solvent	Derivatisation
01	5.027 – 5.178	Sonication	Methanol	Acetic anhydride
02	5.009 – 5.105	Pressurised fluid extraction	Methanol	Acetic anhydride
04	3.701 – 5.256	Sonication	Methanol	Acetic anhydride
05	4.901 – 5.095	Sonication + mechanical shaker	Toluene + H_2SO_4	Acetic anhydride
06	2.0	Sonication	Methanol	Acetic anhydride
08	4.940 – 4.997	Soxhlet	Methanol	Acetic anhydride
09	2.108 – 2.197	Sonication + mechanical shaker	Toluene + H_2SO_4	Acetic anhydride
10	5.0	Sonication	Methanol	No
11	4.509 – 4.775	Sonication	Methanol	Acetic anhydride

5.4 Statistical evaluation of results

The measurement results submitted by the participants in the certification study are listed in Annex 1. They are corrected to dry mass content based on the respective moisture content of the sample determined by the individual participant. The bars in the graphic presentations

indicate the standard deviation of individual results. The bars associated with the also plotted certified values represent the corresponding expanded uncertainties.

Statistical tests and data evaluation were performed with the SoftCRM package. The following tests were carried out and are summarised in Table 4:

Scheffé's multiple t-test: All data sets compatible two-by-two?

Cochran test: Outlying laboratory variances?
(Significance levels 0.01 and 0.05, respectively. Outlying laboratories are indicated.)

Grubbs, Dixon and Nalimov tests: Outlying laboratory means?

Bartlett test: Laboratory variances homogeneous?

Snedecor F-test: Differences between laboratories statistically significant?

Gauss (Kolmogorov-Smirnov-Lilliefors test): Normality of laboratory means distribution?

Tab. 4: Statistical tests carried out on participants' results

Analyte	Number of data sets	Statistical tests				
		Scheffe	Cochran (0.01/0.05)	Grubbs (0.01/0.05)	Dixon (0.01/0.05)	Nalimov (0.01/0.05)
As	9	No	(-/-)	(-/-)	(-/-)	(-/09)
Cd	10	No	(-/-)	(-/-)	(-/-)	(-/05)
Cr	10	No	(-/09)	(-/-)	(-/-)	(-/-)
Cu	10	No	(-/-)	(-/-)	(-/-)	(-/-)
Hg	8	No	(09,04/09,04)	(-/09)	(-/-)	(09/09)
Pb	10	No	(-/-)	(-/-)	(-/-)	(-/-)
PCP	9	No	(-/-)	(04/04)	(04/04)	(04/04)
Moisture	10	No	(05,04/05,04)	(-/11)	(-/11)	(11/11)

Tab. 4 (continued):

Analyte	Statistical tests			Consequences	
	Bartlett (0.01)	Snedecor (0.01)	Gauss (0.05)	Pooling	Data sets to be deleted
As	Yes	Yes	Yes	No	
Cd	Yes	Yes	Yes	No	
Cr	Yes	Yes	Yes	No	
Cu	Yes	Yes	Yes	No	
Hg	No	Yes	No	No	09
Pb	No	Yes	Yes	No	
PCP	Yes	Yes	No	No	04
Moisture	No	Yes	No	No	11

Although the reasons for the outlying results of participants 09 (Hg), 04 (PCP) and 11 (moisture content) could not be identified, these particular results were excluded from further data processing.

5.5 Traceability

In the course of trace element determinations all analyses were carried out with matrix matched calibration solutions prepared either from metals of well-defined purity or from commercial solutions with certified element concentrations.
The certified value for PCP refers to the extractable amount and is conventional to this extent. However, different extraction methods and solvents have been used thus (at least partially) cancelling out systematic biases. The completeness of extraction of PCP from wood material with methanol or toluene/H_2SO_4 was investigated in earlier studies [7]. It was demonstrated that extraction, e.g. with methanol yields a PCP recovery close to 100% [8]. In order to ensure traceability of the extractable content as defined above, certified PCP standards were employed.

5.6 Certified values and uncertainties

The unweighted means of laboratory means were taken as the best estimates w_{char} for the values to be certified. They are expressed on a dry mass basis corresponding to a drying temperature of (103 ± 2) °C. The standard deviations of the mean of laboratory means were taken as the uncertainty contributions u_{char} resulting from interlaboratory comparison.
Additionally the following uncertainty components were taken into account:

- u_{bb} uncertainty due to potentially hidden inhomogeneity of the material (see paragraph 3)
- u_{pur} uncertainty of the certified purity of used calibration standards (whereas a maximum of 0.5 % was taken into account for all analytes)
- u_{dm} uncertainty of dry matter correction carried out by the participants in the certification study (thereby the standard deviation of the mean of 10 laboratory means for the moisture content – see Annex 1 – was attributed with equal value to the mean dry matter content of 92.52 % giving a relative uncertainty $u_{dm,r}$ of approximately 0.15 %)
- u_{lts} uncertainty resulting from stability testing of the material (see paragraph 4)

Relative values of these uncertainty contributions were assembled in a GUM [9] based approach yielding the combined uncertainty $u_{com,r}$:

$$u_{com,r}^2 = u_{char,r}^2 + u_{bb,r}^2 + u_{pur,r}^2 + u_{dm,r}^2 + u_{lts,r}^2$$

Absolute values of the different uncertainty components are given in Table 5.

Tab. 5: Mass fractions and uncertainty components for the analytes in ERM-CD100 (before rounding)

Analyte	w_{char} (mg kg^{-1})	u_{char} (mg kg^{-1})	u_{bb} (mg kg^{-1})	u_{pur} (mg kg^{-1})	u_{dm} (mg kg^{-1})	u_{lts} (mg kg^{-1})	u_{com} (mg kg^{-1})
As	3.126	0.1707	0.1378	0.0156	0.0046	0.0338	0.2226
Cd	3.017	0.0931	0.0665	0.0151	0.0045	0.0299	0.1193
Cr	36.44	0.6903	0.9037	0.1822	0.0539	0.5794	1.2903
Cu	22.89	0.4986	0.5459	0.1145	0.0339	0.3159	0.8128
Hg	0.596	0.0678	0.0070	0.0030	0.0009	0.0089	0.0688
Pb	38.91	1.0548	1.4903	0.1946	0.0576	0.2101	1.8490
PCP	7.888	0.1806	0.1520	0.0394	0.0117	0.1491	0.2822

The expanded uncertainties $U = k \times u_{com}$ were derived using the coverage factor $k = 2$ giving a level of confidence of approximately 95 %.
The certified mass fractions and their corresponding expanded uncertainties are rounded according to the recommendations of the GUM and are given in Table 6.

Tab. 6: Certified mass fractions and expanded uncertainties of analytes in ERM-CD100 (after rounding)

Analyte	Mass fraction (mg/kg)
As	3.1 ± 0.5
Cd	3.02 ± 0.24
Cr	36.4 ± 2.6
Cu	22.9 ± 1.7
Hg	0.60 ± 0.14
Pb	39 ± 4
PCP	7.9 ± 0.6

6 Information on the proper use of ERM - CD100

6.1 Shelf life

The initial stability study after storage of selected units at different temperatures did not reveal any statistically significant deterioration of the certified properties. However, starting with dispatch of the material from BAM the validity of the certificate expires after 12 months. Post-certification measurements will be conducted in appropriate periods to keep this information up to date.

6.2 Transport, storage and use

Transportation of the bottled sample does not require special precautions. The stability of the contents of the relevant analytes allows the dispatch of the material at ambient temperature. Short heating of the closed bottle up to +40 °C for a few days does not affect the quality of ERM-CD100.

On receiving, bottled material has to be stored at (4 ± 2) °C. Before withdrawing a sub-sample, the bottle should be allowed to reach room temperature and mixed thoroughly. Thereafter, the bottle should be closed tightly and stored at (4 ± 2) °C.
The material should be used as it is provided. However, before taking a sub-sample a re-homogenisation by manual shaking of the closed bottle is highly recommended. The bottle shall be left unclosed as shortly as possible.
Analytical results have to be corrected to the dry mass content of the material. In this context it should be noted that under appropriate storage and handling conditions no significant moisture exchange between the bottled material and the ambient atmosphere may occur. Thus, at least at the beginning of the use of the material the required dry mass correction can be made on the basis of the indicated moisture content at the time of certification being 7.48 %. Nevertheless, after repeated use of the material its moisture content should be determined (at least in duplicate) either by Karl Fischer titration method or by heating in an oven at a temperature of (103 ± 2) °C using separate sub-samples.

6.3 Safety instructions

No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with trace elements and pentachlorophenol. Nevertheless, it is strongly recommended to handle and dispose the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal.

6.4 Legal notice

Neither the BAM Federal Institute for Materials Research and Testing nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights, or assume any liability with respect to the use of, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

7 References

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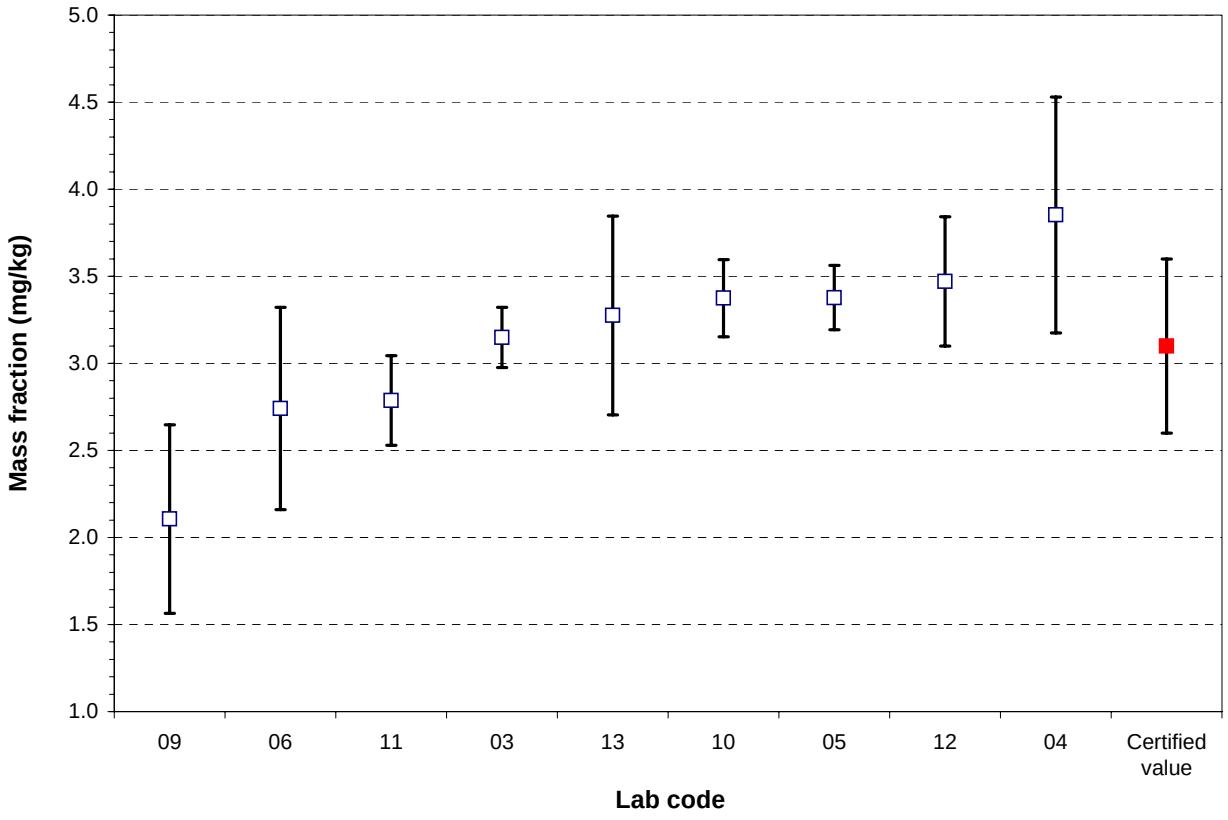
Certification study (measurement results of participating laboratories) **As**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
09	1.74	1.74	3.05	2.07	2.40	1.63	2.106	0.5410	ICP OES
06	3.62	2.10	2.24	3.14	2.46	2.87	2.741	0.5807	ICP OES
11	2.57	2.60	2.84	2.55	3.00	3.16	2.786	0.2572	ICP OES
03	3.10	3.19	3.47	3.03	2.98	3.12	3.149	0.1730	ET AAS
13	3.00	3.89	3.96	3.09	3.25	2.45	3.275	0.5701	ET AAS
10	3.25	3.79	3.14	3.36	3.36	3.36	3.374	0.2210	ICP OES
05	3.24	3.60	3.21	3.46			3.378	0.1844	ICP OES
12	2.87	3.20	3.64	3.49	3.83	3.79	3.470	0.3712	ICP-MS
04	3.83	2.69	3.83	3.91	4.81	4.05	3.852	0.6776	HG ICP OES

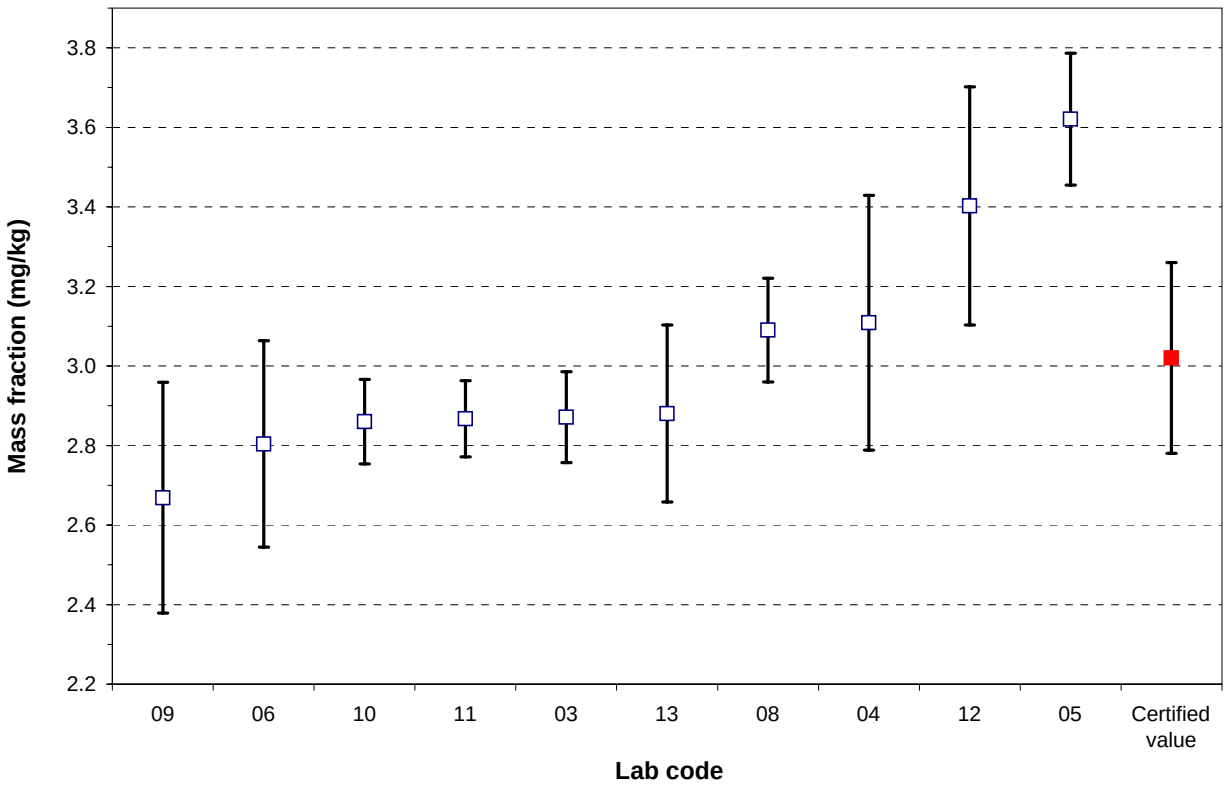
M (mg/kg):	**3.126**
SD_M (mg/kg):	0.5121
$SD_M/\sqrt{N}$ (mg/kg):	0.1707



Certification study (measurement results of participating laboratories) **Cd**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
09	2.61	3.05	2.83	2.40	2.83	2.29	2.669	0.2903	ICP OES
06	2.91	2.98	2.72	2.62	3.15	2.44	2.804	0.2597	ICP OES
10	3.01	2.83	2.96	2.86	2.73	2.78	2.860	0.1060	ICP OES
11	2.78	3.00	2.89	2.91	2.74	2.88	2.867	0.0959	ICP OES
03	2.97	2.84	3.04	2.75	2.77	2.86	2.871	0.1143	ET AAS
13	3.05	2.80	3.07	2.51	3.06	2.80	2.880	0.2226	ET AAS
08	2.89	3.23	2.99	3.08	3.20	3.16	3.090	0.1303	ICP OES
04	3.10	2.63	2.95	3.04	3.47	3.46	3.109	0.3201	ET AAS
12	3.90	3.58	3.11	3.29	3.40	3.13	3.403	0.2995	ICP-MS
05	3.85	3.40	3.61	3.55	3.70		3.621	0.1657	ICP OES

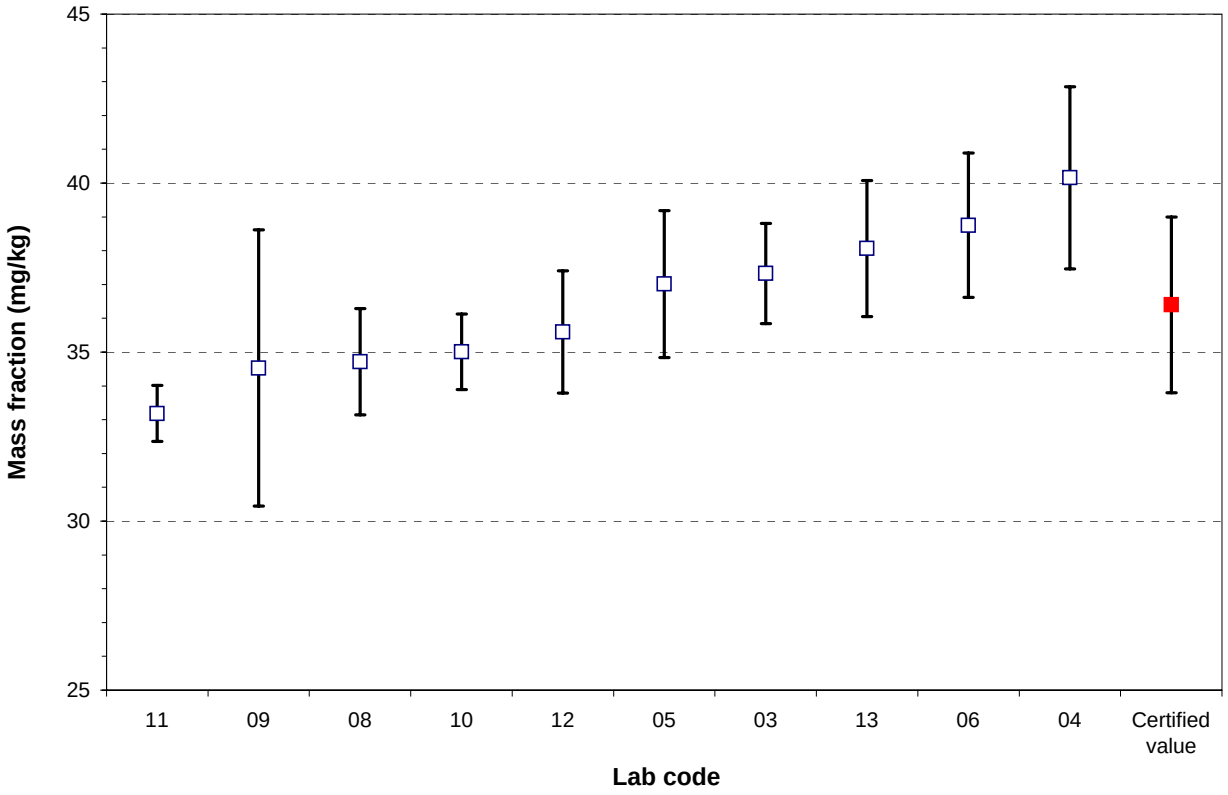
M (mg/kg):	**3.017**
SD_M (mg/kg):	0.2946
$SD_M/\sqrt{N}$ (mg/kg):	0.0931



Certification study (measurement results of participating laboratories) **Cr**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
11	32.3	34.2	33.7	32.3	32.7	33.8	33.19	0.832	ICP OES
09	30.4	36.9	41.4	32.5	34.5	31.5	34.53	4.088	ICP OES
08	33.3	35.4	32.5	36.8	35.1	35.2	34.72	1.576	ICP OES
10	34.6	34.6	33.6	36.8	34.6	35.7	35.01	1.118	ICP OES
12	36.2	34.4	37.6	34.1	37.7	33.7	35.60	1.812	ICP-MS
05	35.9	39.7	34.7	37.8			37.01	2.177	ICP OES
03	39.1	37.8	37.0	38.3	34.8	37.0	37.33	1.483	ICP OES
13	38.8	40.6	36.6	35.6	36.9	39.9	38.06	2.012	ICP OES
06	39.9	42.4	38.7	37.4	36.4	37.7	38.75	2.136	ICP OES
04	42.0	37.5	41.4	41.9	42.1	36.0	40.16	2.698	ICP OES

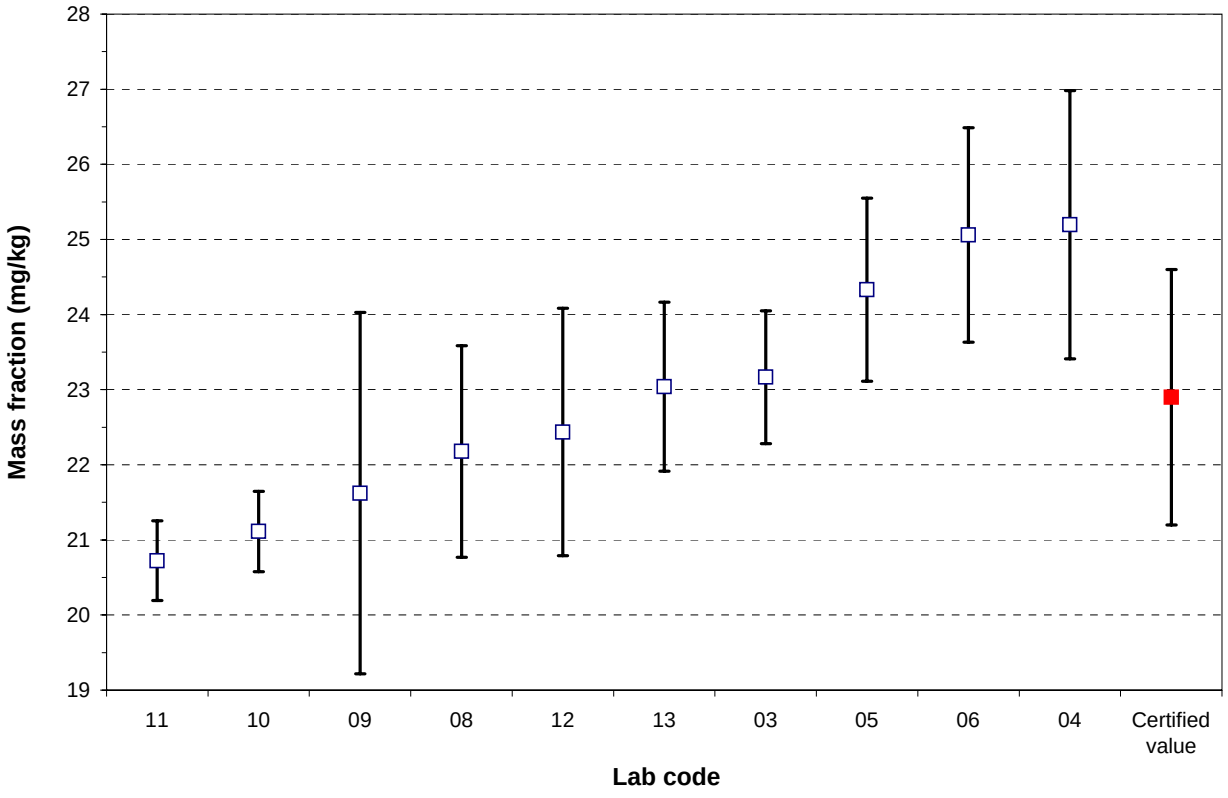
M (mg/kg):	**36.44**
SD_M (mg/kg):	2.183
$SD_M/\sqrt{N}$ (mg/kg):	0.6903



Certification study (measurement results of participating laboratories) **Cu**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
11	20.1	21.5	21.0	20.5	20.3	20.9	20.72	0.529	ICP OES
10	20.9	21.2	20.2	21.9	21.1	21.3	21.11	0.535	ICP OES
09	17.1	23.5	22.2	22.3	23.5	21.0	21.62	2.405	ICP OES
08	21.9	22.1	19.7	23.8	23.2	22.4	22.18	1.409	ICP OES
12	22.1	21.1	25.4	22.0	23.0	21.0	22.44	1.646	ICP-MS
13	22.9	24.6	22.9	21.6	22.2	24.0	23.04	1.124	ICP OES
03	24.1	23.5	22.8	24.0	21.7	22.9	23.17	0.885	ICP OES
05	24.5	25.4	22.6	24.9			24.33	1.220	ICP OES
06	26.2	27.3	24.8	24.1	23.6	24.3	25.06	1.426	ICP OES
04	26.1	23.6	25.6	26.6	26.8	22.4	25.20	1.787	ICP OES

M (mg/kg):	**22.89**
SD_M (mg/kg):	1.577
$SD_M/\sqrt{N}$ (mg/kg):	0.4986

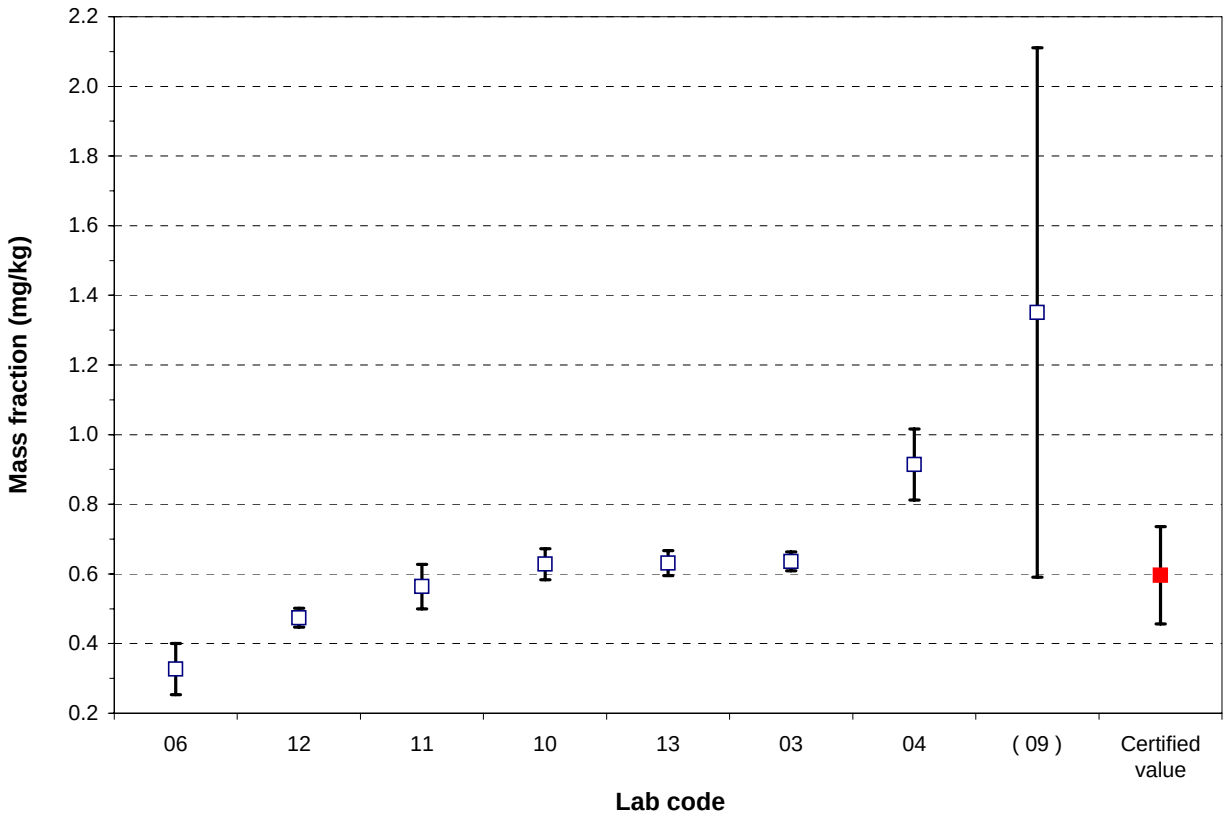


Certification study (measurement results of participating laboratories) **Hg**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
06	0.271	0.260	0.260	0.434	0.358	0.379	0.327	0.0737	CV AAS
12	0.522	0.485	0.458	0.455	0.478	0.447	0.474	0.0273	ICP-MS
11	0.587	0.490	0.512	0.552	0.649	0.594	0.564	0.0638	CV AAS
10	0.660	0.650	0.563	0.585	0.650	0.660	0.628	0.0444	CV AAS
13	0.659	0.641	0.649	0.564	0.651	0.624	0.631	0.0359	CV AFS
03	0.653	0.666	0.653	0.603	0.609	0.632	0.636	0.0272	CV AFS
04	1.099	0.970	0.819	0.894	0.733	0.970	0.914	0.1021	CV AAS
(**09**)	1.089	1.307	1.089	0.763	2.505		1.351	0.7599	CV AAS

The data from lab 09 were not taken into account.
(see chapter "Statistical evaluation")

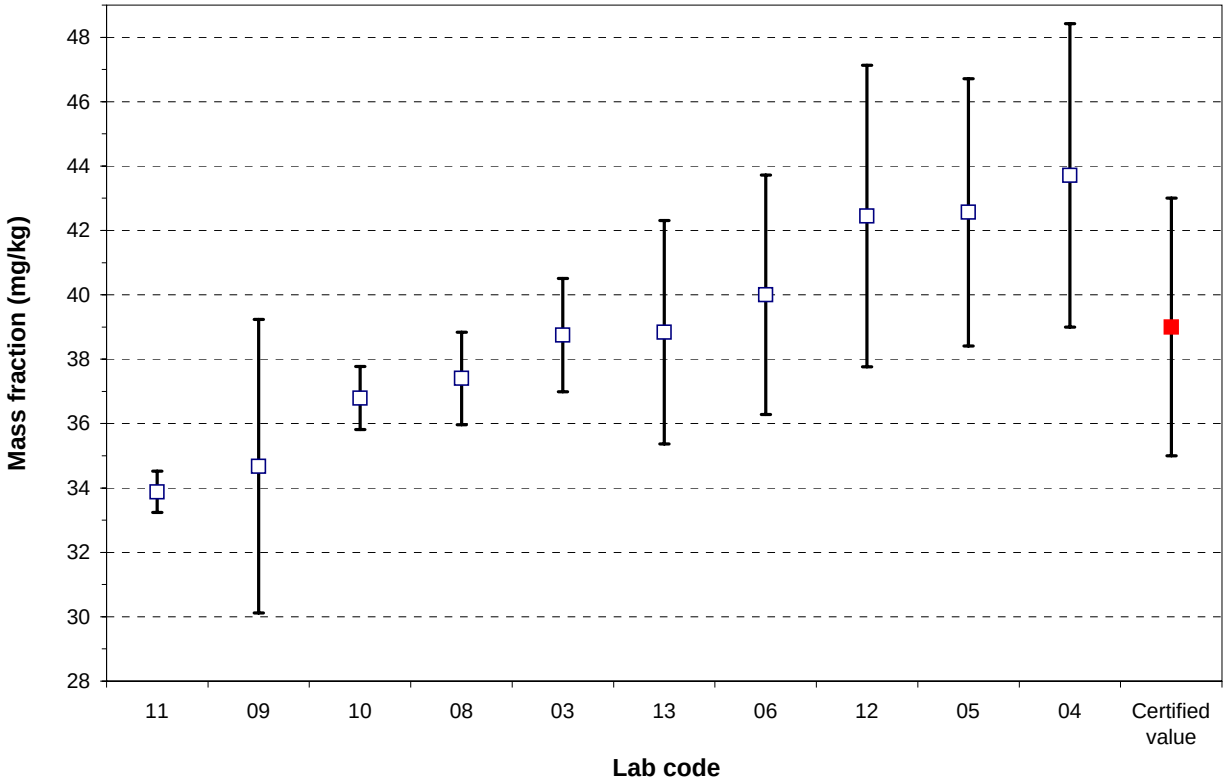
M (mg/kg):	**0.596**
SD_M (mg/kg):	0.1795
$SD_M/\sqrt{N}$ (mg/kg):	0.0678



Certification study (measurement results of participating laboratories) **Pb**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
11	33.5	34.2	34.8	34.3	33.1	33.4	33.88	0.643	ICP OES
09	39.5	41.0	32.8	32.1	33.3	29.3	34.68	4.557	ICP OES
10	37.1	35.3	37.5	37.7	35.8	37.4	36.79	0.981	ICP OES
08	36.3	37.2	35.8	36.9	39.4	38.9	37.40	1.435	ICP OES
03	39.7	39.5	41.5	37.3	37.5	37.1	38.75	1.756	ICP OES
13	42.7	36.4	43.0	35.1	39.7	36.1	38.84	3.467	ICP OES
06	40.3	40.1	43.8	37.7	43.9	34.1	40.00	3.720	ICP OES
12	44.6	47.1	37.9	42.3	46.9	35.9	42.45	4.685	ICP-MS
05	39.1	47.3	40.4	46.9	39.1		42.56	4.154	ICP OES
04	47.6	41.9	43.7	38.6	50.8	39.7	43.71	4.711	ICP OES

M (mg/kg):	**38.91**
SD_M (mg/kg):	3.336
$SD_M/\sqrt{N}$ (mg/kg):	1.0548

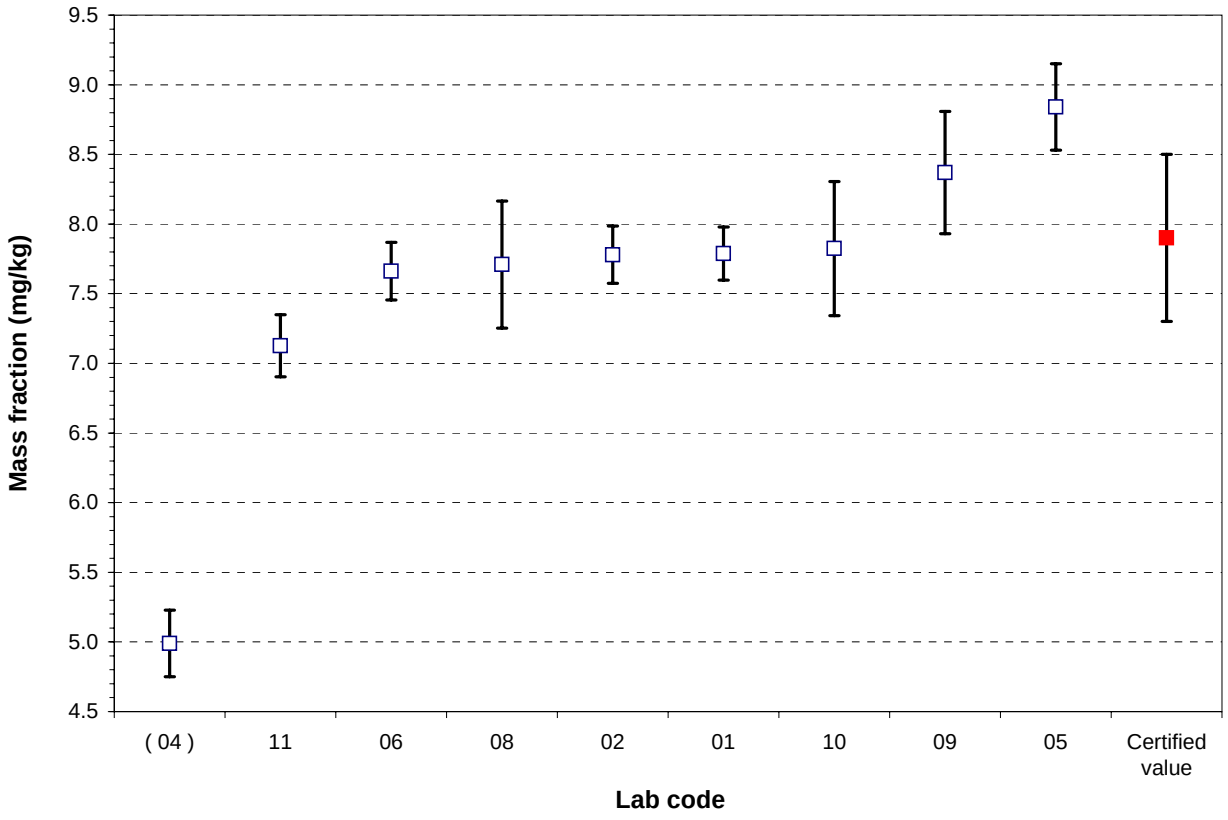


Certification study (measurement results of participating laboratories) **PCP**

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Lab mean (mg/kg)	SD (mg/kg)	Analytical method
(**04**)	5.20	5.31	4.77	5.06	4.76	4.82	4.989	0.2383	GC-MS
11	7.41	7.00	6.81	7.34	7.16	7.04	7.127	0.2232	GC-ECD
06	7.53	7.88	7.47	7.47	7.69	7.94	7.662	0.2069	GC-ECD
08	7.08	7.57	8.36	8.11	7.56	7.57	7.710	0.4561	GC-MS
02	7.97	7.88	7.80	7.86	7.78	7.38	7.780	0.2055	HPLC-MS/MS
01	7.94	7.62	7.71	7.54	7.99	7.94	7.788	0.1907	GC-ECD
10	7.39	7.54	7.65	7.49	8.38	8.49	7.824	0.4810	GC-MS
09	8.16	8.95	8.78	8.47	7.92	7.93	8.369	0.4385	GC-ECD
05	8.63	9.19	8.86	8.44	9.09		8.840	0.3108	GC-ECD

The data from lab 04 were not taken into account.
(see chapter "Statistical evaluation")

M (mg/kg):	**7.888**
SD_M (mg/kg):	0.5107
$SD_M/\sqrt{N}$ (mg/kg):	0.1806

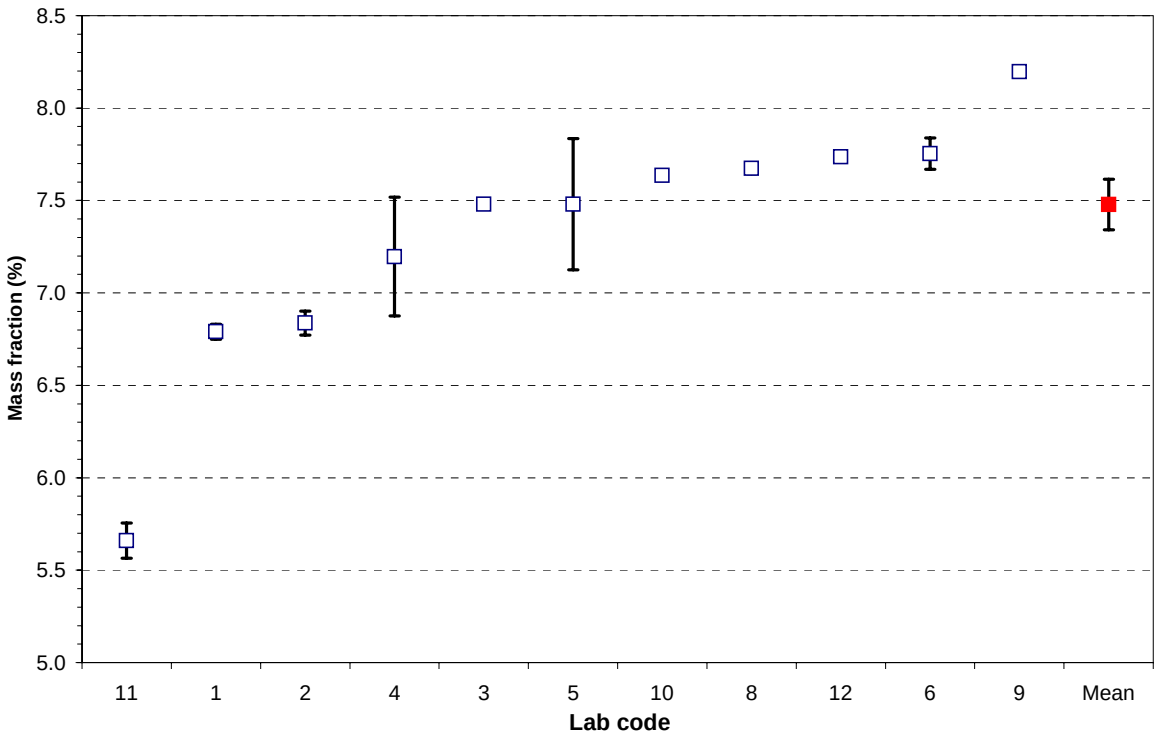


Certification study (measurement results of participating laboratories) **Moisture**

Lab code	#1 (%)	#2 (%)	#3 (%)	Lab mean (%)	SD (%)	Analytical method
(**11**)	5.65	5.76	5.57	5.660	0.0954	ISO 11465
01	6.84	6.78	6.76	6.790	0.0409	MA 30 (IR)
02	6.90	6.77	6.84	6.837	0.0651	KF titration
04	6.86	7.23	7.50	7.197	0.3213	ISO 11465
03	7.49	7.46	7.49	7.480	0.0173	ISO 11465
05	7.89	7.28	7.27	7.480	0.3551	ISO 11465
10	7.65	7.63	7.63	7.636	0.0092	ISO 11465
08	7.69	7.69	7.64	7.673	0.0289	ISO 11465
12	7.72	7.74	7.75	7.736	0.0121	ISO 11465
06	7.69	7.85	7.72	7.753	0.0850	ISO 11465
09	8.20	8.20	8.19	8.197	0.0058	ISO 11465

The data from lab 11 were not taken into account (see chapter "Statistical evaluation").

M (%):	**7.478**
SD_M (%):	0.4328
$SD_M/\sqrt{N}$ (%):	0.1369



Homogeneity study (measurement results) **As**

(1) Sample intake: 2.0 g Analytical method: ET AAS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	3.025	3.062	3.272	3.120	0.1329
028	3.501	2.965	3.374	3.280	0.2800
044	3.215	2.663	2.913	2.930	0.2763
060	2.898	3.361	2.782	3.014	0.3063
076	2.873	3.448	2.953	3.092	0.3115
092	2.600	3.108	3.120	2.943	0.0086
108	3.212	2.782	2.927	2.974	0.1029
124	2.941	3.333	2.874	3.049	0.3248
140	2.578	2.894	2.635	2.702	0.1833
156	3.061	3.153	3.230	3.148	0.0550
172	3.057	3.332	2.793	3.060	0.3810
188	3.119	3.052	3.164	3.112	0.0792

M (mg/kg): **3.035**

SD_M (mg/kg): 0.1428

u_{bb} (% rel.): 2.418

(acc. to ISO Guide 35)

(2) Sample intake: 0.5 g Analytical method: ET AAS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	3.598	3.065	3.472	3.379	0.2787
028	2.787	2.548	3.728	3.021	0.6242
044	2.486	3.279	2.879	2.881	0.3964
060	3.394	3.603	3.177	3.391	0.2131
076	2.710	3.583	4.199	3.497	0.7478
092	3.200	3.701	2.857	3.252	0.5967
108	3.025	3.741	2.614	3.126	0.7969
124	2.622	3.343	3.100	3.022	0.1722
140	3.112	3.592	2.566	3.090	0.7253
156	2.982	3.204	2.530	2.905	0.4762
172	3.092	3.230	3.285	3.202	0.0382
188	3.137	2.550	2.582	2.756	0.0229

M (mg/kg): **3.127**

SD_M (mg/kg): 0.2261

u_{bb} (% rel.): 4.408

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Cd**

(1) Sample intake: 2.0 g Analytical method: ET AAS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	2.754	2.757	2.776	2.762	0.0117
028	2.804	2.647	2.657	2.703	0.0878
044	2.728	2.506	2.798	2.678	0.1526
060	2.829	2.558	2.686	2.691	0.1356
076	2.753	2.452	2.846	2.684	0.2062
092	2.773	2.712	2.677	2.721	0.0248
108	2.806	2.590	2.858	2.752	0.1893
124	2.533	2.690	2.652	2.625	0.0269
140	2.599	2.736	2.748	2.694	0.0081
156	2.727	2.781	2.647	2.718	0.0947
172	2.483	2.614	2.757	2.618	0.1008
188	2.565	2.489	2.813	2.622	0.2295

M (mg/kg): **2.689**

SD_M (mg/kg): 0.0478

u_{bb} (% rel.): 1.413

(acc. to ISO Guide 35)

(2) Sample intake: 0.5 g Analytical method: ET AAS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	2.792	2.795	2.689	2.759	0.0605
028	2.719	2.920	2.559	2.732	0.1807
044	2.513	2.497	2.756	2.589	0.1451
060	2.447	3.050	2.711	2.736	0.3022
076	2.646	2.682	2.491	2.606	0.1012
092	2.859	2.797	2.632	2.763	0.1173
108	2.431	2.383	2.917	2.577	0.3778
124	2.546	2.572	2.687	2.601	0.0811
140	2.716	2.832	3.023	2.857	0.1347
156	2.557	2.548	2.267	2.457	0.1985
172	3.006	2.389	2.691	2.696	0.2139
188	2.606	2.413	2.660	2.560	0.1746

M (mg/kg): **2.661**

SD_M (mg/kg): 0.1131

u_{bb} (% rel.): 2.204

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Cr**

(1) Sample intake: 2.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	34.97	31.83	32.92	33.24	1.591
028	33.69	35.78	36.58	35.35	1.496
044	35.79	34.73	35.27	35.26	0.531
060	34.67	33.75	32.49	33.64	1.095
076	33.96	33.55	35.38	34.30	0.959
092	35.06	34.07	34.46	34.53	0.275
108	33.46	34.20	35.26	34.31	0.755
124	32.26	34.37	35.21	33.94	0.594
140	34.94	34.51	32.58	34.01	1.363
156	32.92	33.33	32.74	33.00	0.416
172	34.46	34.75	33.41	34.21	0.949
188	35.68	33.91	34.15	34.58	0.171

M (mg/kg): **34.20**

SD_M (mg/kg): 0.708

u_{bb} (% rel.): 1.021

(acc. to ISO Guide 35)

(2) Sample intake: 0.5 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	36.35	33.15	34.56	34.69	1.604
028	39.89	30.69	32.14	34.24	4.951
044	32.39	33.03	29.57	31.66	1.840
060	35.50	32.17	29.86	32.51	2.838
076	34.41	34.49	32.02	33.64	1.401
092	38.17	34.60	35.94	36.24	0.948
108	34.53	32.25	39.75	35.51	5.305
124	33.09	39.15	35.25	35.83	2.762
140	33.62	35.71	33.21	34.18	1.764
156	28.36	34.87	32.92	32.05	1.379
172	33.05	38.00	38.49	36.51	0.347
188	34.38	33.98	34.74	34.37	0.537

M (mg/kg): **34.28**

SD_M (mg/kg): 1.603

u_{bb} (% rel.): 2.480

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Cu**

(1) Sample intake: 2.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	22.72	21.02	21.24	21.66	0.925
028	21.45	22.78	22.92	22.38	0.811
044	22.57	21.85	22.08	22.17	0.365
060	23.15	21.73	21.37	22.08	0.938
076	21.68	21.58	22.74	22.00	0.644
092	22.31	22.23	22.50	22.35	0.193
108	21.89	21.84	22.66	22.13	0.581
124	21.00	22.14	22.70	21.94	0.397
140	21.86	22.06	20.91	21.61	0.814
156	21.44	21.77	21.09	21.43	0.482
172	22.31	22.47	21.84	22.21	0.448
188	22.82	21.74	22.29	22.28	0.388

M (mg/kg): **22.02**

SD_M (mg/kg): 0.307

u_{bb} (% rel.): 0.893

(acc. to ISO Guide 35)

(2) Sample intake: 0.5 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	23.23	21.23	23.12	22.53	1.126
028	25.38	19.81	20.48	21.89	3.042
044	20.72	21.02	19.22	20.32	0.968
060	22.62	20.46	19.40	20.83	1.642
076	23.25	22.54	20.09	21.96	1.661
092	23.77	22.57	22.70	23.01	0.094
108	21.74	20.87	26.19	22.93	3.761
124	21.23	25.67	22.37	23.09	2.330
140	21.36	22.62	21.29	21.76	0.937
156	20.44	21.76	20.60	20.93	0.826
172	21.14	23.32	24.01	22.83	0.488
188	22.60	21.98	23.24	22.60	0.892

M (mg/kg): **22.06**

SD_M (mg/kg): 0.943

u_{bb} (% rel.): 2.385

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Hg**

(1) Sample intake: 2.0 g Analytical method: CV AFS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	0.597	0.621	0.596	0.605	0.0140
028	0.595	0.578	0.592	0.588	0.0089
044	0.608	0.584	0.621	0.604	0.0192
060	0.601	0.573	0.593	0.589	0.0141
076	0.624	0.583	0.603	0.603	0.0205
092	0.583	0.602	0.603	0.596	0.0005
108	0.602	0.573	0.609	0.595	0.0258
124	0.595	0.605	0.588	0.596	0.0120
140	0.594	0.626	0.592	0.604	0.0245
156	0.606	0.627	0.589	0.607	0.0270
172	0.617	0.611	0.597	0.608	0.0098
188	0.609	0.582	0.603	0.598	0.0151

M (mg/kg): **0.600**

SD_M (mg/kg): 0.0068

u_{bb} (% rel.): 0.802

(acc. to ISO Guide 35)

(2) Sample intake: 0.5 g Analytical method: CV AFS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	0.626	0.619	0.606	0.617	0.0104
028	0.593	0.616	0.623	0.611	0.0161
044	0.591	0.591	0.639	0.607	0.0278
060	0.585	0.627	0.629	0.614	0.0249
076	0.611	0.604	0.589	0.601	0.0111
092	0.646	0.611	0.598	0.618	0.0095
108	0.582	0.580	0.643	0.602	0.0440
124	0.586	0.586	0.582	0.585	0.0022
140	0.630	0.624	0.648	0.634	0.0166
156	0.587	0.617	0.606	0.603	0.0082
172	0.647	0.563	0.592	0.600	0.0205
188	0.601	0.563	0.570	0.578	0.0049

M (mg/kg): **0.606**

SD_M (mg/kg): 0.0150

u_{bb} (% rel.): 1.180

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Pb**

(1) Sample intake: 2.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	36.73	37.89	34.84	36.49	1.540
028	36.29	36.45	35.32	36.02	0.615
044	35.48	32.93	36.13	34.85	1.691
060	36.22	35.82	37.49	36.51	0.872
076	37.14	34.86	36.73	36.24	1.213
092	35.50	35.89	34.06	35.15	1.300
108	35.31	35.20	38.33	36.28	2.211
124	35.72	35.72	35.79	35.74	0.054
140	34.88	38.08	37.25	36.74	0.584
156	34.61	35.18	33.93	34.57	0.884
172	35.39	36.16	34.98	35.51	0.836
188	36.03	37.95	35.53	36.50	1.712

M (mg/kg): **35.88**

SD_M (mg/kg): 0.718

u_{bb} (% rel.): 1.031

(acc. to ISO Guide 35)

(2) Sample intake: 0.5 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	39.77	39.68	38.34	39.26	0.802
028	39.15	38.79	32.12	36.69	3.962
044	36.88	33.68	38.44	36.33	2.430
060	34.02	40.80	38.43	37.75	3.443
076	35.66	33.78	30.61	33.35	2.554
092	38.47	33.82	37.96	36.75	2.925
108	34.39	32.60	37.81	34.93	3.683
124	33.06	35.62	36.36	35.01	0.522
140	35.60	37.35	37.42	36.79	0.056
156	34.00	33.58	30.51	32.69	2.171
172	38.47	36.22	34.49	36.39	1.230
188	33.33	32.67	34.70	33.56	1.436

M (mg/kg): **35.79**

SD_M (mg/kg): 1.933

u_{bb} (% rel.): 3.830

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **PCP**

Sample intake: 4.0 g Analytical method: GC-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	7.502	6.799	7.620	7.307	0.4437
028	7.014	6.833	7.315	7.054	0.2432
044	6.889	7.771	8.143	7.601	0.6437
060	7.744	7.164	7.333	7.414	0.2983
076	7.460	8.006	6.777	7.414	0.6154
092	7.178	7.677	6.974	7.276	0.4976
108	7.180	6.966	6.920	7.022	0.0321
124	6.466	7.902	6.997	7.122	0.6397
140	7.716	7.455	7.952	7.708	0.3513
156	6.840	7.212	7.083	7.045	0.0914
172	7.601	7.249	8.090	7.647	0.5942
188	7.709	6.917	6.497	7.041	0.2967

M (mg/kg): **7.304**

SD_M (mg/kg): 0.2532

u_{bb} (% rel.): 1.927

(acc. to ISO Guide 35)

Stability study (measurement results) **As**

Sample intake: 2.0 g Analytical method: ICP-MS

Sample I.D.	Storage conditions	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
160	-20 °C	3.055	3.468	3.335	3.286	0.2109
161	-20 °C	3.003	2.944	3.381	3.109	0.2370
166	4 °C, 1 month	3.055	3.092	3.085	3.077	0.0195
167	4 °C, 3 months	3.307	3.258	3.483	3.349	0.1186
168	4 °C, 6 months	3.137	3.439	3.003	3.193	0.2234
169	4 °C, 12 months	3.292	3.313	2.995	3.200	0.1777
173	23 °C, 1 month	2.833	3.330	2.609	2.924	0.3691
174	23 °C, 3 months	3.761	3.282	3.539	3.527	0.2399
175	23 °C, 6 months	3.001	3.267	3.072	3.113	0.1376
176	23 °C, 12 months	3.181	2.832	3.581	3.198	0.3748
179	40 °C, 1 month	3.197	3.144	3.550	3.297	0.2207
180	40 °C, 3 months	3.562	3.214	2.625	3.134	0.4736
181	40 °C, 6 months	3.322	3.131	3.237	3.230	0.0957
182	40 °C, 12 months	3.044	3.219	3.087	3.117	0.0909
183	60 °C, 1 month	3.499	3.030	3.654	3.394	0.3246
184	60 °C, 3 months	3.255	2.985	2.737	2.993	0.2590

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.0985	0.9624 ± 0.0673	1.0474 ± 0.0818	0.9985 ± 0.0986	1.0007 ± 0.0892
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.0985	0.9144 ± 0.1318	1.1031 ± 0.1074	0.9736 ± 0.0803	1.0001 ± 0.1364
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.0985	1.0311 ± 0.0996	0.9800 ± 0.1631	1.0101 ± 0.0765	0.9747 ± 0.0737
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.0985	1.0615 ± 0.1257	0.9358 ± 0.1040		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0036
R(+23 °C)	No	No	0.0081
R(+40 °C)	No	No	0.0022
R(+60 °C)	No	No	0.0308

Stability study (measurement results) **Cd**

Sample intake: 2.0 g Analytical method: ICP-MS

Sample I.D.	Storage conditions	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
160	-20 °C	2.730	2.574	2.706	2.670	0.0840
161	-20 °C	2.597	2.710	2.743	2.683	0.0763
166	4 °C, 1 month	2.703	2.879	2.731	2.771	0.0945
167	4 °C, 3 months	2.549	2.537	2.686	2.591	0.0825
168	4 °C, 6 months	2.824	2.738	2.779	2.780	0.0431
169	4 °C, 12 months	2.754	3.015	2.550	2.773	0.2331
173	23 °C, 1 month	2.821	2.872	2.749	2.814	0.0622
174	23 °C, 3 months	2.814	2.885	3.029	2.909	0.1099
175	23 °C, 6 months	2.878	2.750	2.744	2.791	0.0760
176	23 °C, 12 months	2.664	2.765	2.752	2.727	0.0552
179	40 °C, 1 month	2.937	2.844	2.604	2.795	0.1718
180	40 °C, 3 months	2.755	2.782	3.057	2.865	0.1669
181	40 °C, 6 months	2.734	2.628	2.670	2.677	0.0536
182	40 °C, 12 months	2.698	2.886	2.586	2.723	0.1520
183	60 °C, 1 month	2.812	2.870	2.828	2.837	0.0303
184	60 °C, 3 months	2.646	2.857	3.029	2.844	0.1917

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.0382	1.0352 ± 0.0450	0.9679 ± 0.0405	1.0387 ± 0.0323	1.0360 ± 0.0915
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.0382	1.0513 ± 0.0366	1.0869 ± 0.0504	1.0426 ± 0.0399	1.0188 ± 0.0343
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.0382	1.0442 ± 0.0701	1.0702 ± 0.0688	1.0002 ± 0.0336	1.0174 ± 0.0629
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.0382	1.0598 ± 0.0307	1.0625 ± 0.0772		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0033
R(+23 °C)	No	No	0.0039
R(+40 °C)	No	No	0.0036
R(+60 °C)	No	No	0.0145

Stability study (measurement results) **Cr**

Sample intake: 2.0 g Analytical method: ICP-MS

Sample I.D.	**Storage conditions**	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
160	-20 °C	33.78	37.14	33.39	34.77	2.060
161	-20 °C	33.36	35.06	35.79	34.74	1.249
166	4 °C, 1 month	29.74	32.77	30.99	31.17	1.525
167	4 °C, 3 months	36.33	32.67	36.00	35.00	2.028
168	4 °C, 6 months	35.88	35.27	33.21	34.79	1.404
169	4 °C, 12 months	34.06	34.21	34.27	34.18	0.106
173	23 °C, 1 month	31.13	33.55	35.09	33.25	1.996
174	23 °C, 3 months	34.21	31.04	37.29	34.18	3.124
175	23 °C, 6 months	35.75	36.19	37.36	36.44	0.832
176	23 °C, 12 months	33.05	32.33	34.47	33.29	1.089
179	40 °C, 1 month	32.87	36.04	36.23	35.05	1.886
180	40 °C, 3 months	35.57	34.35	32.88	34.27	1.343
181	40 °C, 6 months	36.28	33.84	34.96	35.02	1.226
182	40 °C, 12 months	31.59	34.12	32.40	32.70	1.295
183	60 °C, 1 month	33.57	34.78	39.02	35.79	2.861
184	60 °C, 3 months	36.04	31.82	33.38	33.75	2.134

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.0620	0.8968 ± 0.0589	1.0071 ± 0.0731	1.0010 ± 0.0596	0.9835 ± 0.0432
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.0620	0.9569 ± 0.0711	0.9835 ± 0.0997	1.0483 ± 0.0518	0.9577 ± 0.0524
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.0620	1.0084 ± 0.0700	0.9860 ± 0.0581	1.0079 ± 0.0565	0.9410 ± 0.0555
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.0620	1.0298 ± 0.0939	0.9710 ± 0.0747		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0053
R(+23 °C)	No	No	0.0045
R(+40 °C)	No	No	0.0019
R(+60 °C)	No	No	0.0147

Stability study (measurement results) **Cu**

Sample intake: 2.0 g Analytical method: ICP-MS

Sample I.D.	**Storage conditions**	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
160	-20 °C	21.88	22.88	21.33	22.03	0.789
161	-20 °C	21.00	22.20	22.33	21.84	0.733
166	4 °C, 1 month	19.00	21.02	19.41	19.81	1.067
167	4 °C, 3 months	22.29	20.76	22.04	21.70	0.822
168	4 °C, 6 months	22.29	20.76	22.04	21.70	0.822
169	4 °C, 12 months	21.38	21.71	21.29	21.46	0.225
173	23 °C, 1 month	19.89	21.27	21.32	20.83	0.815
174	23 °C, 3 months	21.50	20.79	23.58	21.95	1.451
175	23 °C, 6 months	21.75	22.12	22.69	22.19	0.475
176	23 °C, 12 months	20.83	20.30	21.29	20.81	0.492
179	40 °C, 1 month	20.90	22.17	22.39	21.82	0.808
180	40 °C, 3 months	22.00	21.27	20.12	21.13	0.945
181	40 °C, 6 months	22.20	21.15	21.60	21.65	0.524
182	40 °C, 12 months	20.53	21.41	19.75	20.56	0.828
183	60 °C, 1 month	21.20	22.04	21.92	21.72	0.454
184	60 °C, 3 months	23.13	20.39	20.65	21.39	1.512

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.0443	0.9031 ± 0.0563	0.9891 ± 0.0486	0.9891 ± 0.0486	0.9783 ± 0.0323
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.0443	0.9494 ± 0.0475	1.0009 ± 0.0732	1.0114 ± 0.0383	0.9485 ± 0.0373
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.0443	0.9947 ± 0.0481	0.9632 ± 0.0527	0.9869 ± 0.0392	0.9374 ± 0.0479
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.0443	0.9901 ± 0.0373	0.9751 ± 0.0754		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0046
R(+23 °C)	No	No	0.0034
R(+40 °C)	No	No	0.0016
R(+60 °C)	No	No	0.0006

Stability study (measurement results) **Hg**

Sample intake: 2.0 g Analytical method: ICP-MS

Sample I.D.	**Storage conditions**	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
160	-20 °C	0.6235	0.5504	0.5847	0.5862	0.03655
161	-20 °C	0.5574	0.5777	0.5838	0.5730	0.01383
166	4 °C, 1 month	0.6422	0.5995	0.5815	0.6077	0.03118
167	4 °C, 3 months	0.5261	0.5505	0.5489	0.5418	0.01366
168	4 °C, 6 months	0.5879	0.5837	0.6043	0.5920	0.01086
169	4 °C, 12 months	0.6231	0.5919	0.5293	0.5814	0.04774
173	23 °C, 1 month	0.5894	0.5975	0.5741	0.5870	0.01186
174	23 °C, 3 months	0.5850	0.5962	0.6072	0.5961	0.01110
175	23 °C, 6 months	0.6025	0.5715	0.5632	0.5791	0.02070
176	23 °C, 12 months	0.5881	0.5983	0.5873	0.5913	0.00611
179	40 °C, 1 month	0.5867	0.5943	0.5631	0.5814	0.01625
180	40 °C, 3 months	0.5841	0.5689	0.6102	0.5878	0.02091
181	40 °C, 6 months	0.5656	0.5702	0.5660	0.5672	0.00255
182	40 °C, 12 months	0.5694	0.5858	0.5579	0.5710	0.01405
183	60 °C, 1 month	0.5919	0.5985	0.5943	0.5949	0.00332
184	60 °C, 3 months	0.5999	0.5965	0.6066	0.6010	0.00514

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.0629	1.0486 ± 0.0712	0.9349 ± 0.0478	1.0214 ± 0.0491	1.0032 ± 0.0937
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.0629	1.0128 ± 0.0495	1.0286 ± 0.0496	1.0201 ± 0.0466	1.0001 ± 0.1364
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.0629	1.0031 ± 0.0527	1.0141 ± 0.0577	0.9788 ± 0.0437	0.9853 ± 0.0500
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.0629	1.0264 ± 0.0460	1.0370 ± 0.0470		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0050
R(+23 °C)	No	No	0.0015
R(+40 °C)	No	No	0.0013
R(+60 °C)	No	No	0.0052

Stability study (measurement results) **Pb**

Sample intake: 2.0 g Analytical method: ICP-MS

Sample I.D.	**Storage conditions**	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
160	-20 °C	36.79	34.30	35.81	35.63	1.252
161	-20 °C	34.56	35.48	38.57	36.20	2.098
166	4 °C, 1 month	34.87	37.47	36.30	36.21	1.299
167	4 °C, 3 months	34.08	35.47	36.65	35.40	1.287
168	4 °C, 6 months	37.73	37.03	36.29	37.02	0.721
169	4 °C, 12 months	34.09	39.86	35.53	36.49	3.002
173	23 °C, 1 month	35.74	37.85	36.18	36.59	1.110
174	23 °C, 3 months	36.32	37.56	37.83	37.24	0.802
175	23 °C, 6 months	36.96	35.21	34.63	35.60	1.209
176	23 °C, 12 months	34.46	35.18	37.22	35.62	1.432
179	40 °C, 1 month	36.25	37.00	35.04	36.10	0.990
180	40 °C, 3 months	34.78	36.91	39.84	37.18	2.538
181	40 °C, 6 months	38.67	34.70	35.64	36.34	2.077
182	40 °C, 12 months	35.58	38.58	33.98	36.04	2.336
183	60 °C, 1 month	35.20	37.96	37.40	36.85	1.458
184	60 °C, 3 months	35.10	35.88	39.13	36.71	2.140

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.0622	1.0082 ± 0.0572	0.9856 ± 0.0562	1.0306 ± 0.0495	1.0160 ± 0.0948
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.0622	1.0187 ± 0.0545	1.0367 ± 0.0508	0.9911 ± 0.0551	0.9917 ± 0.0591
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.0622	1.0050 ± 0.0520	1.0350 ± 0.0841	1.0116 ± 0.0729	1.0036 ± 0.0786
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.0622	1.0260 ± 0.0607	1.0219 ± 0.0746		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0018
R(+23 °C)	No	No	0.0020
R(+40 °C)	No	No	0.0017
R(+60 °C)	No	No	0.0070

Stability study (measurement results) **PCP**

Sample intake: 4.0 g Analytical method: GC-MS

Sample I.D.	**Storage conditions**	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
160	-20 °C	6.995	6.361	7.348	6.901	0.5003
161	-20 °C	5.992	6.892	7.169	6.684	0.6159
166	4 °C, 1 month	7.540	7.677	7.649	7.622	0.0725
167	4 °C, 3 months	7.833	7.995	7.618	7.815	0.1893
168	4 °C, 6 months	8.327	7.662	7.660	7.883	0.3849
169	4 °C, 12 months	7.409	8.259	7.884	7.850	0.4261
173	23 °C, 1 month	7.598	7.817	8.361	7.926	0.3929
174	23 °C, 3 months	7.932	7.216	6.712	7.287	0.6131
175	23 °C, 6 months	7.160	8.391	8.241	7.930	0.6715
176	23 °C, 12 months	7.610	7.631	7.765	7.669	0.0844
179	40 °C, 1 month	7.508	7.266	7.748	7.507	0.2411
180	40 °C, 3 months	7.821	7.929	7.116	7.622	0.4413
181	40 °C, 6 months	7.572	7.981	7.432	7.662	0.2855
182	40 °C, 12 months	7.813	7.908	7.690	7.804	0.1091
183	60 °C, 1 month	7.864	8.218	8.405	8.162	0.2748
184	60 °C, 3 months	8.029	8.123	7.554	7.902	0.3052

Ratio of means table:

	Storage time (months)				
	0	1	3	6	12
R(+4 °C) ± u(+4 °C)	1.0000 ± 0.1073	1.1221 ± 0.0858	1.1505 ± 0.0916	1.1605 ± 0.1047	1.1557 ± 0.1078
R(+23 °C) ± u(+23 °C)	1.0000 ± 0.1073	1.1667 ± 0.1057	1.0727 ± 0.1215	1.1675 ± 0.1328	1.1289 ± 0.0866
R(+40 °C) ± u(+40 °C)	1.0000 ± 0.1073	1.1052 ± 0.0911	1.1221 ± 0.1071	1.1279 ± 0.0953	1.1488 ± 0.0886
R(+60 °C) ± u(+60 °C)	1.0000 ± 0.1073	1.2016 ± 0.0997	1.1633 ± 0.0990		

Slope of the linear regression significantly different from zero?

	a = 99 %	a = 95 %	relative standard uncertainty of the slope
R(+4 °C)	No	No	0.0063
R(+23 °C)	No	No	0.0077
R(+40 °C)	No	No	0.0049
R(+60 °C)	No	No	0.0546