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Certification Report

Certified Reference Material ERM®-CC018

Trace elements in contaminated sandy soil

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Summary

This report describes the certification of a reference material for the determination of aqua regia extractable mass fractions of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn in a contaminated sandy soil.
The certified reference material ERM®-CC018 is intended for the verification of analytical results obtained by standardised procedures as well as for the validation of modified or new analytical methods.

The following mass fractions were certified:

Analyte	Aqua regia extractable mass fraction in mg/kg [1] (extraction according to ISO 11466)	
	Certified value [2]	Uncertainty [3]
Arsenic	22.9	± 1.3
Cadmium	5.4	± 0.5
Chromium	129	± 6
Cobalt	5.9	± 0.4
Copper	80	± 4
Lead	289	± 10
Mercury	1.38	± 0.06
Nickel	25.8	± 1.8
Vanadium	19.4	± 1.0
Zinc	313	± 13

[1] All results are corrected to the dry mass content of the material determined after drying to constant mass at (105 ± 2) °C.

[2] Unweighted mean value of the means of accepted sets of data obtained in different BAM working groups using different methods of determination. The certified values are traceable to the SI (Système International d'Unites) via calibration using substances with certified purity.

[3] Estimated expanded uncertainty *U* with a coverage factor *k* = 2.5, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008).

ERM®-CC018 is provided as a powder with particle sizes below 63 µm in a 100 mL screw-capped brown glass bottle containing (55 ± 1) g. The minimum amount of sample to be used for the determination of aqua regia extractable mass fractions of elements is 3 g (as prescribed by ISO 11466).

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

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1 Introduction

The determination of element contents of soils after extraction with aqua regia according to ISO 11466 [1] is a very common analytical task in the daily practice of testing laboratories involved in the assessment of environmental pollution. In many countries it is prescribed by legislation which also demands that the reliability of measurement results must be assured by appropriate quality control.
A very useful tool for internal quality assurance is the analysis of certified reference materials (CRM). However, in this context it is important to note that the used CRMs should match the matrix composition of the samples to be tested as close as possible. Given the wide variation of “real world” soils in terms of their mineral components, organic matter and anthropogenic contamination, there is a need for a wide range of different soil reference materials. Hence, ERM®-CC018 was certified to complement available offers of appropriate CRMs for inorganic soil analysis.

2 Candidate material

The starting material for preparing ERM®-CC018 was a sandy soil collected from a stockpile excavated during a remediation campaign on an industrial wasteland in the Berlin region (Germany). The raw material was dried at ambient air to constant mass and afterwards the fraction passing a 2 mm screen was ground in a ball mill (with grinding bowls and balls made of zirconia) completely to particle sizes below 63 µm. Homogenisation and bottling of the ground material was performed using a spinning riffler according to the so-called “cross-riffling scheme” [2]. A total of 256 bottles each containing (55 ± 1) g was produced in March 2009 and stored at (20 ± 3) °C.

3 Homogeneity study

10 bottles were chosen using a random sample picking scheme following the sequence of bottling. The selected units were analysed in duplicate each using sample intakes of 3 g and also of 0.5 g. For trace element determination the soil material was extracted

(a) with aqua regia according to ISO 11466 under reflux conditions using a sample intake of 3 g,
(b) with aqua regia (9 mL HCl + 3 mL HNO_3) using a closed vessel microwave system and a sample intake of 0.5 g.

Solutions obtained according to (a) or (b) were analysed under repeatability conditions after randomisation in one run with one calibration, respectively. All measurement results and used analytical methods are given in Annex 2.
The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budgets were calculated according to ISO Guide 35 using Eq. (1) and (2):

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

$$u^*_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

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

s_{bb} signifies the between-bottle standard deviation, whereas u^*_{bb} denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). In any case the larger of the two values was used as u_{bb}. Eq. (1) does not apply if MS_{within} is larger than MS_{among}.
The calculated relative values of s_{bb}, u^*_{bb}, and u_{bb} referring to the different sample intakes are given in the following table.

Table 1: Relative uncertainty contributions $s_{bb,r}$, $u^*_{bb,r}$, and $u_{bb,r}$

Analyte	Sample intake 3 g (a)			Sample intake 0.5 g (b)		
	$s_{bb,r}$ (%)	$u^*_{bb,r}$ (%)	$u_{bb,r}$ (%)	$s_{bb,r}$ (%)	$u^*_{bb,r}$ (%)	$u_{bb,r}$ (%)
Arsenic	0.81	0.77	0.81	$MS_{among} < MS_{within}$	1.54	1.54
Cadmium	$MS_{among} < MS_{within}$	0.62	0.62	$MS_{among} < MS_{within}$	1.51	1.51
Chromium	$MS_{among} < MS_{within}$	0.26	0.26	$MS_{among} < MS_{within}$	1.44	1.44
Cobalt	1.04	0.59	1.04	$MS_{among} < MS_{within}$	1.23	1.23
Copper	$MS_{among} < MS_{within}$	0.37	0.37	$MS_{among} < MS_{within}$	1.30	1.30
Lead	$MS_{among} < MS_{within}$	0.43	0.43	$MS_{among} < MS_{within}$	1.26	1.26
Mercury	1.03	0.80	1.03	$MS_{among} < MS_{within}$	2.94	2.94
Nickel	0.53	0.81	0.81	$MS_{among} < MS_{within}$	1.35	1.35
Vanadium	0.43	0.50	0.50	0.38	1.31	1.31
Zinc	$MS_{among} < MS_{within}$	0.16	0.16	$MS_{among} < MS_{within}$	1.52	1.52

As could be expected, larger $u_{bb,r}$ values were obtained for all analytes when the smaller sample intake was used for extraction. Nevertheless, taking into account the analytical protocol prescribed by ISO 11466, the uncertainty contributions u_{bb} which were included in the calculation of the expanded uncertainties of the certified mass fractions refer to a sample intake of 3 g.

4 Stability study

Based on many years of experience gained at BAM with reference materials for inorganic soil analysis it is very unlikely that aqua regia extractable mass fractions of elements will change if the samples are stored and handled properly. For this reason only a reduced stability check of the bottled material was performed.
Immediately after bottling selected units were stored at temperatures of -20 °C, +20 °C and +40 °C, respectively. After a storage time of 12 months two bottles per temperature were analysed in duplicate for aqua regia extractable mass fractions applying extraction procedure (a). The extraction solutions were analysed under repeatability conditions in one run with one calibration. The measurement results (see Annex 3) were evaluated for each analyte calculating the ratios R_t (3) and their uncertainties u_t (4):

$$R_t = X_t \,/\, X_{-20\,°C} \qquad (3)$$

$$u_t = (CV_t^2 + CV_{-20\,°C}^2)^{1/2} * R_t \qquad (4)$$

where X_t and $X_{-20\,°C}$ are the mean values of four analyses of samples stored at temperature t (+20 °C or +40 °C) and of samples stored at the reference temperature -20 °C, respectively. CV_t and $CV_{-20\,°C}$ are the corresponding coefficients of variation.

If one postulates that aqua regia extractable mass fractions of samples stored at -20 °C do not change over time, in case of ideal sample stability at a higher storage temperature *t* the ratio R_t should be 1. In reality, however, unavoidable random variations of measurement results have to be taken into account. Thus, a material can be considered stable at storage temperature *t* if the value 1 is comprised between $R_t - u_t$ and $R_t + u_t$. This precondition is fulfilled for all analytes and storage temperatures under test.

Table 2: Results of the stability test after a storage time of 12 months

Analyte	$R_t \pm u_t$	
	Samples stored at 20 °C	Samples stored at 40 °C
Arsenic	0.9964 ± 0.0090	1.0016 ± 0.0092
Cadmium	1.0238 ± 0.0243	1.0206 ± 0.0227
Chromium	0.9961 ± 0.0061	1.0000 ± 0.0022
Cobalt	1.0065 ± 0.0215	1.0002 ± 0.0254
Copper	0.9975 ± 0.0115	1.0005 ± 0.0071
Lead	0.9997 ± 0.0133	1.0010 ± 0.0157
Mercury	1.0165 ± 0.0383	0.9935 ± 0.0116
Nickel	0.9996 ± 0.0206	0.9996 ± 0.0221
Vanadium	1.0125 ± 0.0271	1.0105 ± 0.0294
Zinc	1.0017 ± 0.0072	0.9973 ± 0.0061

As no trend and no statistically significant impact of storage conditions on the stability of the certified properties could be detected and taking into account the small uncertainties u_t, an expansion of the total uncertainty of the certified values by a long-term uncertainty contribution u_{lts} was not considered necessary.
Stability testing will be continued by further measurements of units stored at -20 °C, +20 °C and +40 °C over the period of availability of the material. Thus, the validity of the expiration date of one year after dispatch given in the certificate is maintained by post-certification measurements starting at BAM.

5 Certification study

5.1 Participants and used analytical methods

Three BAM working groups with a total of 12 independent operator/equipment combinations were involved in the characterisation of the candidate material. All of them are operating a quality management system accredited to ISO/IEC 17025 [4].

The following analytical methods were used:

- Cold-vapour atomic absorption spectrometry (CV AAS)
- Cold-vapour atomic fluorescence spectrometry (CV AFS)
- Electrothermal atomic absorption spectrometry (ET AAS)
- Flame atomic absorption spectrometry (F AAS)
- Hydride generation atomic absorption spectrometry (HG AAS)
- Inductively coupled plasma optical emission spectrometry (ICP OES)
- Inductively coupled plasma mass spectrometry (ICP-MS)
- Solid sampling advanced mercury analyzer (AMA)

As aqua regia extractable mass fractions of elements are operationally-defined parameters, extraction of the soil sample was performed strictly following the analytical protocol prescribed by ISO standard 11466 [1].

Each participating working group received two units of the bottled candidate material and had to analyse two independent sub-samples from each unit. In addition, the dry mass content of the material had to be determined on separate sub-samples by drying to constant mass at (105 ± 2) °C according to ISO 11465 [5]. All reported aqua regia extractable mass fraction were corrected to the dry mass content of the soil sample.

5.2 Statistical evaluation of results

The measurement results obtained with the different operator/equipment combinations (identified by a "WG & method code") are compiled in Annex 1. 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 using software SoftCRM version 1.2.2 [6]. The following tests were carried out:

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

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

Grubbs, Dixon and Nalimov tests: Outlying means?

Bartlett test: Variances homogeneous?

Snedecor F-test: Differences between data sets statistically significant?

Gauß (Kolmogorov-Smirnov-Lilliefors test): Normality of the distribution of the means?

The results of these tests are summarised in Table 4.

Table 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)
Arsenic	7	No	(-/-)	(-/-)	(-/-)	(-/-)
Cadmium	5	No	(-/-)	(-/-)	(-/-)	(-/-)
Chromium	6	No	(-/-)	(-/-)	(-/-)	(-/-)
Cobalt	5	No	(-/06)	(-/-)	(-/-)	(-/-)
Copper	5	No	(-/-)	(-/-)	(-/-)	(-/-)
Lead	6	No	(-/-)	(-/-)	(-/-)	(-/-)
Mercury	4	No	(-/-)	(-/-)	(-/-)	(-/-)
Nickel	6	No	(-/05)	(-/-)	(-/-)	(-/-)
Vanadium	6	No	(-/-)	(-/-)	(-/-)	(-/-)
Zinc	5	No	(-/-)	(-/-)	(-/-)	(-/-)

Table 4 (continued): Statistical tests carried out on participants' results

Analyte	Statistical tests			Consequence
	Bartlett (0.01/0.05)	Snedecor (0.01/0.05)	Gauß (0.01/0.05)	
Arsenic	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Cadmium	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Chromium	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Cobalt	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Copper	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Lead	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Mercury	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Nickel	Yes/No	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Vanadium	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Zinc	Yes/Yes	Yes/Yes	Yes/Yes	Pooling of individual data not allowed

As no technical reasons could be identified for "suspicious" data sets (none of them was flagged as a statistical outlier with a level of confidence of 99 %), all data sets were retained for further data processing.

6 Certified values and uncertainties

The unweighted means of accepted data set 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 (105 ± 2) °C. The standard deviations of the means of accepted data set means were taken as uncertainty contributions u_{char} resulting from the characterisation exercise. The different contributions to the overall uncertainties of the certified mass fractions were combined using the following equation:

$$u_{CRM} = \sqrt{u_{char}^2 + u_{bb}^2} \qquad (5)$$

Calculated aqua regia extractable mass fractions w_{char} and absolute values of the different uncertainty components are given in Table 5.

Table 5: Mass fractions and uncertainty components for the analytes in ERM®-CC018 (before rounding)

Analyte	w_{char} (mg/kg)	u_{char} (mg/kg)	u_{bb} (mg/kg)	u_{CRM} (mg/kg)
Arsenic	22.94	0.4842	0.1851	0.5184
Cadmium	5.378	0.1684	0.0332	0.1718
Chromium	129.1	2.3243	0.3357	2.3484
Cobalt	5.872	0.1408	0.0610	0.1534
Copper	80.21	1.5546	0.2936	1.5821
Lead	289.4	3.7036	1.2386	3.9052
Mercury	1.379	0.0158	0.0142	0.0212
Nickel	25.84	0.6681	0.2091	0.7001
Vanadium	19.42	0.3559	0.0971	0.3689
Zinc	313.3	4.8629	0.4856	4.8871

The expanded uncertainties U were obtained by multiplying the combined uncertainties u_{CRM} by a coverage factor k:

$$U = k \times u_{CRM} \qquad (6)$$

The value of the coverage factor k was chosen to give a level of confidence of approximately 95 % to be associated with the interval ± U around the certified values. For approximation of k the effective degrees of freedom ν_{eff} of the linear combinations of u_{char} and u_{bb} were calculated using the Welch-Satterthwaite formula (see [7], Annex G.4). The obtained values for ν_{eff} and the corresponding factors $t_{95}(\nu_{eff})$ taken from Student's distribution and giving a level of confidence of 95 % are listed in the following table.

Table 6: Effective degrees of freedom of u_{CRM} and corresponding factors $t_{95}(\nu_{eff})$

Analyte	ν_{eff}	$t_{95}(\nu_{eff})$
Arsenic	7.77	2.36
Cadmium	4.31	2.78
Chromium	5.21	2.57
Cobalt	5.56	2.57
Copper	4.29	2.78
Lead	6.14	2.45
Mercury	8.05	2.31
Nickel	6.00	2.57
Vanadium	5.74	2.57
Zinc	4.08	2.78

Because all factors $t_{95}(\nu_{eff})$ were well below 3 and most of them close to 2.5, a coverage factor k = 2.5 was chosen for all analytes to give the desired level of confidence of approximately 95 %.

The certified mass fractions and their corresponding expanded uncertainties were rounded according to DIN 1333 [8].

Table 7: Certified mass fractions and expanded uncertainties of analytes in ERM®-CC018 (after rounding)

Analyte	Aqua regia extractable mass fraction (mg/kg)
Arsenic	22.9 ± 1.3
Cadmium	5.4 ± 0.5
Chromium	129 ± 6
Cobalt	5.9 ± 0.4
Copper	80 ± 4
Lead	289 ± 10
Mercury	1.38 ± 0.06
Nickel	25.8 ± 1.8
Vanadium	19.4 ± 1.0
Zinc	313 ± 13

7 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.
However, due to the fact that an extraction step is necessary prior to the analytical determination it is important to note that the certified mass fractions of ERM®-CC018 are operationally defined referring to the analytical protocol prescribed by ISO 11466 [1].

8 Additional data

The main matrix constituents of the bottled material were determined by semi-quantitative X-ray fluorescence analysis giving the following non-certified results:

Element	Si	Al	Ca	Fe	K
Mass fraction in %	38.8	2.1	2.6	1.4	0.9

Further informative analytical results obtained in the course of sample characterisation:

Parameter	Mass fraction in %	Analytical method
Dry mass content at 105 °C	99.1	ISO 11465 [5]
Loss on ignition at 550 °C	4.6	EN 12879 [9]
Total organic carbon (TOC)	2.4	ISO 10694 [10]
Total inorganic carbon (TIC)	0.4	ISO 10694 [10]

pH values in water and $CaCl_2$ solution (acc. to ISO 10390 [11]): 7.6 and 7.5, respectively.

In October 2009 bottled units of the candidate material were used as test items in the course of a proficiency test (PT) organised for accredited German laboratories. Participants had to analyse the soil sample in duplicate for aqua regia extractable mass fractions. They were requested to follow the extraction procedure prescribed by ISO 11466 [1] but they were free in choosing analytical methods for the determination of the elements under test.
The PT results were evaluated using a robust method of data analysis according to DIN 38402-45 [12]. A summary is given in the following table:

Analyte	PT mean (mg/kg)	s_R in %	s_r in %	N
Arsenic	22.45	7.56	1.80	65
Cadmium	5.423	6.71	1.13	66
Chromium	129.7	5.31	1.46	66
Cobalt	5.977	12.75	1.62	57
Copper	80.35	5.19	1.24	66
Lead	286.9	6.73	1.38	66
Mercury	1.392	9.37	2.73	65
Nickel	25.96	7.71	2.83	66
Vanadium	18.94	8.85	2.16	52
Zinc	313.4	5.36	1.62	66

s_R relative reproducibility standard deviation of laboratory means

s_r relative repeatability standard deviation

N number of participating laboratories

The PT results agree within the respective uncertainties with those obtained in the course of the internal BAM certification exercise. Hence, they can be regarded as an additional confirmation of validity of the certified values.

9 Information on the proper use of ERM®-CC018

9.1 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.

9.2 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®-CC018.

On receiving, bottled material has to be stored at (20 ± 3) °C in the dark. 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. BAM cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

Analytical results have to be corrected to the dry mass content of the material which shall be determined according to ISO 11465 [5] using a separate sub-sample. The dry mass content of 99.1 % (see chapter “Additional data”) should be regarded as being indicative only.

9.3 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. 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.

9.4 Legal notice

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

10 References

[1] ISO 11466 (1995): Soil quality – Extraction of trace elements soluble in aqua regia

[2] A.M.H. van der Veen and D.A.G. Natter: Sample preparation from bulk samples: an overview, *Fuel Processing Technology*, 36 (1993) 1 - 7

[3] ISO Guide 35: Reference materials – General and statistical principles for certification Edition: 3, ISO/REMCO, Geneva 2006

[4] EN ISO/IEC 17025 (2005): General requirements for the competence of testing and calibration laboratories

[5] ISO 11465 (1993): Soil quality – Determination of dry matter and water content on a mass basis. Gravimetric method

[6] SoftCRM v. 1.2.2 (download: www.eie.gr/iopc/softcrm/index.html); for details see: G. Bonas, M. Zervou, T. Papaeoannou and M. Lees: "SoftCRM": a new software for the Certification of Reference Materials, *Accred Qual Assur* (2003) 8:101-107

[7] ISO/IEC Guide 98-3 (2008): Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement (GUM)

[8] DIN 1333 (1992): Zahlenangaben (*Presentation of numerical data*)

[9] EN 12879 (2000): Characterization of sludges – Determination of the loss on ignition of dry mass

[10] ISO 10694 (1995): Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis)

[11] ISO 10390 (2005): Soil quality – Determination of pH

[12] DIN 38402-45 (2003): Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Allgemeine Angaben (Gruppe A) – Teil 45: Ringversuche zur externen Qualitätskontrolle von Laboratorien (A 45)
(*German standard methods for the examination of water, waste water and sludge; General information (Group A) – Part 45: Interlaboratory comparisons for proficiency testing of laboratories (A 45)*)

11 Annexes

Annex 1: Certification study (measurement results of participants)

Annex 2: Homogeneity study (measurement results)

Annex 3: Stability study (measurement results)

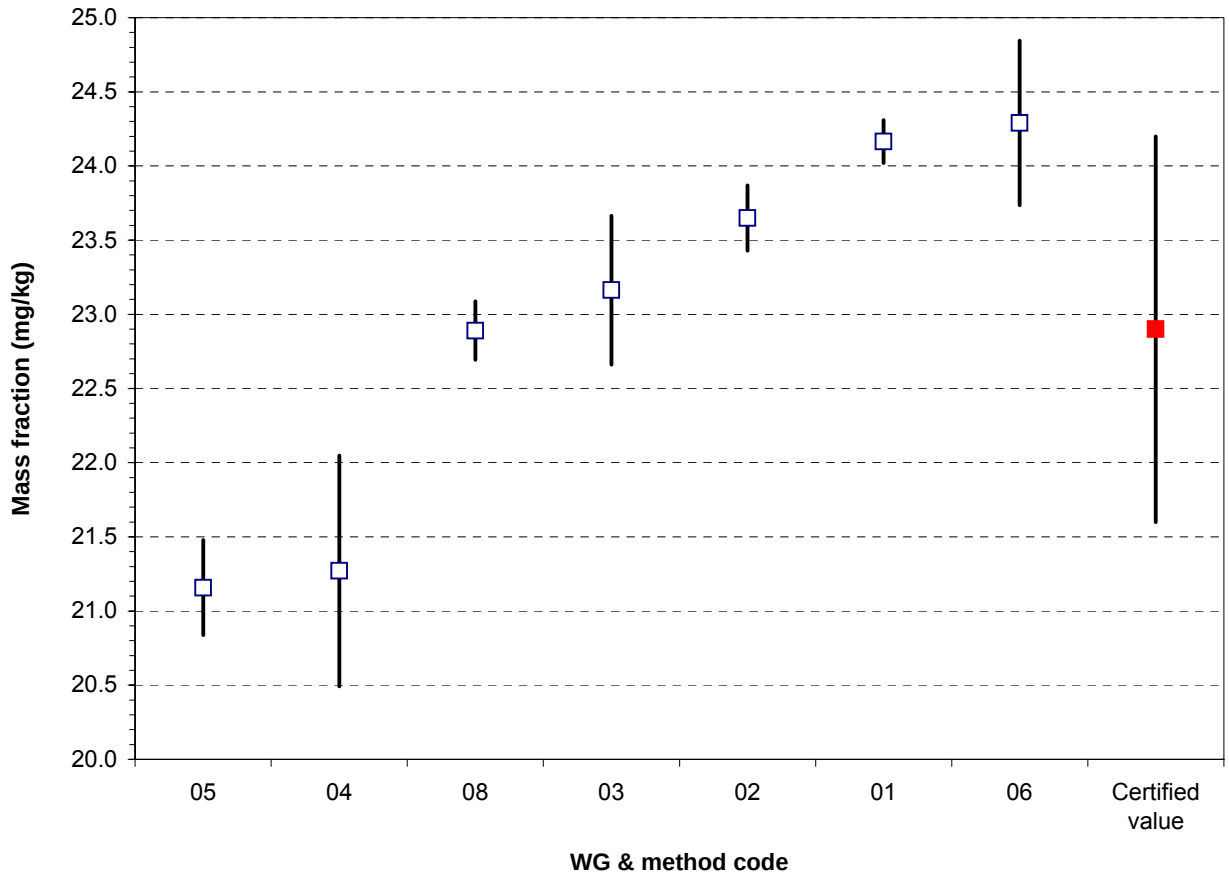
List of used abbreviations
(if not explained elsewhere in the report)

M arithmetic mean of means
N number of individual data sets
SD standard deviation of an individual data set
SD_M standard deviation of the mean of data set means

Certification study (measurement results of participants) **Arsenic**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
05	21.14	21.38	20.71	21.40	21.16	0.321	ICP OES
04	21.44	22.24	21.01	20.39	21.27	0.777	ET AAS
08	23.10	22.68	23.01	22.77	22.89	0.197	HG AAS
03	23.70	23.12	22.50	23.33	23.16	0.503	ICP OES
02	23.58	23.89	23.38	23.75	23.65	0.220	ICP OES
01	24.22	24.14	24.32	23.98	24.17	0.144	ICP-MS
06	24.51	24.96	23.73	23.96	24.29	0.554	ET AAS

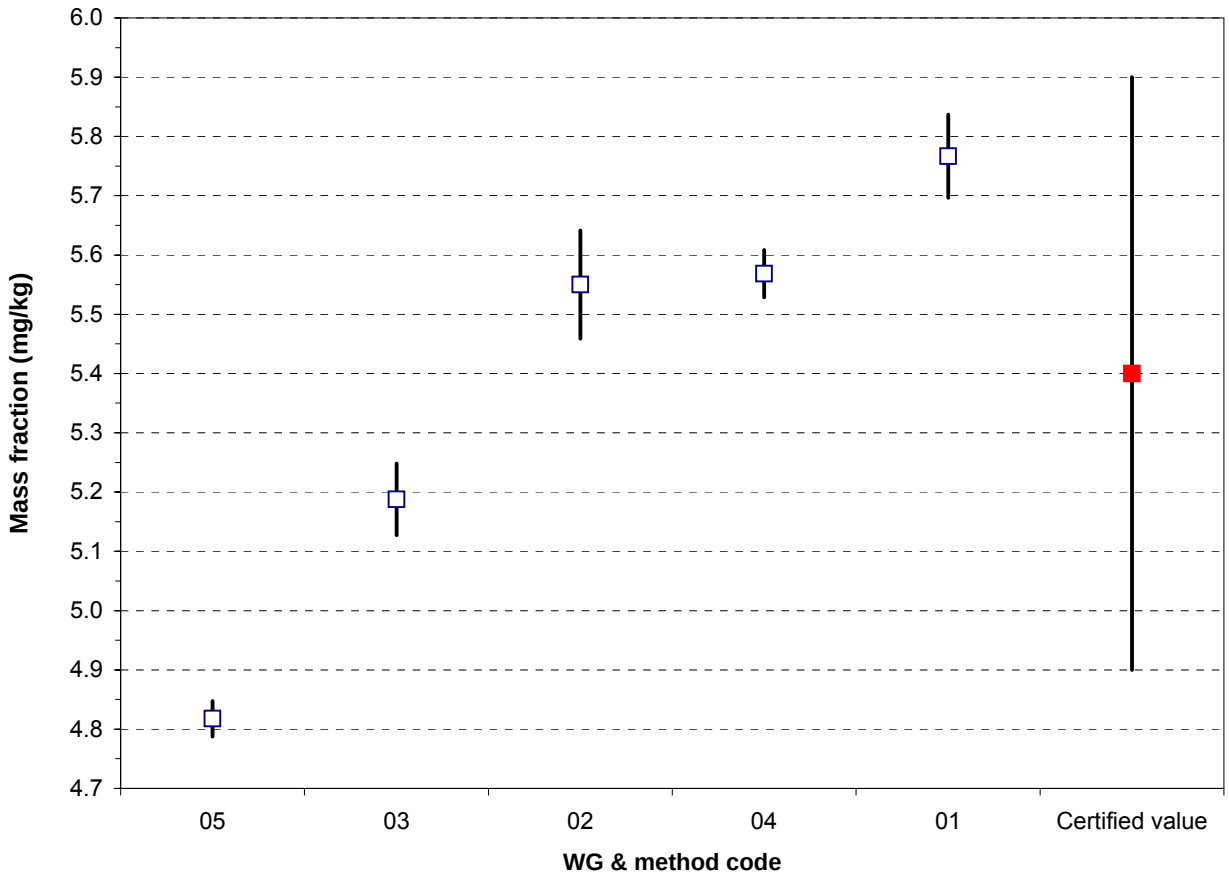
M (mg/kg):	**22.94**
SD_M (mg/kg):	1.281
$SD_M/\sqrt{N}$ (mg/kg):	0.4842



Certification study (measurement results of participants) **Cadmium**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
05	4.810	4.790	4.810	4.860	4.818	0.0299	ICP OES
03	5.166	5.183	5.130	5.272	5.188	0.0604	ICP OES
02	5.415	5.577	5.596	5.612	5.550	0.0911	ICP OES
04	5.520	5.618	5.569	5.567	5.569	0.0400	ET AAS
01	5.826	5.734	5.823	5.683	5.767	0.0701	ICP-MS

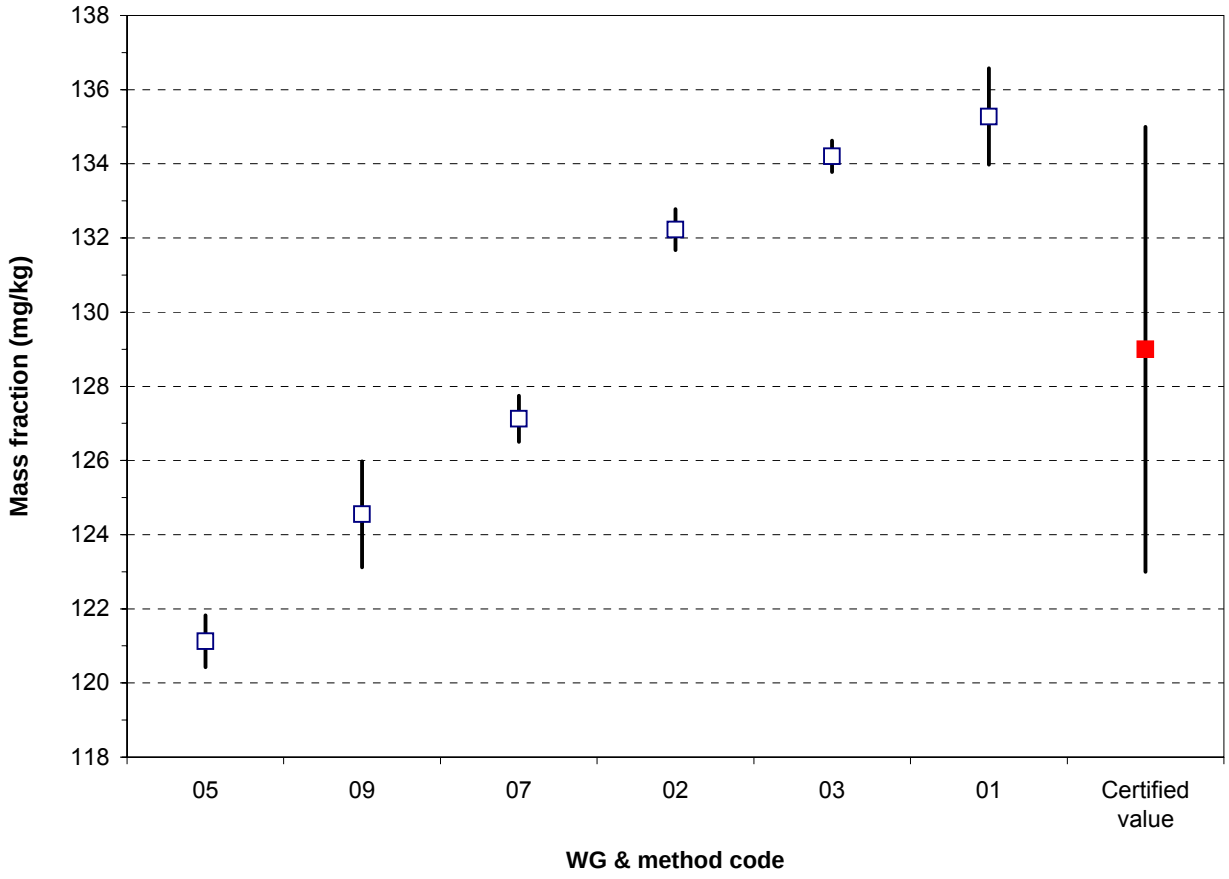
M (mg/kg):	**5.378**
SD_M (mg/kg):	0.3766
$SD_M/\sqrt{N}$ (mg/kg):	0.1684



Certification study (measurement results of participants) **Chromium**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
05	121.0	121.2	120.3	122.0	121.1	0.70	ICP OES
09	124.6	126.0	125.0	122.6	124.6	1.43	F AAS
07	127.8	127.1	126.3	127.3	127.1	0.62	F AAS
02	132.7	131.8	132.7	131.7	132.2	0.55	ICP OES
03	133.6	134.5	134.2	134.5	134.2	0.42	ICP OES
01	134.9	136.2	136.4	133.6	135.3	1.30	ICP-MS

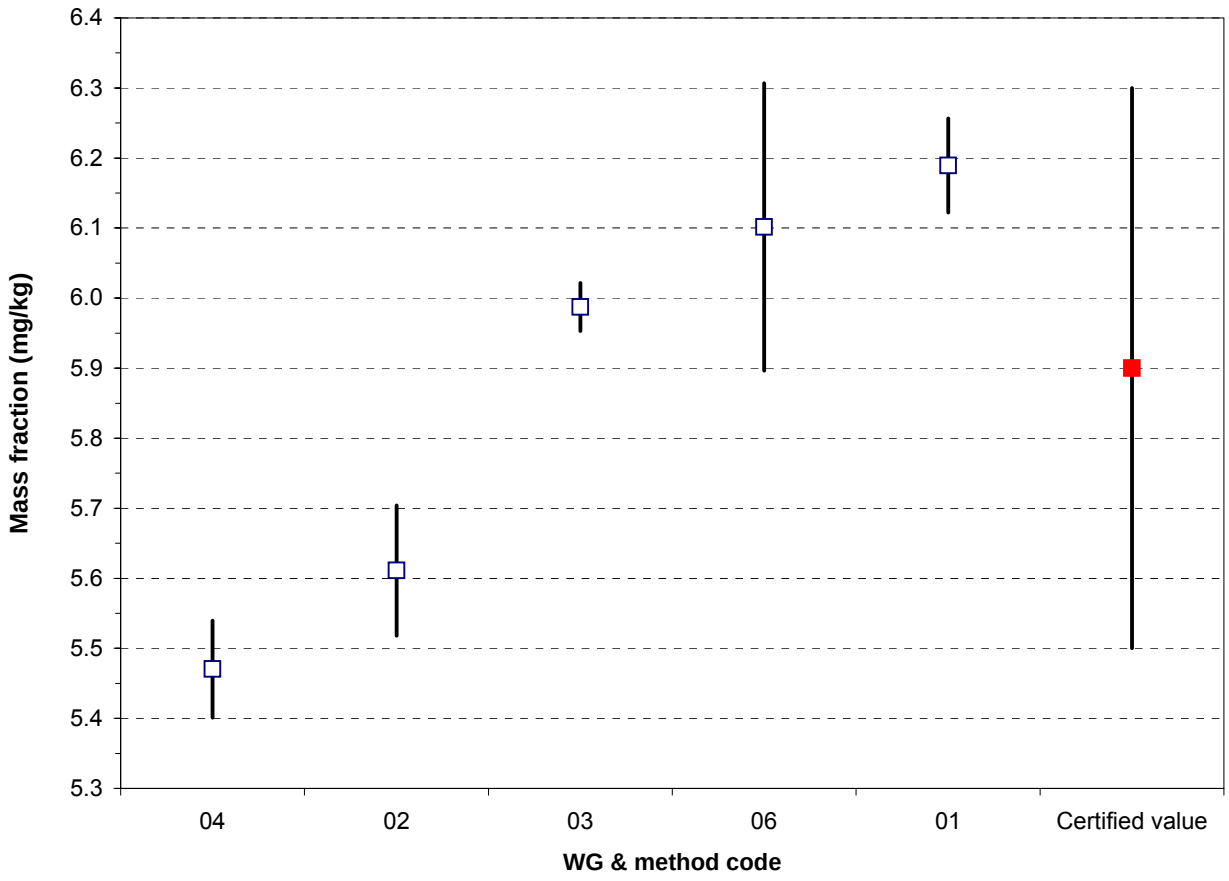
M (mg/kg):	**129.1**
SD_M (mg/kg):	5.69
$SD_M/\sqrt{N}$ (mg/kg):	2.3243



Certification study (measurement results of participants) **Cobalt**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
04	5.416	5.422	5.565	5.478	5.470	0.0691	ET AAS
02	5.643	5.533	5.540	5.728	5.611	0.0928	ICP OES
03	6.024	5.945	5.976	6.004	5.987	0.0344	ICP OES
06	6.056	6.269	6.251	5.830	6.102	0.2051	ET AAS
01	6.122	6.272	6.214	6.150	6.190	0.0671	ICP-MS

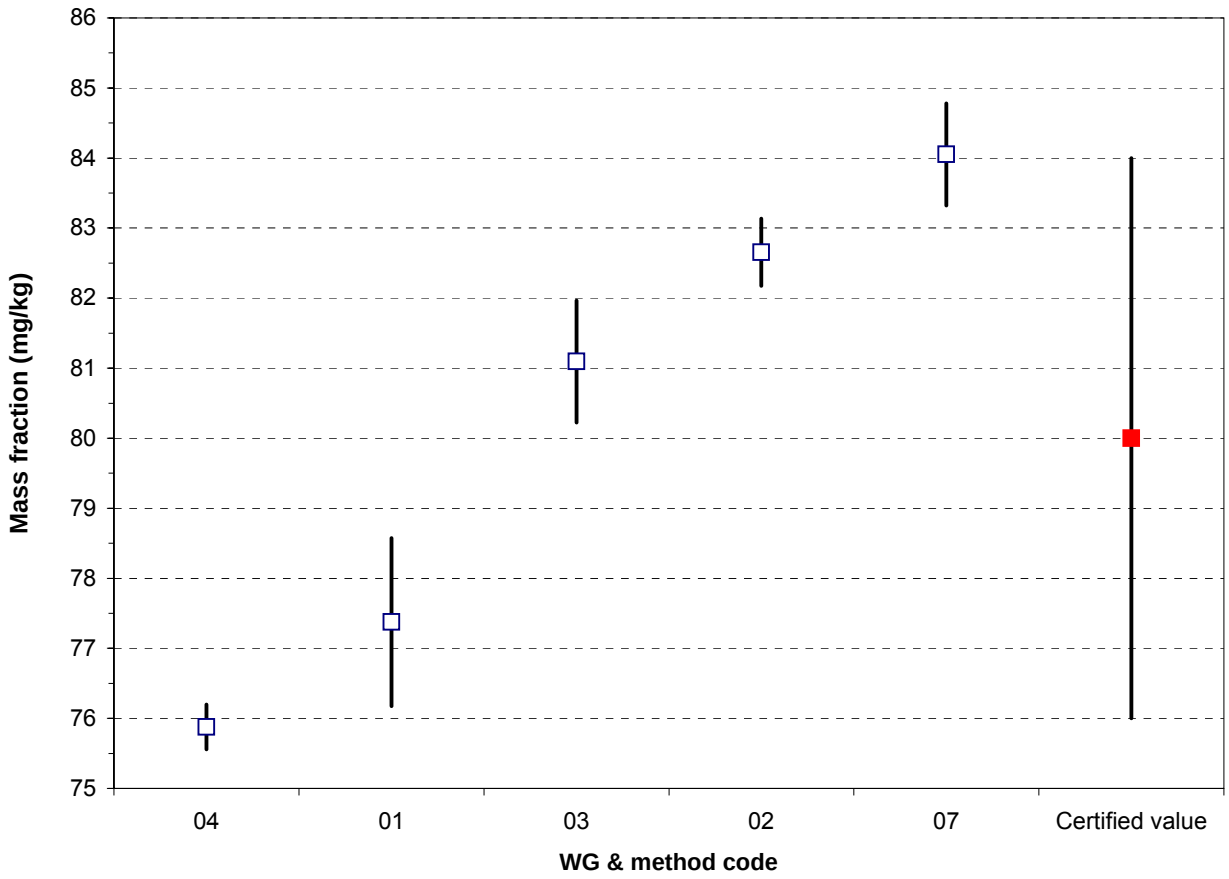
M (mg/kg):	**5.872**
SD_M (mg/kg):	0.3148
$SD_M/\sqrt{N}$ (mg/kg):	0.1408



Certification study (measurement results of participants) **Copper**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
04	75.83	75.70	75.64	76.34	75.88	0.318	ET AAS
01	77.34	78.92	77.25	75.99	77.38	1.200	ICP-MS
03	80.49	82.18	80.30	81.41	81.10	0.871	ICP OES
02	82.26	83.34	82.62	82.40	82.66	0.480	ICP OES
07	82.97	84.43	84.53	84.28	84.05	0.729	F AAS

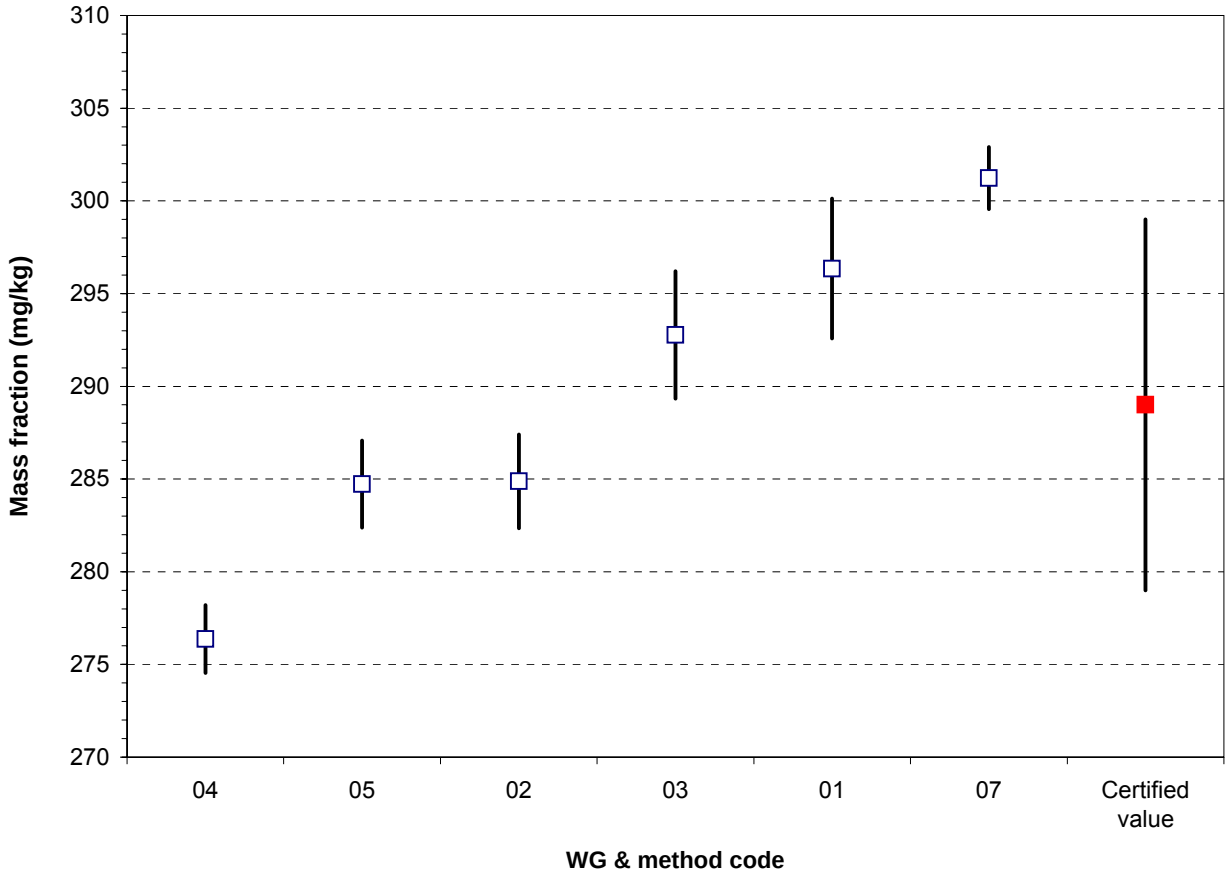
M (mg/kg):	**80.21**
SD_M (mg/kg):	3.476
$SD_M/\sqrt{N}$ (mg/kg):	1.5546



Certification study (measurement results of participants) **Lead**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
04	278.5	277.3	274.7	275.0	276.4	1.83	ET AAS
05	287.7	283.4	282.4	285.4	284.7	2.34	ICP OES
02	282.0	286.1	287.7	283.7	284.9	2.53	ICP OES
03	294.4	288.6	291.6	296.5	292.8	3.43	ICP OES
01	298.1	300.6	294.7	292.0	296.4	3.78	ICP-MS
07	301.2	303.6	300.1	300.0	301.2	1.67	F AAS

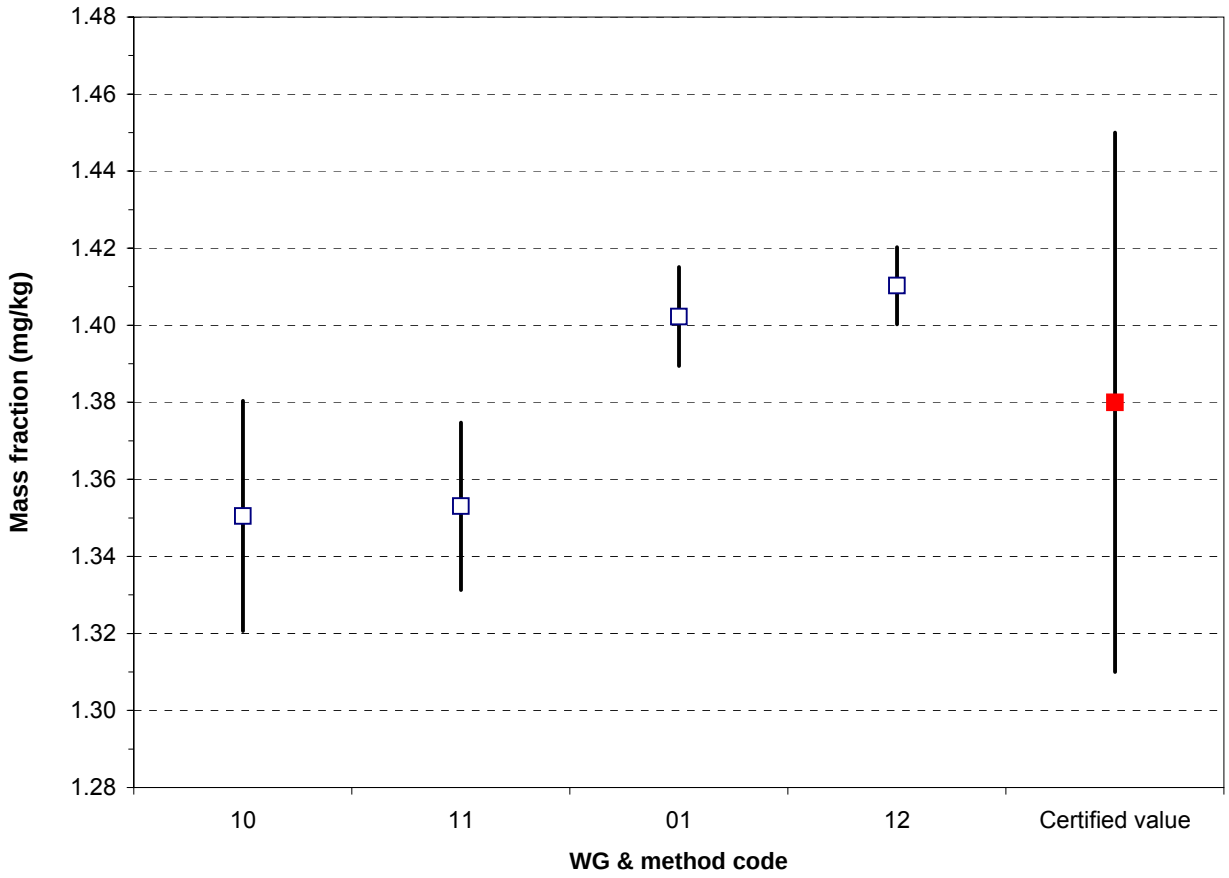
M (mg/kg):	**289.4**
SD_M (mg/kg):	9.07
$SD_M/\sqrt{N}$ (mg/kg):	3.7036



Certification study (measurement results of participants) **Mercury**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
10	1.349	1.368	1.376	1.309	1.351	0.0299	CV AAS
11	1.332	1.382	1.342	1.356	1.353	0.0217	CV AFS
01	1.423	1.410	1.386	1.390	1.402	0.0129	ICP-MS
12	1.395	1.423	1.404	1.419	1.410	0.0100	AMA

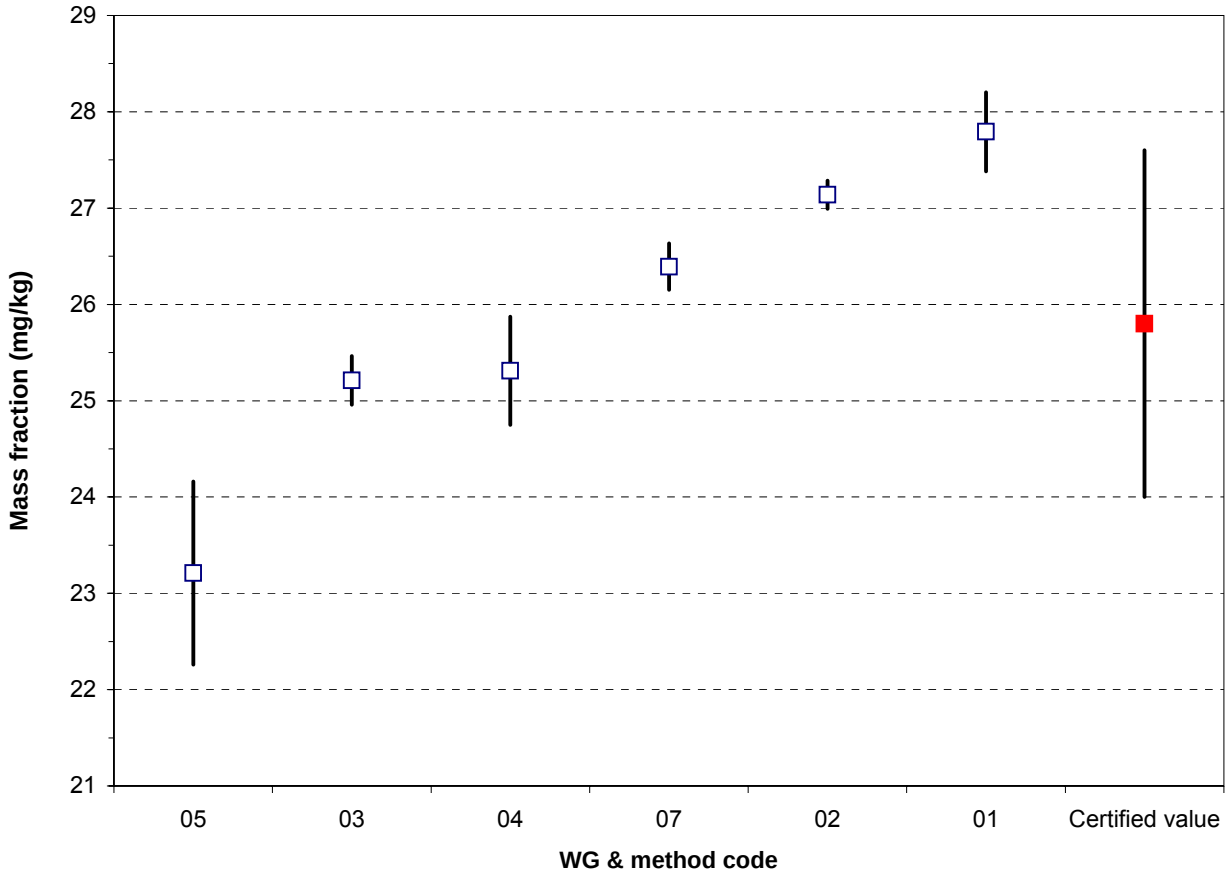
M (mg/kg):	**1.379**
SD_M (mg/kg):	0.0317
$SD_M/\sqrt{N}$ (mg/kg):	0.0158



Certification study (measurement results of participants) **Nickel**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
05	24.58	23.08	22.44	22.74	23.21	0.950	ICP OES
03	25.18	25.57	25.12	24.98	25.21	0.253	ICP OES
04	25.29	24.72	26.07	25.16	25.31	0.562	ET AAS
07	26.26	26.59	26.60	26.12	26.39	0.241	F AAS
02	27.24	27.20	27.19	26.92	27.14	0.147	ICP OES
01	27.22	27.77	28.12	28.06	27.79	0.411	ICP-MS

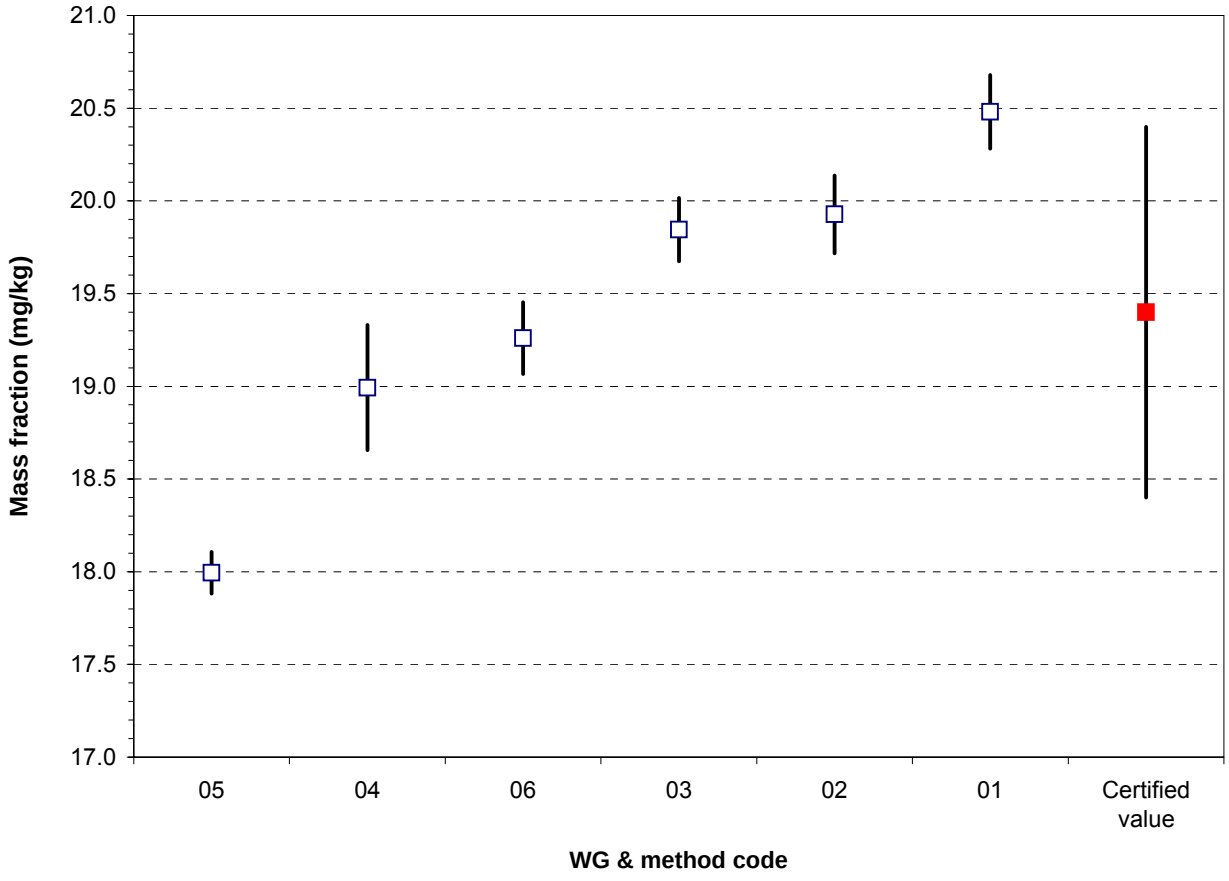
M (mg/kg):	**25.84**
SD_M (mg/kg):	1.637
$SD_M/\sqrt{N}$ (mg/kg):	0.6681



Certification study (measurement results of participants) **Vanadium**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
05	18.06	18.02	17.83	18.07	18.00	0.112	ICP OES
04	18.99	18.73	19.47	18.78	18.99	0.338	ET AAS
06	19.54	19.14	19.12	19.24	19.26	0.194	ET AAS
03	19.80	20.06	19.65	19.87	19.85	0.170	ICP OES
02	19.98	19.73	20.20	19.80	19.93	0.210	ICP OES
01	20.72	20.52	20.24	20.44	20.48	0.199	ICP-MS

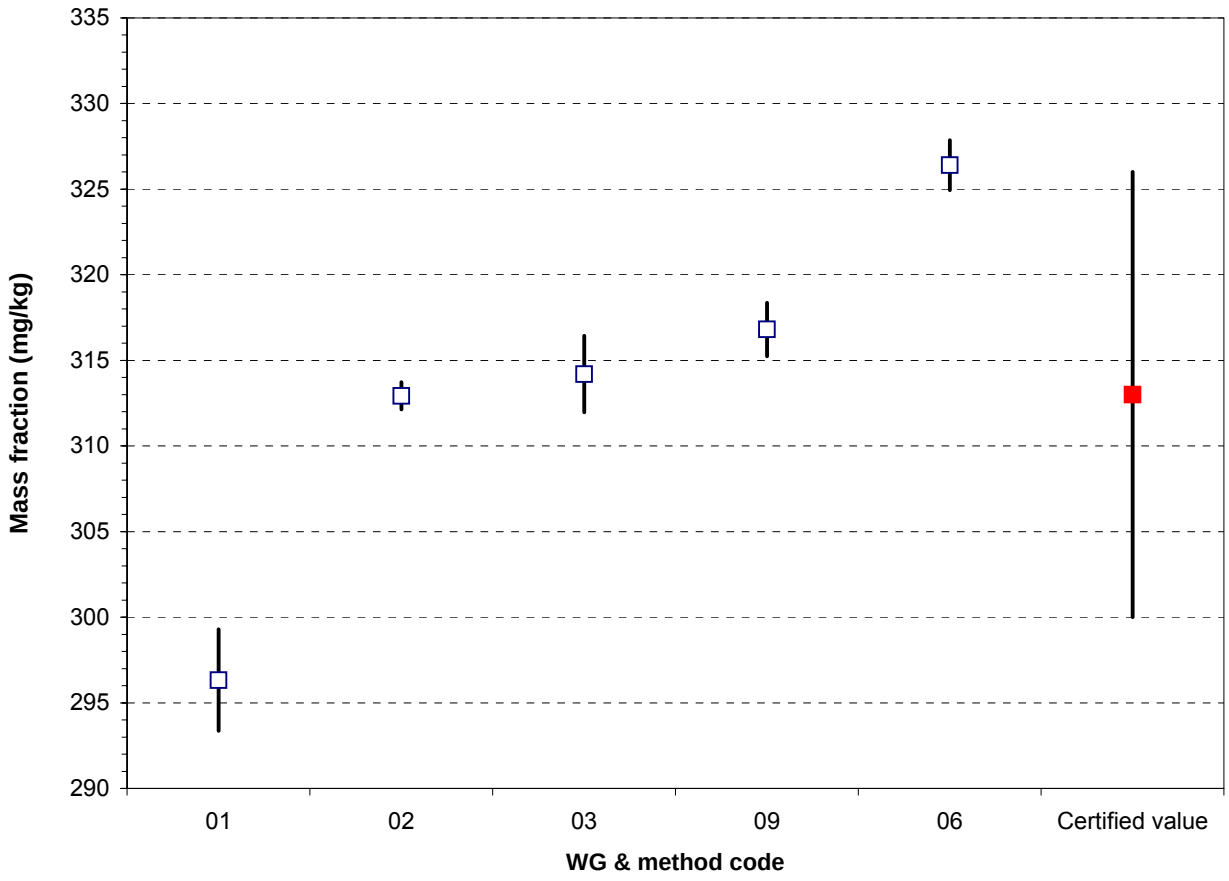
M (mg/kg):	**19.42**
SD_M (mg/kg):	0.872
$SD_M/\sqrt{N}$ (mg/kg):	0.3559



Certification study (measurement results of participants) **Zinc**

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
01	295.2	300.3	296.5	293.3	296.3	2.96	ICP-MS
02	313.9	312.7	313.1	312.0	312.9	0.79	ICP OES
03	312.3	317.0	312.5	315.0	314.2	2.23	ICP OES
09	317.9	318.3	315.0	316.0	316.8	1.56	F AAS
06	328.5	325.1	326.1	325.9	326.4	1.47	F AAS

M (mg/kg):	**313.3**
SD_M (mg/kg):	10.87
$SD_M/\sqrt{N}$ (mg/kg):	4.8629



Homogeneity study (measurement results) **Arsenic**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	22.82	22.79	22.81	0.019
045	22.18	22.75	22.47	0.404
072	22.97	23.36	23.16	0.272
105	22.93	22.63	22.78	0.208
124	23.58	23.17	23.38	0.288
140	23.28	22.83	23.05	0.315
166	23.31	23.42	23.37	0.078
204	23.66	23.26	23.46	0.285
226	23.01	23.67	23.34	0.466
251	22.66	23.79	23.22	0.800

M (mg/kg): **23.10**

SD_M (mg/kg): 0.324

u_{bb} (% rel.): 0.807

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	25.78	26.72	26.25	0.666
045	24.14	26.58	25.36	1.724
072	26.49	27.23	26.86	0.526
105	26.53	26.94	26.74	0.287
124	24.56	26.82	25.69	1.596
140	26.45	26.40	26.42	0.035
166	26.40	25.28	25.84	0.793
204	26.26	25.50	25.88	0.536
226	26.15	26.42	26.28	0.189
251	26.66	26.67	26.66	0.009

M (mg/kg): **26.20**

SD_M (mg/kg): 0.494

u_{bb} (% rel.): 1.540

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Cadmium**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	5.504	5.547	5.526	0.0299
045	5.539	5.448	5.494	0.0642
072	5.566	5.486	5.526	0.0563
105	5.561	5.438	5.499	0.0872
124	5.481	5.614	5.548	0.0942
140	5.483	5.511	5.497	0.0200
166	5.550	5.428	5.489	0.0859
204	5.519	5.444	5.482	0.0529
226	5.561	5.404	5.483	0.1105
251	5.524	5.434	5.479	0.0638

M (mg/kg): **5.502**

SD_M (mg/kg): 0.0230

u_{bb} (% rel.): 0.617

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	5.575	5.683	5.629	0.0766
045	5.158	5.598	5.378	0.3111
072	5.674	5.543	5.609	0.0932
105	5.797	5.674	5.735	0.0867
124	5.295	5.664	5.480	0.2609
140	5.573	5.526	5.549	0.0333
166	5.663	5.372	5.517	0.2058
204	5.606	5.316	5.461	0.2054
226	5.478	5.757	5.618	0.1976
251	5.526	5.556	5.541	0.0209

M (mg/kg): **5.552**

SD_M (mg/kg): 0.1013

u_{bb} (% rel.): 1.505

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Chromium**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	132.4	132.0	132.2	0.25
045	131.5	132.7	132.1	0.87
072	132.1	134.4	133.2	1.63
105	132.1	131.7	131.9	0.28
124	132.5	132.6	132.5	0.04
140	131.9	132.0	132.0	0.06
166	132.7	131.0	131.9	1.22
204	132.5	132.0	132.3	0.40
226	131.8	131.8	131.8	0.02
251	132.0	132.4	132.2	0.25

M (mg/kg): **132.2**

SD_M (mg/kg): 0.41

u_{bb} (% rel.): 0.260

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	139.8	144.9	142.4	3.63
045	132.8	146.0	139.4	9.36
072	144.0	146.5	145.2	1.80
105	143.7	145.3	144.5	1.10
124	133.9	143.5	138.7	6.79
140	144.2	141.7	143.0	1.80
166	140.9	136.9	138.9	2.82
204	142.0	135.4	138.7	4.68
226	142.4	143.4	142.9	0.73
251	143.3	142.9	143.1	0.24

M (mg/kg): **141.7**

SD_M (mg/kg): 2.50

u_{bb} (% rel.): 1.435

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Cobalt**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	5.720	5.947	5.833	0.1608
045	5.689	5.732	5.711	0.0301
072	5.707	5.831	5.769	0.0873
105	5.713	5.606	5.659	0.0751
124	5.730	5.743	5.737	0.0092
140	5.736	5.731	5.733	0.0031
166	5.696	5.679	5.687	0.0116
204	5.651	5.671	5.661	0.0136
226	5.677	5.668	5.673	0.0066
251	5.468	5.613	5.541	0.1029

M (mg/kg): **5.700**

SD_M (mg/kg): 0.0778

u_{bb} (% rel.): 1.039

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	6.378	6.383	6.381	0.0039
045	6.010	6.601	6.305	0.4174
072	6.471	6.578	6.525	0.0759
105	6.428	6.556	6.492	0.0904
124	6.135	6.421	6.278	0.2023
140	6.475	6.309	6.392	0.1175
166	6.253	6.219	6.236	0.0242
204	6.376	6.138	6.257	0.1684
226	6.421	6.476	6.448	0.0392
251	6.449	6.465	6.457	0.0112

M (mg/kg): **6.377**

SD_M (mg/kg): 0.1033

u_{bb} (% rel.): 1.226

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Copper**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	81.23	82.19	81.71	0.678
045	81.07	82.05	81.56	0.691
072	81.49	82.32	81.91	0.588
105	81.81	80.32	81.07	1.057
124	82.00	80.97	81.49	0.732
140	81.64	80.81	81.23	0.587
166	81.55	80.62	81.08	0.656
204	82.22	82.00	82.11	0.153
226	81.82	81.16	81.49	0.463
251	81.15	80.94	81.05	0.147

M (mg/kg): **81.47**

SD_M (mg/kg): 0.368

u_{bb} (% rel.): 0.366

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	82.69	84.03	83.36	0.950
045	81.00	85.34	83.17	3.066
072	82.53	87.38	84.96	3.428
105	85.50	84.02	84.76	1.047
124	79.94	83.61	81.77	2.598
140	83.93	82.64	83.29	0.913
166	82.32	80.21	81.26	1.490
204	85.35	79.39	82.37	4.217
226	82.47	84.01	83.24	1.089
251	83.01	83.28	83.14	0.188

M (mg/kg): **83.13**

SD_M (mg/kg): 1.154

u_{bb} (% rel.): 1.297

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Lead**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	280.6	286.5	283.5	4.22
045	281.3	284.5	282.9	2.21
072	281.7	286.4	284.1	3.30
105	282.6	280.4	281.5	1.56
124	288.4	283.8	286.1	3.19
140	284.6	287.2	285.9	1.85
166	287.4	283.4	285.4	2.85
204	286.7	284.9	285.8	1.30
226	286.1	282.4	284.3	2.60
251	283.2	283.7	283.4	0.36

M (mg/kg): **284.3**

SD_M (mg/kg): 1.49

u_{bb} (% rel.): 0.428

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	270.9	277.3	274.1	4.55
045	263.1	281.4	272.2	12.90
072	283.6	281.0	282.3	1.87
105	285.9	279.0	282.5	4.86
124	267.4	282.6	275.0	10.73
140	282.0	281.9	281.9	0.07
166	283.3	265.8	274.6	12.36
204	276.1	265.3	270.7	7.63
226	275.7	273.1	274.4	1.88
251	277.8	277.7	277.7	0.10

M (mg/kg): **276.5**

SD_M (mg/kg): 4.32

u_{bb} (% rel.): 1.261

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Mercury**

(a) Sample intake: 3.0 g Analytical method: CV AFS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	1.321	1.299	1.310	0.0157
045	1.325	1.366	1.346	0.0290
072	1.321	1.356	1.339	0.0253
105	1.345	1.379	1.362	0.0243
124	1.372	1.370	1.371	0.0009
140	1.338	1.327	1.333	0.0074
166	1.321	1.374	1.348	0.0377
204	1.313	1.357	1.335	0.0312
226	1.397	1.375	1.386	0.0157
251	1.342	1.363	1.353	0.0154

M (mg/kg): **1.348**

SD_M (mg/kg): 0.0213

u_{bb} (% rel.): 1.032

(acc. to ISO Guide 35)

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

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	1.387	1.394	1.390	0.0049
045	1.284	1.388	1.336	0.0733
072	1.389	1.446	1.417	0.0403
105	1.350	1.445	1.397	0.0673
124	1.230	1.531	1.381	0.2124
140	1.378	1.417	1.398	0.0275
166	1.392	1.322	1.357	0.0489
204	1.336	1.383	1.360	0.0331
226	1.434	1.315	1.374	0.0837
251	1.430	1.324	1.377	0.0751

M (mg/kg): **1.379**

SD_M (mg/kg): 0.0236

u_{bb} (% rel.): 2.941

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Nickel**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	27.26	27.30	27.28	0.024
045	26.83	28.61	27.72	1.261
072	27.49	27.46	27.48	0.021
105	26.66	26.75	26.71	0.065
124	27.00	27.01	27.00	0.003
140	27.31	26.89	27.10	0.300
166	26.85	26.72	26.78	0.095
204	27.03	26.52	26.78	0.364
226	27.07	26.29	26.68	0.555
251	26.85	26.74	26.80	0.076

M (mg/kg): **27.03**

SD_M (mg/kg): 0.357

u_{bb} (% rel.): 0.809

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	27.77	28.44	28.11	0.470
045	26.44	29.05	27.74	1.843
072	28.49	29.24	28.87	0.529
105	28.58	29.12	28.85	0.383
124	27.12	28.80	27.96	1.190
140	28.57	27.86	28.22	0.504
166	28.18	28.38	28.28	0.145
204	28.42	27.19	27.81	0.872
226	28.36	28.54	28.45	0.124
251	28.85	28.72	28.78	0.094

M (mg/kg): **28.31**

SD_M (mg/kg): 0.421

u_{bb} (% rel.): 1.349

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Vanadium**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	19.86	20.06	19.96	0.141
045	19.85	20.17	20.01	0.228
072	19.86	20.36	20.11	0.354
105	19.67	19.69	19.68	0.010
124	19.86	19.65	19.75	0.145
140	19.74	19.81	19.77	0.046
166	19.90	19.35	19.62	0.388
204	19.75	19.57	19.66	0.129
226	19.77	19.51	19.64	0.186
251	19.81	19.64	19.72	0.127

M (mg/kg): **19.79**

SD_M (mg/kg): 0.171

u_{bb} (% rel.): 0.500

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	22.07	23.04	22.55	0.689
045	21.63	23.39	22.51	1.242
072	23.15	23.64	23.40	0.349
105	22.78	23.40	23.09	0.434
124	21.56	22.94	22.25	0.977
140	23.01	22.69	22.85	0.228
166	22.25	22.08	22.17	0.121
204	22.70	21.74	22.22	0.684
226	22.96	23.21	23.08	0.178
251	23.00	23.43	23.22	0.303

M (mg/kg): **22.73**

SD_M (mg/kg): 0.452

u_{bb} (% rel.): 1.306

(acc. to ISO Guide 35)

Homogeneity study (measurement results) **Zinc**

(a) Sample intake: 3.0 g Analytical method: ICP OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	311.2	310.0	310.6	0.84
045	310.3	311.9	311.1	1.13
072	310.7	312.4	311.6	1.21
105	310.9	310.9	310.9	0.02
124	312.8	311.3	312.1	1.07
140	310.7	312.3	311.5	1.10
166	311.4	309.1	310.2	1.62
204	312.3	310.4	311.4	1.38
226	309.8	310.0	309.9	0.14
251	310.4	310.7	310.6	0.26

M (mg/kg): **311.0**

SD_M (mg/kg): 0.67

u_{bb} (% rel.): 0.155

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
031	321.6	334.5	328.0	9.15
045	309.1	338.3	323.7	20.66
072	331.5	341.8	336.7	7.24
105	329.0	333.5	331.3	3.19
124	308.4	335.4	321.9	19.09
140	329.0	330.7	329.9	1.18
166	325.7	315.3	320.5	7.37
204	328.1	314.7	321.4	9.48
226	326.2	329.0	327.6	2.02
251	327.7	333.3	330.5	3.93

M (mg/kg): **327.1**

SD_M (mg/kg): 5.21

u_{bb} (% rel.): 1.518

(acc. to ISO Guide 35)

Stability study (measurement results)

(Analyses were performed after a storage time of 12 months)

Arsenic

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	25.03	24.66	24.81	24.58	24.77	0.198	ICP-MS
+20 °C	24.60	24.82	24.60	24.72	24.69	0.106	
+40 °C	24.65	24.83	24.90	24.87	24.81	0.112	

Cadmium

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	5.694	5.772	5.655	5.577	5.675	0.0813	ICP-MS
+20 °C	5.913	5.860	5.658	5.809	5.810	0.1099	
+40 °C	5.694	5.925	5.748	5.803	5.792	0.0988	

Chromium

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	127.7	127.6	128.0	127.5	127.7	0.21	ICP OES
+20 °C	126.3	128.0	127.4	127.0	127.2	0.75	
+40 °C	127.7	127.6	127.6	128.0	127.7	0.18	

Cobalt

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	6.583	6.388	6.566	6.315	6.463	0.1322	ICP-MS
+20 °C	6.513	6.526	6.534	6.445	6.505	0.0408	
+40 °C	6.485	6.553	6.491	6.327	6.464	0.0967	

Copper

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	80.93	81.00	80.84	81.58	81.09	0.336	ICP OES
+20 °C	80.41	82.19	80.54	80.42	80.89	0.868	
+40 °C	81.73	80.66	81.24	80.90	81.13	0.463	

Stability study (measurement results)

(Analyses were performed after a storage time of 12 months)

Lead

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	303.5	306.5	299.3	298.9	302.1	3.62	ICP OES
+20 °C	304.4	302.2	300.8	300.7	302.0	1.73	
+40 °C	297.8	304.2	303.5	303.9	302.4	3.05	

Mercury

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	1.331	1.340	1.456	1.420	1.387	0.0610	CV AFS
+20 °C	1.410	1.476	1.402	1.345	1.408	0.0538	
+40 °C	1.386	1.419	1.344	1.418	1.392	0.0354	

Nickel

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	28.19	27.29	27.30	28.18	27.74	0.514	ICP-MS
+20 °C	27.55	28.09	27.73	27.55	27.73	0.251	
+40 °C	27.54	28.18	27.78	27.43	27.73	0.333	

Vanadium

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	20.51	20.08	20.30	19.99	20.22	0.232	ICP-MS
+20 °C	20.15	20.66	20.20	20.25	20.32	0.235	
+40 °C	20.15	20.63	20.44	19.88	20.28	0.326	

Zinc

Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X_t (mg/kg)	SD_t (mg/kg)	Analytical method
-20 °C	298.4	301.3	300.8	300.2	300.2	1.26	ICP OES
+20 °C	298.6	302.6	301.5	300.1	300.7	1.74	
+40 °C	299.8	301.0	298.8	297.9	299.4	1.32	