



Certification Report

Certified Reference Material ERM[®]-CC020

Trace elements in contaminated river sediment

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ERM[®]-CC020 (Certification Report)

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 river sediment.

The certified reference material ERM[®]-CC020 is intended for the verification of measurement results obtained by standardised analytical protocols as well as for the validation of modified or new analytical procedures.

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	56.6	± 2.6
Cadmium	20.8	± 0.5
Chromium	290	± 8
Cobalt	32.8	± 1.5
Copper	560	± 11
Lead	255	± 11
Mercury	27.4	± 0.6
Nickel	158	± 6
Vanadium	53	± 4
Zinc	2030	± 40

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 operationally defined by the analytical protocol given in ISO 11466 and 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 of $k = 2.5$, 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[®]-CC020 is provided as a powder with particle sizes below 63 µm in a 100 mL screw-capped brown glass bottle containing (52 ± 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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Contents

	Page
1 Introduction	1
2 Candidate material	1
3 Homogeneity study	1
4 Stability study	3
5 Certification study	4
5.1 Participants and used analytical methods	4
5.2 Statistical evaluation of results	4
6 Certified values and uncertainties	6
7 Traceability	7
8 Additional data	8
9 Information on the proper use of ERM [®] -CC020	9
9.1 Shelf life	9
9.2 Transport, storage and use	9
9.3 Safety instructions	9
9.4 Legal notice	9
10 References	10
11 Annexes	11
Annex I: Homogeneity study (measurement results)	12
Annex II: Stability study (measurement results)	22
Annex III: Certification study (measurement results of participants)	26

1 Introduction

Europe-wide, the volume of dredged river and channel sediments amounts to several million cubic meters per year. For dredged material management, solutions like placement on river embankments, beneficial use as construction material or for agricultural soil enrichment are the first options to consider. However, these solutions are only acceptable if the contamination of the dredged sediments is below given regulatory limits. If sediments are contaminated to such an extent that a beneficial use is not allowed or restricted, the dredged material must be disposed of in confined disposal facilities (landfills) at much higher costs. Thus, for decision-making with respect to dredged sediment utilisation, reliable analytical data are needed and – due to their great economic and environmental impact – must be assured by appropriate quality control.

As for soils, the determination of element contents of sediments 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.

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 dredged materials in terms of their mineral components, organic matter and anthropogenic contamination, there is a need for a wide range of different reference materials. Hence, ERM[®]-CC020 was certified to complement available offers of appropriate CRMs for use in the determination of environmentally relevant elements in sediments, soils, or materials of a similar matrix.

2 Candidate material

The starting material for preparing ERM[®]-CC020 was a mixture of sediments collected at different locations in the eastern part of Germany (river Elbe near Magdeburg, river Weiße Elster near Leipzig, Finow Canal near Eberswalde). The raw material was freeze-dried 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 were performed using a spinning riffler according to the so-called “cross-riffing scheme” [2]. A total of 256 bottles each containing (52 ± 1) g was produced in March 2010 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 sediment 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 HNO₃) 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 I.

The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budgets were calculated according to ISO Guide 35 [3] using Eq. (1) and Eq. (2):

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

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

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 Table 1.

Table 1: Results of the homogeneity study

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	1.55	0.76	1.55	1.78	0.88	1.78
Cadmium	$MS_{among} < MS_{within}$	0.65	0.65	0.43	0.35	0.43
Chromium	$MS_{among} < MS_{within}$	0.44	0.44	0.49	0.52	0.52
Cobalt	0.64	0.53	0.64	1.02	0.41	1.02
Copper	0.44	0.44	0.44	0.33	0.26	0.33
Lead	$MS_{among} < MS_{within}$	0.62	0.62	$MS_{among} < MS_{within}$	0.72	0.72
Mercury	0.16	0.62	0.62	$MS_{among} < MS_{within}$	0.33	0.33
Nickel	0.09	0.41	0.41	0.25	0.16	0.25
Vanadium	$MS_{among} < MS_{within}$	0.65	0.65	0.24	0.24	0.24
Zinc	$MS_{among} < MS_{within}$	0.37	0.37	0.24	0.26	0.26

A general influence of sample intake (3 g versus 0.5 g) on $u_{bb,r}$ could not be proven. 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.

NOTE: When optimising the measurement conditions for homogeneity testing, the main focus was on precision rather than on trueness of measurement results. Hence, the differences between results obtained with extraction procedures (a) and (b) – see Annex I – should not be overrated. However, there is some evidence that the efficiency of extracting elements with aqua regia from the sediment matrix depends more or less strongly on process conditions (this is most clearly pronounced for vanadium). In any case it should be kept in mind that aqua regia extractable mass fractions of elements in sediments are operationally-defined parameters.

4 Stability study

Based on many years of experience gained at BAM with reference materials of similar matrix composition, it is very unlikely that aqua regia extractable mass fractions of elements will change if the samples are stored and handled properly. That's why only a reduced stability check of the bottled material was performed.

Immediately after bottling selected units were stored at a temperature of -20 °C, +20 °C and +40 °C, respectively. After a storage time of 6 and 12 months, respectively, 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 II) were evaluated for each analyte calculating the ratios R_t (3) and their uncertainties u_t (4):

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

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

where X_t and $X_{-20\text{ °C}}$ 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 $CV_{-20\text{ °C}}$ are the corresponding coefficients of variation.

Table 2: Results of the stability test after a storage time of 6 and 12 months

Analyte	Storage time	$R_t \pm u_t$	
		Samples stored at 20 °C	Samples stored at 40 °C
Arsenic	6 months	1.0120 ± 0.0327	1.0073 ± 0.0327
	12 months	1.0047 ± 0.0269	1.0056 ± 0.0212
Cadmium	6 months	0.9986 ± 0.0229	1.0019 ± 0.0172
	12 months	0.9963 ± 0.0164	1.0028 ± 0.0155
Chromium	6 months	0.9986 ± 0.0048	0.9966 ± 0.0089
	12 months	0.9997 ± 0.0072	1.0017 ± 0.0098
Cobalt	6 months	0.9975 ± 0.0118	0.9949 ± 0.0141
	12 months	0.9946 ± 0.0202	1.0023 ± 0.0214
Copper	6 months	1.0040 ± 0.0124	0.9981 ± 0.0100
	12 months	0.9966 ± 0.0071	1.0015 ± 0.0067
Lead	6 months	1.0031 ± 0.0194	0.9988 ± 0.0179
	12 months	0.9909 ± 0.0149	0.9992 ± 0.0100
Mercury	6 months	1.0081 ± 0.0156	1.0046 ± 0.0153
	12 months	1.0068 ± 0.0203	1.0061 ± 0.0094
Nickel	6 months	0.9975 ± 0.0039	1.0006 ± 0.0046
	12 months	0.9932 ± 0.0158	1.0000 ± 0.0130
Vanadium	6 months	0.9987 ± 0.0138	1.0013 ± 0.0148
	12 months	1.0011 ± 0.0092	1.0096 ± 0.0149
Zinc	6 months	0.9985 ± 0.0097	0.9980 ± 0.0112
	12 months	0.9966 ± 0.0086	0.9995 ± 0.0067

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.

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 performed at BAM.

5 Certification study

5.1 Participants and used analytical methods

Three BAM working groups with a total of 13 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:

- Advanced mercury analyzer (AMA)
- 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)

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

Each participating working group received two units of the bottled candidate material and had to analyse three 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 fractions were corrected to the dry mass content of the sediment 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 III. 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 3.

Table 3: 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	(-/-)	(-/-)	(-/-)	(-/08)
Cadmium	6	No	(-/-)	(-/-)	(-/-)	(-/-)
Chromium	6	No	(08/08)	(-/-)	(-/-)	(-/-)
Cobalt	7	No	(-/-)	(-/-)	(-/-)	(-/-)
Copper	5	No	(-/-)	(-/-)	(-/-)	(-/-)
Lead	5	No	(-/-)	(-/-)	(-/-)	(-/-)
Mercury	6	No	(03,04/03,04)	(-/-)	(-/-)	(-/-)
Nickel	6	No	(-/-)	(-/-)	(-/-)	(-/-)
Vanadium	6	No	(-/-)	(-/-)	(-/-)	(-/07)
Zinc	5	No	(-/-)	(-/-)	(-/-)	(-/-)

Table 3 (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	No/No	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/No	Yes/Yes	Yes/Yes	Pooling of individual data not allowed
Mercury	No/No	No/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 the means was flagged as a statistical outlier with a level of confidence of 99 %), all data sets were retained for further data processing. The results of the Cochran test were ignored because all the intralaboratory standard deviations were at acceptable low levels (with a maximum of 3.1 % rel. for Hg results of participant 03).

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 $(105 \pm 2) ^\circ\text{C}$. 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:

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

Calculated aqua regia extractable mass fractions w_{char} and absolute values of the different uncertainty components are given in Table 4.

Table 4: Mass fractions and uncertainty components for the analytes in ERM[®]-CC020 (before rounding)

Analyte	w_{char} (mg/kg)	u_{char} (mg/kg)	u_{bb} (mg/kg)	u_{CRM} (mg/kg)
Arsenic	56.64	0.513	0.878	1.017
Cadmium	20.84	0.147	0.136	0.200
Chromium	290.1	2.757	1.276	3.041
Cobalt	32.84	0.544	0.210	0.583
Copper	559.8	3.202	2.463	4.038
Lead	255.4	3.789	1.584	4.108
Mercury	27.40	0.131	0.170	0.215
Nickel	158.3	2.238	0.649	2.332
Vanadium	52.81	1.349	0.343	1.392
Zinc	2034	12.011	7.526	14.165

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

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

The value of the coverage factor k was chosen to give a level of confidence of approximately 95 % to be associated with the interval $\pm U$ 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 5.

Table 5: Effective degrees of freedom of u_{CRM} and corresponding factors $t_{95}(v_{eff})$

Analyte	v_{eff}	$t_{95}(v_{eff})$
Arsenic	13.8	2.16
Cadmium	12.6	2.18
Chromium	7.2	2.37
Cobalt	7.8	2.37
Copper	7.5	2.37
Lead	5.5	2.57
Mercury	14.9	2.15
Nickel	5.9	2.57
Vanadium	5.7	2.57
Zinc	7.3	2.37

Because all factors $t_{95}(v_{eff})$ 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 6: Certified mass fractions and expanded uncertainties of analytes in ERM[®]-CC020 (after rounding)

Analyte	Aqua regia extractable mass fraction (mg/kg)
Arsenic	56.6 ± 2.6
Cadmium	20.8 ± 0.5
Chromium	290 ± 8
Cobalt	32.8 ± 1.5
Copper	560 ± 11
Lead	255 ± 11
Mercury	27.4 ± 0.6
Nickel	158 ± 6
Vanadium	53 ± 4
Zinc	2030 ± 40

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[®]-CC020 are operationally-defined referring to the analytical protocol prescribed by ISO 11466.

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	Mg
Mass fraction in %	25.3	5.5	2.9	5.1	1.7	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	96.2	ISO 11465
Loss on ignition at 550 °C	18.5	EN 12879 [9]
Total organic carbon (TOC)	9.7	ISO 10694 [10]
Total inorganic carbon (TIC)	0.2	ISO 10694 [10]

pH values in water and CaCl₂ solution (acc. to ISO 10390 [11]): 6.8 and 6.7, respectively.

In October 2010 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 sediment sample in duplicate for aqua regia extractable mass fractions. They were requested to follow the extraction procedure prescribed by ISO 11466 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	53.95	8.17	1.39	57
Cadmium	20.34	7.11	1.94	57
Chromium	282.9	6.75	1.81	46
Cobalt	31.91	7.31	1.93	57
Copper	552.5	6.25	1.28	57
Lead	255.0	6.82	1.63	57
Mercury	26.70	8.26	3.06	57
Nickel	152.9	6.55	2.30	57
Vanadium	52.13	13.57	2.10	43
Zinc	1974	6.69	1.26	57

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[®]-CC020

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[®]-CC020.

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 using a separate sub-sample. The dry mass content of 96.2 % (see chapter "Additional data") should be regarded as being indicative only.

It is explicitly stressed that the certified values are not valid if there are deviations from the extraction procedure prescribed by ISO standard 11466. In particular, extraction with aqua regia using microwave assisted closed vessel procedures is prone to result in higher mass fractions.

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

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(*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 I: Homogeneity study (measurement results)

Annex II: Stability study (measurement results)

Annex III: Certification study (measurement results of participants)

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

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)
041	55.23	57.16	56.19	1.36
061	58.08	58.06	58.07	0.01
081	56.65	55.40	56.02	0.89
101	55.53	56.36	55.95	0.59
121	55.72	54.21	54.96	1.07
141	54.86	55.62	55.24	0.54
161	55.29	56.06	55.68	0.54
181	57.14	58.84	57.99	1.21
201	54.47	56.00	55.23	1.08
221	55.31	56.52	55.92	0.86

M (mg/kg): 56.13

SD_M (mg/kg): 1.08 u_{bb} (% rel.): 1.55

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	59.84	58.27	59.05	1.11
061	59.12	58.60	58.86	0.37
081	60.65	61.32	60.98	0.48
101	57.81	60.79	59.30	2.11
121	59.38	58.25	58.81	0.80
141	59.38	58.25	58.81	0.80
161	61.72	60.71	61.22	0.72
181	59.04	59.40	59.22	0.26
201	58.09	55.24	56.67	2.01
221	58.18	57.91	58.05	0.19

M (mg/kg): 59.10

SD_M (mg/kg): 1.31 u_{bb} (% rel.): 1.78

(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)
041	20.52	20.92	20.72	0.29
061	20.53	20.43	20.48	0.07
081	20.90	20.70	20.80	0.14
101	20.70	20.78	20.74	0.05
121	20.51	20.57	20.54	0.04
141	20.56	20.84	20.70	0.20
161	20.42	21.08	20.75	0.46
181	20.52	20.59	20.56	0.06
201	19.78	20.60	20.19	0.58
221	20.53	20.94	20.74	0.29

M (mg/kg): 20.62

SD_M (mg/kg): 0.18 u_{bb} (% rel.): 0.65

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	20.79	20.84	20.81	0.03
061	20.62	20.74	20.68	0.08
081	20.53	20.96	20.74	0.31
101	20.56	20.75	20.66	0.14
121	20.71	20.74	20.73	0.02
141	20.53	20.53	20.53	0.00
161	20.46	20.76	20.61	0.21
181	20.40	20.22	20.31	0.13
201	20.66	20.51	20.58	0.11
221	20.49	20.76	20.63	0.19

M (mg/kg): 20.63

SD_M (mg/kg): 0.14 u_{bb} (% rel.): 0.43

(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)
041	286.5	285.0	285.7	1.1
061	285.5	285.9	285.7	0.3
081	284.5	286.2	285.4	1.2
101	284.0	284.7	284.4	0.5
121	284.1	283.5	283.8	0.4
141	283.9	284.2	284.0	0.2
161	282.5	284.0	283.2	1.0
181	285.4	285.2	285.3	0.2
201	276.1	287.6	281.9	8.1
221	287.6	287.5	287.5	0.1

M (mg/kg): 284.7

SD_M (mg/kg): 1.6 u_{bb} (% rel.): 0.44

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	292.9	293.5	293.2	0.4
061	293.0	293.9	293.5	0.7
081	294.8	294.9	294.8	0.1
101	292.2	292.1	292.1	0.0
121	292.7	292.4	292.6	0.2
141	292.9	288.6	290.8	3.0
161	296.6	294.2	295.4	1.7
181	306.7	293.5	300.1	9.3
201	292.3	290.2	291.2	1.5
221	293.7	292.0	292.8	1.2

M (mg/kg): 293.6

SD_M (mg/kg): 2.7 u_{bb} (% rel.): 0.52

(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)
041	34.62	34.48	34.55	0.10
061	34.98	34.97	34.98	0.00
081	34.60	34.72	34.66	0.09
101	34.66	34.17	34.42	0.35
121	34.06	33.73	33.90	0.24
141	34.62	34.58	34.60	0.03
161	34.08	34.05	34.06	0.02
181	35.04	34.10	34.57	0.66
201	33.51	34.84	34.18	0.94
221	35.00	34.88	34.94	0.08

M (mg/kg): 34.48

SD_M (mg/kg): 0.35 u_{bb} (% rel.): 0.64

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	36.38	36.49	36.44	0.08
061	36.18	35.63	35.91	0.38
081	34.72	35.74	35.23	0.73
101	34.96	34.93	34.95	0.02
121	35.47	35.36	35.42	0.08
141	35.15	35.75	35.45	0.43
161	35.39	35.42	35.40	0.02
181	35.91	35.94	35.92	0.02
201	35.46	35.81	35.64	0.25
221	35.43	35.25	35.34	0.13

M (mg/kg): 35.57

SD_M (mg/kg): 0.42 u_{bb} (% rel.): 1.02

(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)
041	577.4	571.4	574.4	4.2
061	576.0	576.8	576.4	0.6
081	571.3	569.7	570.5	1.1
101	571.9	563.0	567.5	6.3
121	561.7	567.4	564.5	4.0
141	566.0	564.1	565.1	1.3
161	564.5	568.0	566.3	2.4
181	569.5	571.9	570.7	1.7
201	557.0	576.8	566.9	14.0
221	577.4	575.3	576.3	1.5

M (mg/kg): 569.8

SD_M (mg/kg): 4.5 u_{bb} (% rel.): 0.44

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	563.9	567.2	565.6	2.3
061	564.3	567.0	565.7	2.0
081	565.3	565.0	565.2	0.2
101	564.3	561.5	562.9	2.0
121	568.9	569.0	568.9	0.1
141	560.9	566.1	563.5	3.7
161	566.3	568.9	567.6	1.8
181	567.5	569.7	568.6	1.6
201	558.9	562.1	560.5	2.2
221	567.1	556.3	561.7	7.6

M (mg/kg): 565.0

SD_M (mg/kg): 2.9 u_{bb} (% rel.): 0.33

(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)
041	263.3	261.5	262.4	1.3
061	263.4	267.0	265.2	2.6
081	262.2	266.4	264.3	3.0
101	270.1	265.5	267.8	3.3
121	272.7	263.1	267.9	6.8
141	260.1	266.9	263.5	4.8
161	270.3	265.3	267.8	3.5
181	262.8	265.2	264.0	1.7
201	259.7	263.7	261.7	2.8
221	265.3	267.1	266.2	1.2

M (mg/kg): 265.1

SD_M (mg/kg): 2.3 u_{bb} (% rel.): 0.62

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	271.6	277.5	274.5	4.1
061	273.9	266.9	270.4	4.9
081	266.4	274.6	270.5	5.8
101	265.4	269.6	267.5	3.0
121	267.7	269.4	268.5	1.2
141	268.9	261.1	265.0	5.6
161	263.0	271.1	267.0	5.7
181	268.7	270.6	269.7	1.4
201	269.7	266.5	268.1	2.3
221	273.3	268.3	270.8	3.5

M (mg/kg): 269.2

SD_M (mg/kg): 2.6 u_{bb} (% rel.): 0.72

(acc. to ISO Guide 35)

Homogeneity study (measurement results)

Mercury

(a) Sample intake: 3.0 g

Analytical method: CV AAS

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	28.06	28.93	28.49	0.61
061	28.47	29.06	28.76	0.42
081	28.62	29.36	28.99	0.52
101	28.83	29.34	29.09	0.36
121	28.65	29.32	28.98	0.48
141	28.87	28.52	28.70	0.25
161	28.69	28.27	28.48	0.29
181	28.63	28.37	28.50	0.18
201	28.54	28.50	28.52	0.03
221	28.45	28.08	28.27	0.26

M (mg/kg): 28.68

SD_M (mg/kg): 0.27 u_{bb} (% rel.): 0.62

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: CV AAS

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	28.33	28.44	28.39	0.08
061	28.82	28.19	28.51	0.45
081	28.64	28.38	28.51	0.19
101	28.26	28.27	28.26	0.01
121	28.52	28.40	28.46	0.08
141	28.43	28.38	28.41	0.03
161	28.34	28.20	28.27	0.10
181	28.27	28.37	28.32	0.07
201	28.10	28.25	28.18	0.10
221	28.35	28.82	28.59	0.33

M (mg/kg): 28.39

SD_M (mg/kg): 0.13 u_{bb} (% rel.): 0.33

(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)
041	164.9	163.0	164.0	1.3
061	163.7	163.9	163.8	0.2
081	163.4	164.4	163.9	0.7
101	164.1	163.7	163.9	0.2
121	162.5	162.0	162.2	0.4
141	162.8	163.1	162.9	0.2
161	163.1	163.4	163.2	0.3
181	163.8	166.1	164.9	1.6
201	159.1	164.6	161.9	3.9
221	164.9	164.9	164.9	0.0

M (mg/kg): 163.6

SD_M (mg/kg): 1.0 u_{bb} (% rel.): 0.41

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	168.7	169.6	169.1	0.6
061	169.6	168.8	169.2	0.5
081	168.4	168.9	168.7	0.4
101	169.1	167.9	168.5	0.9
121	168.8	169.0	168.9	0.1
141	168.5	167.3	167.9	0.8
161	168.3	169.6	168.9	0.9
181	169.2	168.9	169.1	0.2
201	167.6	168.1	167.9	0.3
221	169.9	169.6	169.7	0.2

M (mg/kg): 168.8

SD_M (mg/kg): 0.6 u_{bb} (% rel.): 0.25

(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)
041	60.30	60.30	60.30	0.00
061	59.44	60.74	60.09	0.92
081	59.94	60.82	60.38	0.62
101	59.35	60.01	59.68	0.47
121	59.34	58.68	59.01	0.47
141	59.65	58.83	59.24	0.58
161	58.77	59.45	59.11	0.48
181	59.42	59.96	59.69	0.38
201	58.44	61.37	59.91	2.07
221	59.72	59.62	59.67	0.07

M (mg/kg): 59.71

SD_M (mg/kg): 0.48 u_{bb} (% rel.): 0.65

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	78.63	79.43	79.03	0.56
061	79.06	78.99	79.02	0.04
081	79.17	79.74	79.45	0.40
101	78.80	78.08	78.44	0.50
121	79.01	79.39	79.20	0.26
141	79.42	78.58	79.00	0.60
161	79.48	79.49	79.49	0.01
181	79.37	79.66	79.52	0.21
201	78.81	78.75	78.78	0.04
221	79.68	78.81	79.25	0.61

M (mg/kg): 79.12

SD_M (mg/kg): 0.34 u_{bb} (% rel.): 0.24

(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)
041	2044	2044	2044	1
061	2028	2025	2027	2
081	2026	2047	2036	15
101	2035	2042	2039	5
121	2031	2038	2034	5
141	2041	2036	2038	4
161	2018	2026	2022	6
181	2036	2029	2032	5
201	1982	2046	2014	45
221	2031	2042	2036	8

M (mg/kg): 2032

SD_M (mg/kg): 9 u_{bb} (% rel.): 0.37

(acc. to ISO Guide 35)

(b) Sample intake: 0.5 g

Analytical method: ICP OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
041	2027	2048	2038	14
061	2039	2026	2032	9
081	2028	2043	2035	10
101	2025	2011	2018	10
121	2026	2033	2029	5
141	2035	2018	2027	12
161	2026	2053	2040	19
181	2054	2039	2046	10
201	2035	2040	2038	3
221	2058	2041	2050	12

M (mg/kg): 2035

SD_M (mg/kg): 9 u_{bb} (% rel.): 0.26

(acc. to ISO Guide 35)

ERM[®]-CC020 (Certification Report, Annex II)

Stability study (measurement results)

(Analyses were performed after a storage time of 6 and 12 months, respectively)

Arsenic

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	58.18	56.05	59.34	56.36	57.48	1.55	ICP-OES
	+20 °C	58.75	59.32	57.27	57.32	58.17	1.03	
	+40 °C	57.73	58.67	58.71	56.49	57.90	1.04	
12 months	-20 °C	55.86	57.90	57.14	58.47	57.34	1.13	
	+20 °C	57.67	58.58	56.14	58.04	57.61	1.05	
	+40 °C	57.73	57.83	57.03	58.04	57.66	0.44	

Cadmium

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	21.26	21.93	21.90	21.32	21.60	0.36	ICP-OES
	+20 °C	21.53	21.93	21.12	21.68	21.57	0.34	
	+40 °C	21.73	21.64	21.54	21.66	21.64	0.08	
12 months	-20 °C	21.34	21.53	21.59	21.87	21.58	0.22	
	+20 °C	21.38	21.34	21.92	21.37	21.50	0.28	
	+40 °C	21.42	21.53	21.58	22.01	21.64	0.26	

Chromium

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	293.7	293.4	291.4	293.2	292.9	1.0	ICP-OES
	+20 °C	293.6	292.2	291.4	292.9	292.5	0.9	
	+40 °C	291.8	292.8	288.7	294.4	291.9	2.4	
12 months	-20 °C	294.9	292.6	290.3	293.1	292.7	1.9	
	+20 °C	291.5	292.6	293.7	292.6	292.6	0.9	
	+40 °C	292.0	296.3	291.5	293.1	293.2	2.2	

ERM[®]-CC020 (Certification Report, Annex II)

Stability study (measurement results)

(Analyses were performed after a storage time of 6 and 12 months, respectively)

Cobalt

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	35.25	35.17	35.69	35.97	35.52	0.38	ICP-OES
	+20 °C	35.27	35.69	35.34	35.40	35.43	0.18	
	+40 °C	35.70	34.93	35.24	35.47	35.34	0.33	
12 months	-20 °C	35.01	34.99	36.06	35.76	35.46	0.54	
	+20 °C	35.86	35.21	34.71	35.30	35.27	0.47	
	+40 °C	35.05	35.12	35.89	36.09	35.54	0.53	

Copper

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	574.1	582.8	581.2	587.3	581.4	5.5	ICP-OES
	+20 °C	586.2	579.2	589.0	580.5	583.7	4.6	
	+40 °C	577.7	581.9	581.8	579.7	580.3	2.0	
12 months	-20 °C	578.2	584.4	584.0	578.6	581.3	3.4	
	+20 °C	578.2	582.5	576.8	579.7	579.3	2.4	
	+40 °C	584.7	580.1	581.6	582.3	582.2	1.9	

Lead

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	258.7	257.0	264.8	256.3	259.2	3.9	ICP-OES
	+20 °C	259.1	264.6	258.9	257.3	260.0	3.2	
	+40 °C	260.4	258.1	255.6	261.3	258.9	2.6	
12 months	-20 °C	265.1	263.0	264.2	262.5	263.7	1.2	
	+20 °C	261.4	263.2	264.5	256.0	261.3	3.7	
	+40 °C	264.3	262.6	266.3	260.8	263.5	2.4	

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Stability study (measurement results)

(Analyses were performed after a storage time of 6 and 12 months, respectively)

Mercury

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	28.62	28.34	28.31	28.02	28.32	0.25	CV-AAS
	+20 °C	28.15	28.93	28.34	28.78	28.55	0.37	
	+40 °C	28.08	28.74	28.21	28.77	28.45	0.36	
12 months	-20 °C	27.61	28.13	27.78	27.77	27.82	0.22	
	+20 °C	27.50	27.96	27.85	28.73	28.01	0.52	
	+40 °C	28.09	28.03	28.04	27.78	27.99	0.14	

Nickel

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	160.6	161.1	161.8	161.2	161.2	0.5	ICP-OES
	+20 °C	160.9	160.6	160.3	161.2	160.8	0.4	
	+40 °C	161.7	161.6	161.4	160.5	161.3	0.5	
12 months	-20 °C	161.9	160.7	163.9	160.2	161.7	1.6	
	+20 °C	159.1	161.5	158.8	162.9	160.6	2.0	
	+40 °C	160.9	161.9	160.6	163.5	161.7	1.3	

Vanadium

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	56.42	55.45	55.12	56.57	55.89	0.71	ICP-OES
	+20 °C	55.83	56.22	55.72	55.51	55.82	0.30	
	+40 °C	55.79	56.58	55.65	55.82	55.96	0.42	
12 months	-20 °C	54.80	54.70	55.38	55.55	55.11	0.42	
	+20 °C	55.34	55.22	54.75	55.35	55.17	0.28	
	+40 °C	55.53	56.53	55.67	54.82	55.64	0.70	

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Stability study (measurement results)

(Analyses were performed after a storage time of 6 and 12 months, respectively)

Zinc

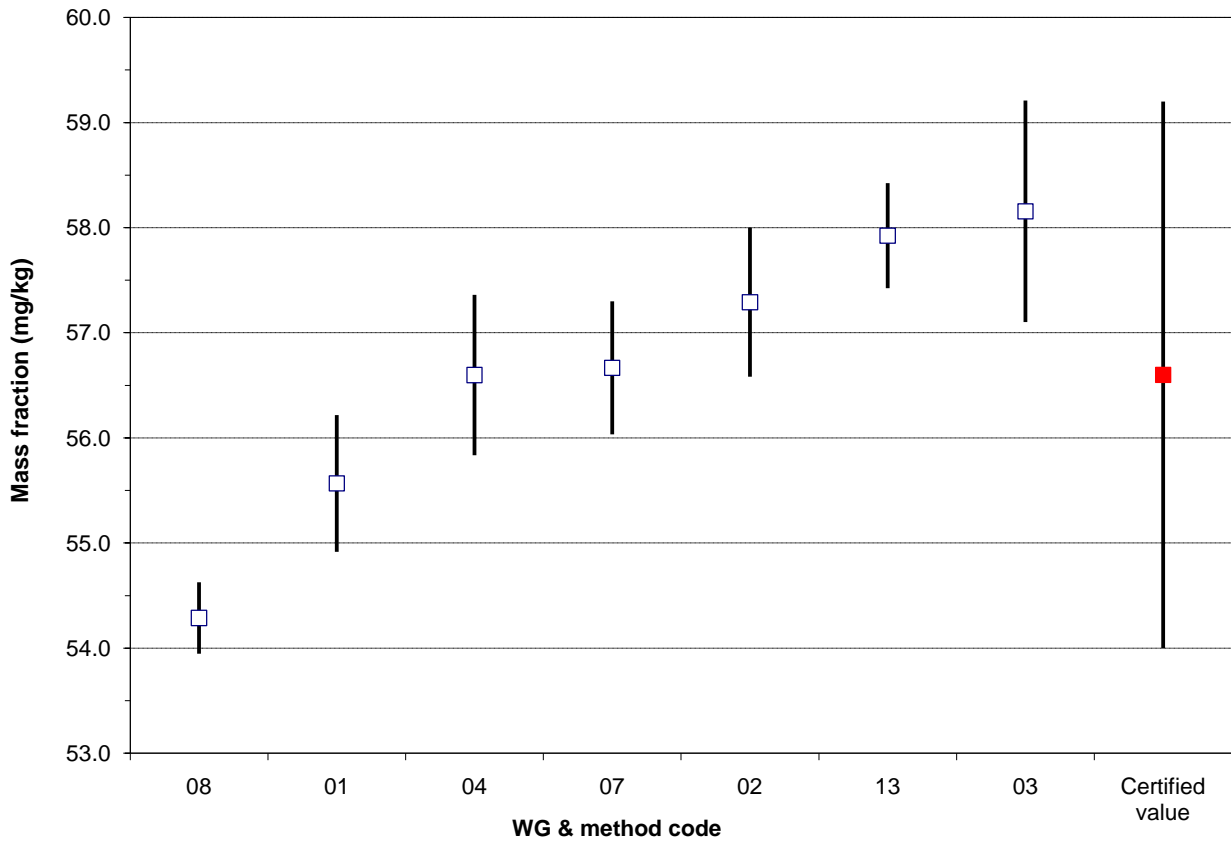
Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	X _t (mg/kg)	SD _t (mg/kg)	Analytical method
6 months	-20 °C	2067	2044	2038	2023	2043	18	ICP-OES
	+20 °C	2040	2045	2029	2045	2040	8	
	+40 °C	2055	2023	2034	2045	2039	14	
12 months	-20 °C	2038	2032	2036	2060	2042	13	
	+20 °C	2022	2030	2037	2051	2035	12	
	+40 °C	2044	2041	2033	2045	2041	5	

Certification study (measurement results of participants)

Arsenic

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
08	54.13	54.70	54.19	54.68	53.83	54.19	54.29	0.34	ET AAS
01	55.94	55.69	55.62	54.73	54.93	56.49	55.57	0.65	ICP OES
04	57.27	57.22	56.69	56.09	55.32	57.00	56.60	0.76	ICP OES
07	56.15	56.08	56.48	56.38	57.33	57.58	56.67	0.63	ET AAS
02	56.40	56.96	56.78	57.40	58.02	58.19	57.29	0.71	ICP-MS
13	57.95	58.57	57.16	57.57	58.06	58.24	57.92	0.50	HG AAS
03	57.42	58.31	59.10	57.17	57.26	59.68	58.16	1.05	ICP OES

M (mg/kg): 56.64
 SD_M (mg/kg): 1.36
 SD_M/√N (mg/kg): 0.51

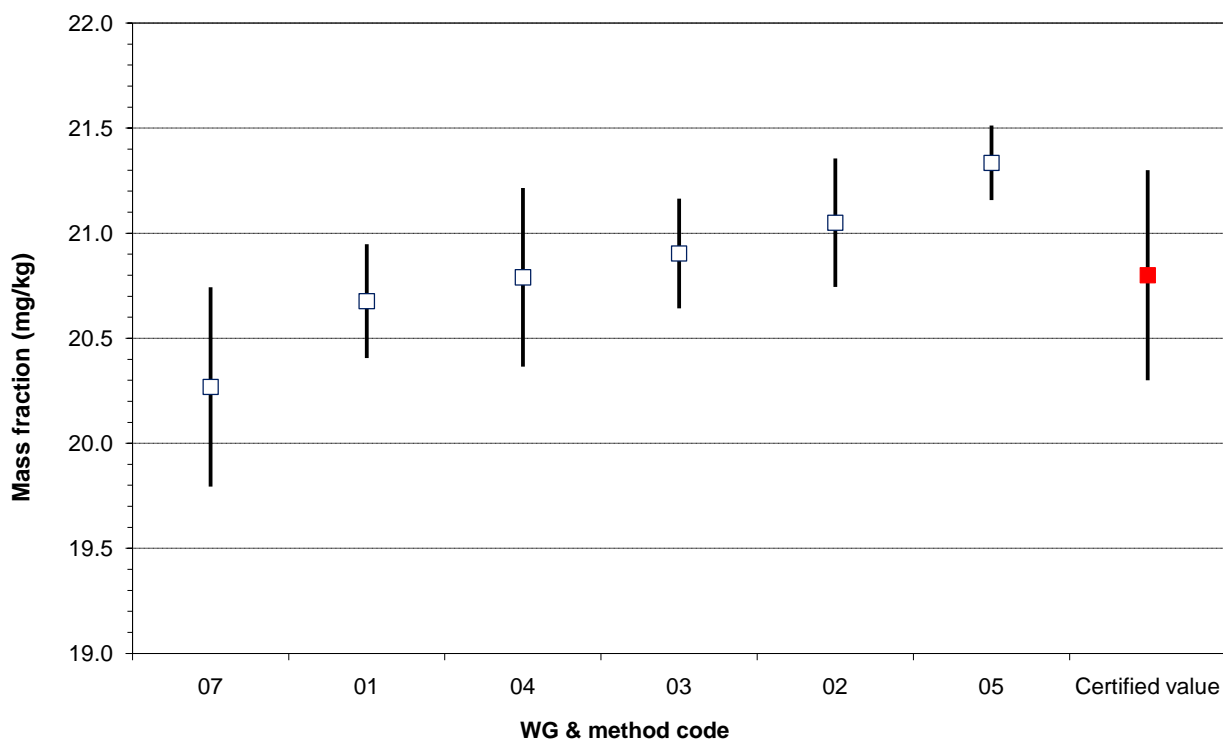


Certification study (measurement results of participants)

Cadmium

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
07	19.68	20.27	20.74	20.70	20.51	19.71	20.27	0.47	ET AAS
01	20.52	20.28	20.82	20.71	20.65	21.08	20.68	0.27	ICP OES
04	20.36	21.02	20.64	21.02	21.39	20.31	20.79	0.43	ICP OES
03	21.05	20.92	21.03	20.39	21.10	20.93	20.90	0.26	ICP OES
02	20.74	20.85	21.45	21.40	21.03	20.83	21.05	0.31	ICP-MS
05	21.37	21.16	21.19	21.25	21.40	21.64	21.34	0.18	F AAS

M (mg/kg): 20.84
 SD_M (mg/kg): 0.36
 SD_M/√N (mg/kg): 0.15

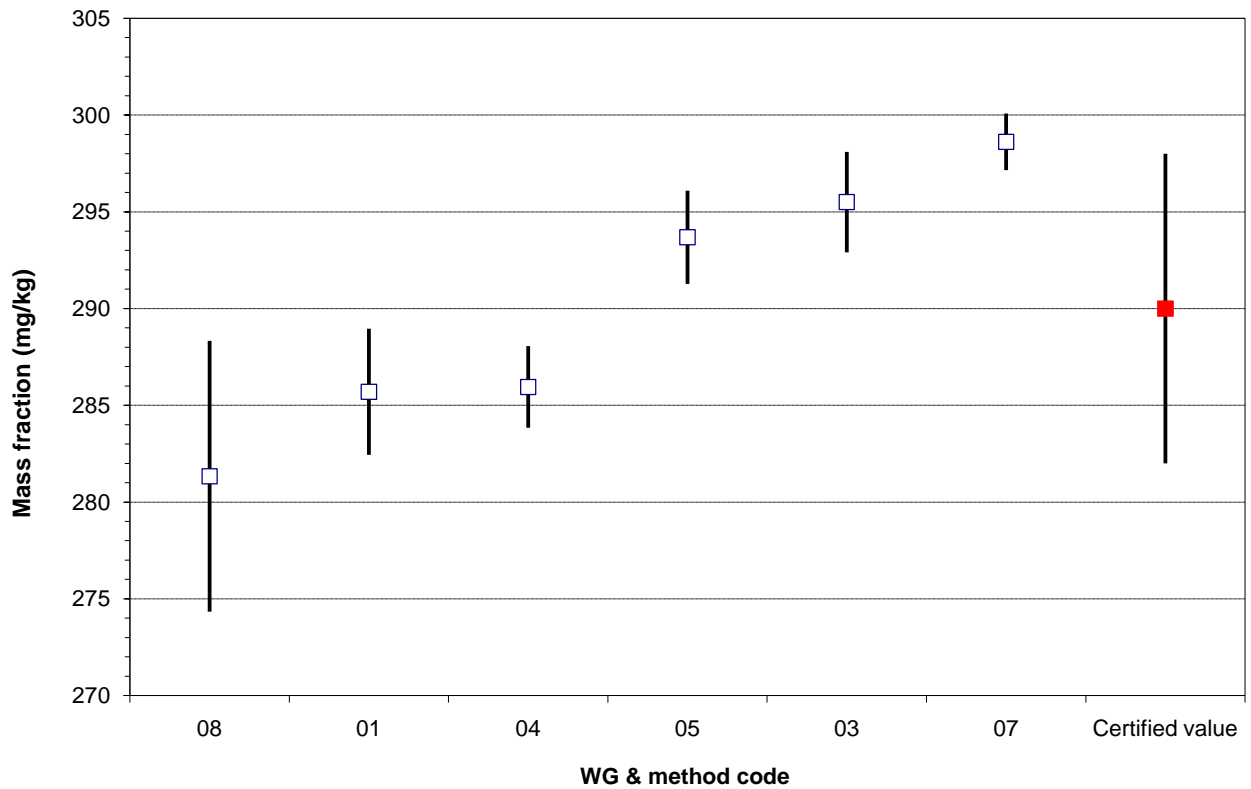


Certification study (measurement results of participants)

Chromium

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
08	275.0	282.4	278.8	273.1	290.0	288.7	281.3	7.0	ET AAS
01	284.1	282.9	283.6	285.2	286.6	291.8	285.7	3.3	ICP OES
04	286.4	283.0	284.4	285.4	288.4	288.1	286.0	2.1	ICP OES
05	295.7	295.6	293.4	290.6	291.0	295.8	293.7	2.4	F AAS
03	293.7	293.9	292.8	295.9	296.9	299.8	295.5	2.6	ICP OES
07	299.3	297.4	299.6	299.6	299.6	296.2	298.6	1.5	ET AAS

M (mg/kg): 290.1
 SD_M (mg/kg): 6.8
 SD_M/√N (mg/kg): 2.8

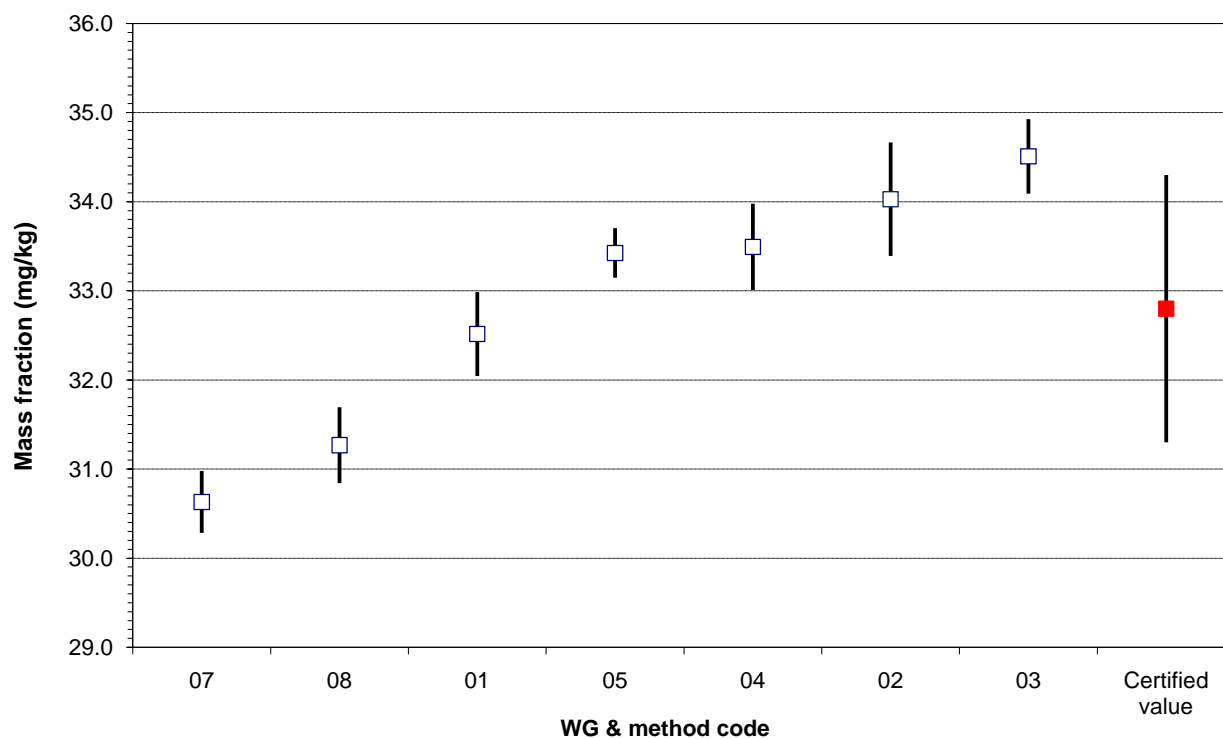


Certification study (measurement results of participants)

Cobalt

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
07	30.32	31.26	30.62	30.33	30.73	30.53	30.63	0.35	ET AAS
08	31.68	30.98	30.91	31.57	31.70	30.77	31.27	0.43	ET AAS
01	32.44	31.91	32.70	32.22	32.52	33.30	32.52	0.47	ICP OES
05	33.78	33.66	33.30	33.53	33.23	33.05	33.43	0.28	F AAS
04	33.37	33.27	32.72	33.62	33.96	34.02	33.49	0.48	ICP OES
02	34.23	33.13	34.32	34.47	33.34	34.68	34.03	0.64	ICP-MS
03	34.55	35.03	34.38	34.02	34.95	34.12	34.51	0.42	ICP OES

M (mg/kg): 32.84
 SD_M (mg/kg): 1.44
 SD_M/√N (mg/kg): 0.54

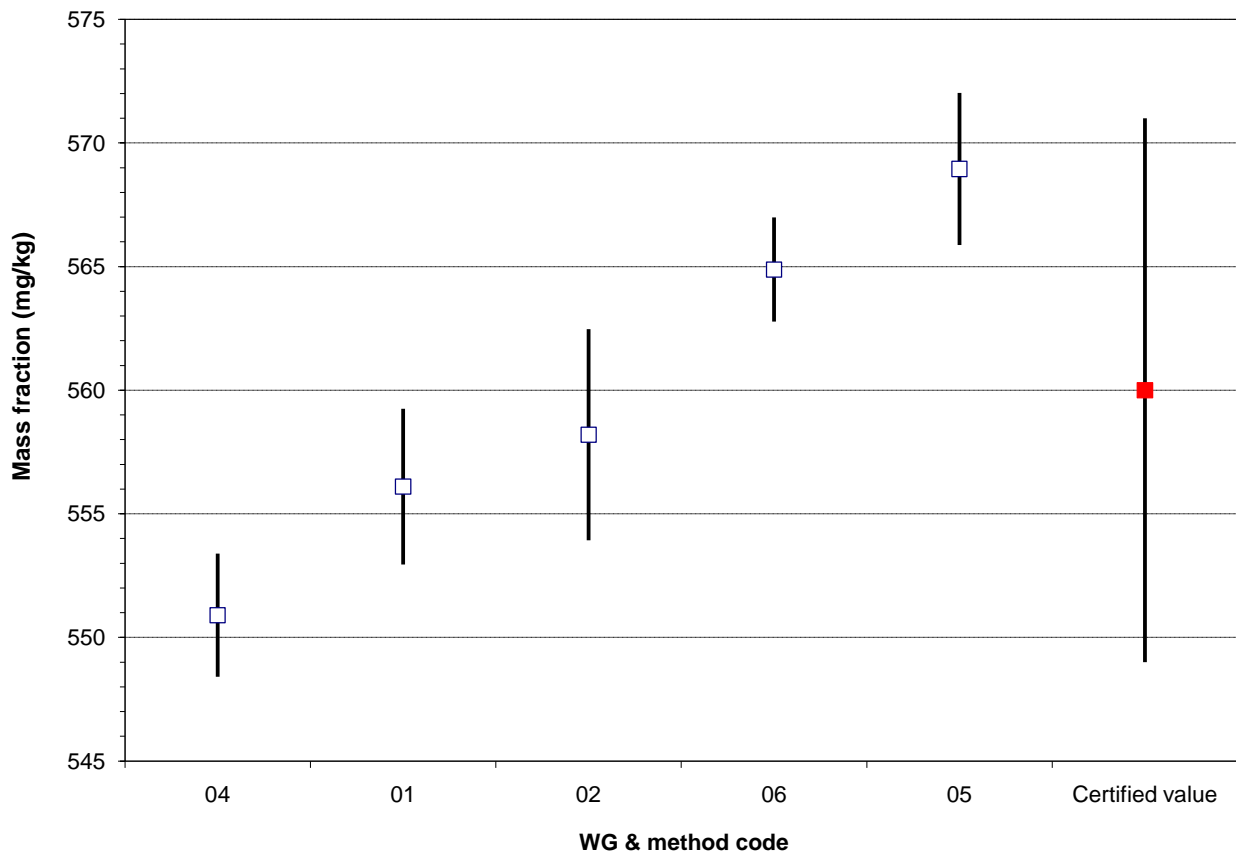


Certification study (measurement results of participants)

Copper

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
04	554.1	549.1	547.2	550.5	552.4	552.1	550.9	2.5	ICP OES
01	555.1	559.4	556.5	558.8	556.2	550.6	556.1	3.1	ICP OES
02	555.8	557.7	557.0	559.6	553.3	565.8	558.2	4.3	ICP-MS
06	567.9	564.1	561.8	566.2	563.9	565.4	564.9	2.1	F AAS
05	566.2	572.2	567.8	567.7	566.4	573.4	569.0	3.1	F AAS

M (mg/kg): 559.8
 SD_M (mg/kg): 7.2
 SD_M/√N (mg/kg): 3.2

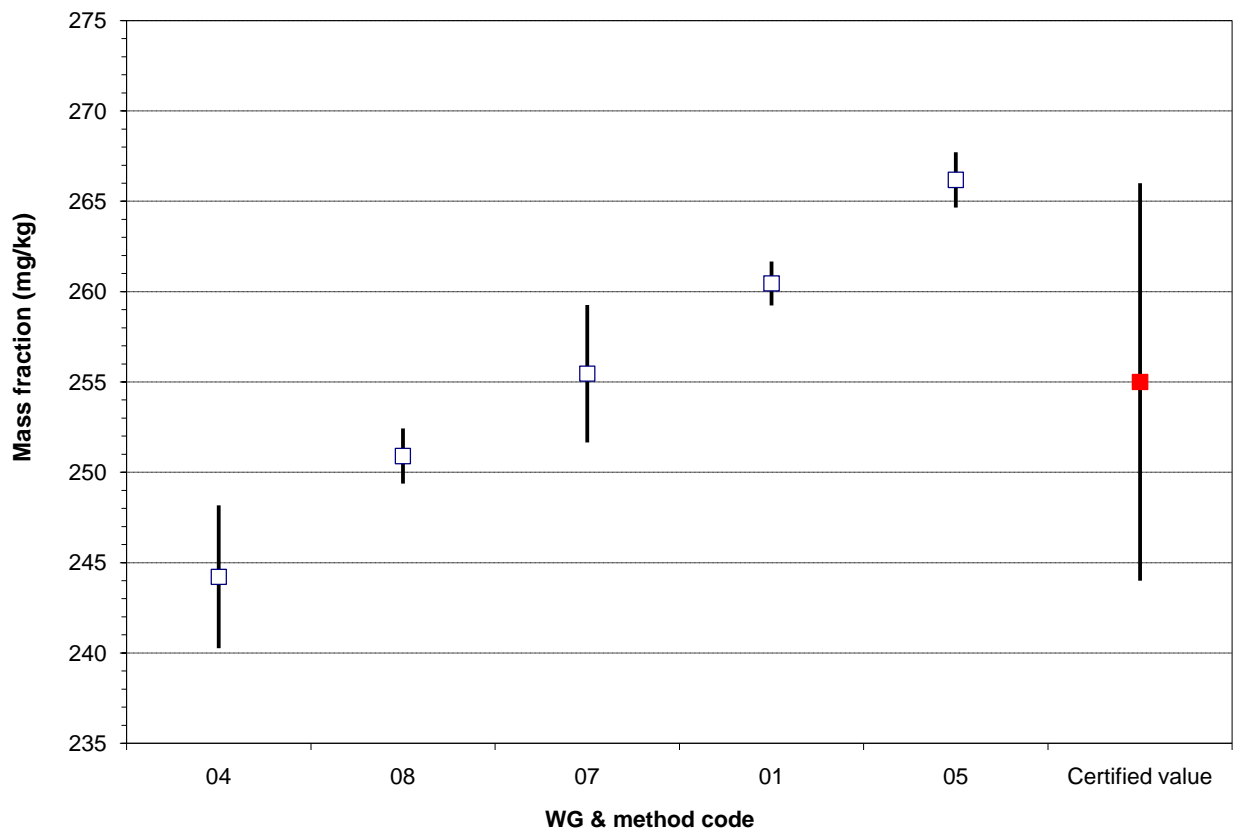


Certification study (measurement results of participants)

Lead

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
04	248.4	239.1	246.1	241.3	248.4	242.0	244.2	4.0	ICP OES
08	251.7	249.4	249.2	251.6	253.2	250.3	250.9	1.5	ET AAS
07	249.2	253.3	256.2	260.1	257.9	256.1	255.5	3.8	ET AAS
01	260.9	258.7	260.0	262.3	259.9	260.9	260.5	1.2	ICP OES
05	267.6	265.9	264.6	265.3	268.5	265.2	266.2	1.5	F AAS

M (mg/kg): 255.4
 SD_M (mg/kg): 8.5
 SD_M/√N (mg/kg): 3.8

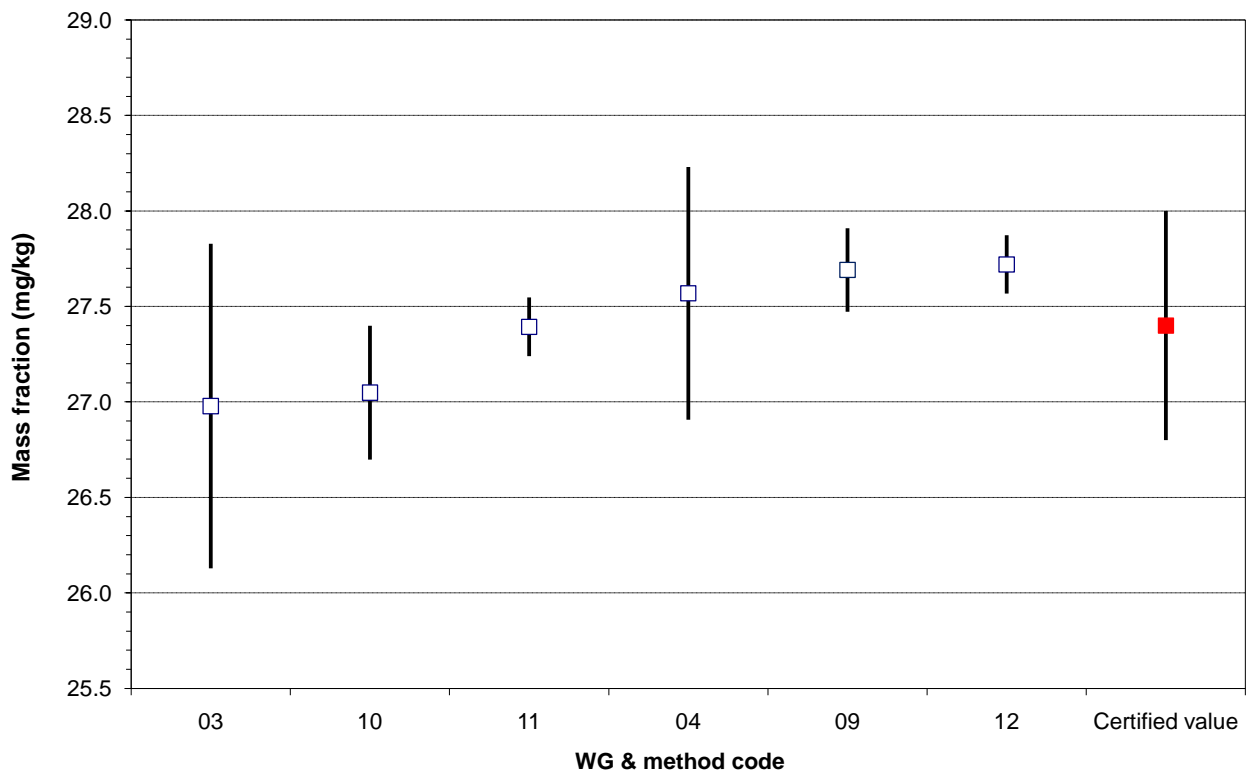


Certification study (measurement results of participants)

Mercury

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
03	26.39	26.69	25.87	27.08	27.63	28.21	26.98	0.85	ICP OES
10	27.35	26.66	26.67	27.37	27.36	26.88	27.05	0.35	CV AFS
11	27.29	27.48	27.57	27.15	27.49	27.38	27.39	0.15	CV AAS
04	27.73	27.38	26.45	28.19	28.25	27.41	27.57	0.66	ICP OES
09	27.52	27.46	27.72	27.95	27.55	27.95	27.69	0.22	CV AAS
12	27.94	27.74	27.79	27.55	27.76	27.54	27.72	0.15	AMA

M (mg/kg): 27.40
 SD_M (mg/kg): 0.32
 SD_M/√N (mg/kg): 0.13

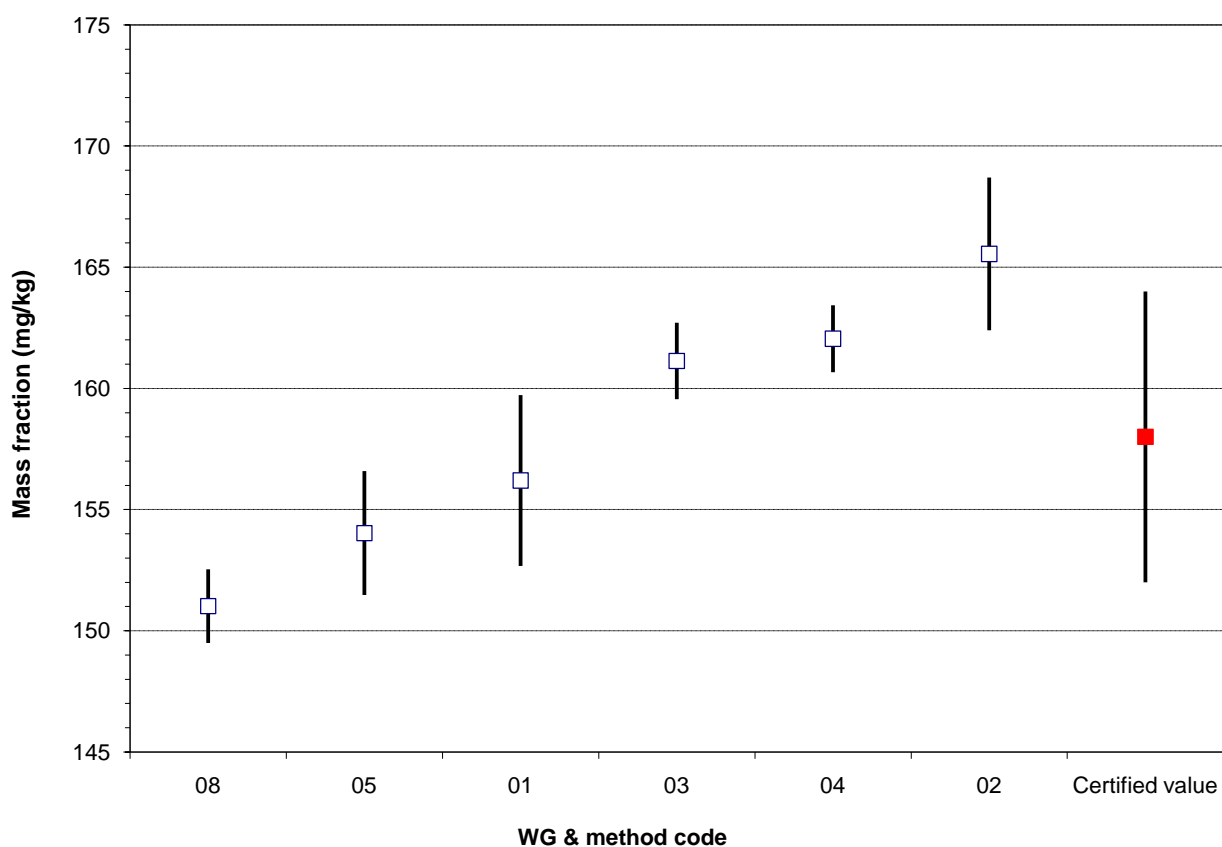


Certification study (measurement results of participants)

Nickel

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
08	151.7	153.5	149.5	151.0	151.0	149.4	151.0	1.5	ET AAS
05	156.8	156.8	154.0	154.2	150.4	152.0	154.0	2.6	F AAS
01	156.1	156.5	149.5	157.0	158.7	159.4	156.2	3.5	ICP OES
03	159.3	159.2	161.3	161.6	162.4	163.0	161.1	1.6	ICP OES
04	162.3	159.8	161.2	162.2	163.3	163.5	162.1	1.4	ICP OES
02	166.4	161.9	167.2	167.9	161.3	168.6	165.6	3.2	ICP-MS

M (mg/kg): 158.3
 SD_M (mg/kg): 5.5
 SD_M/√N (mg/kg): 2.2

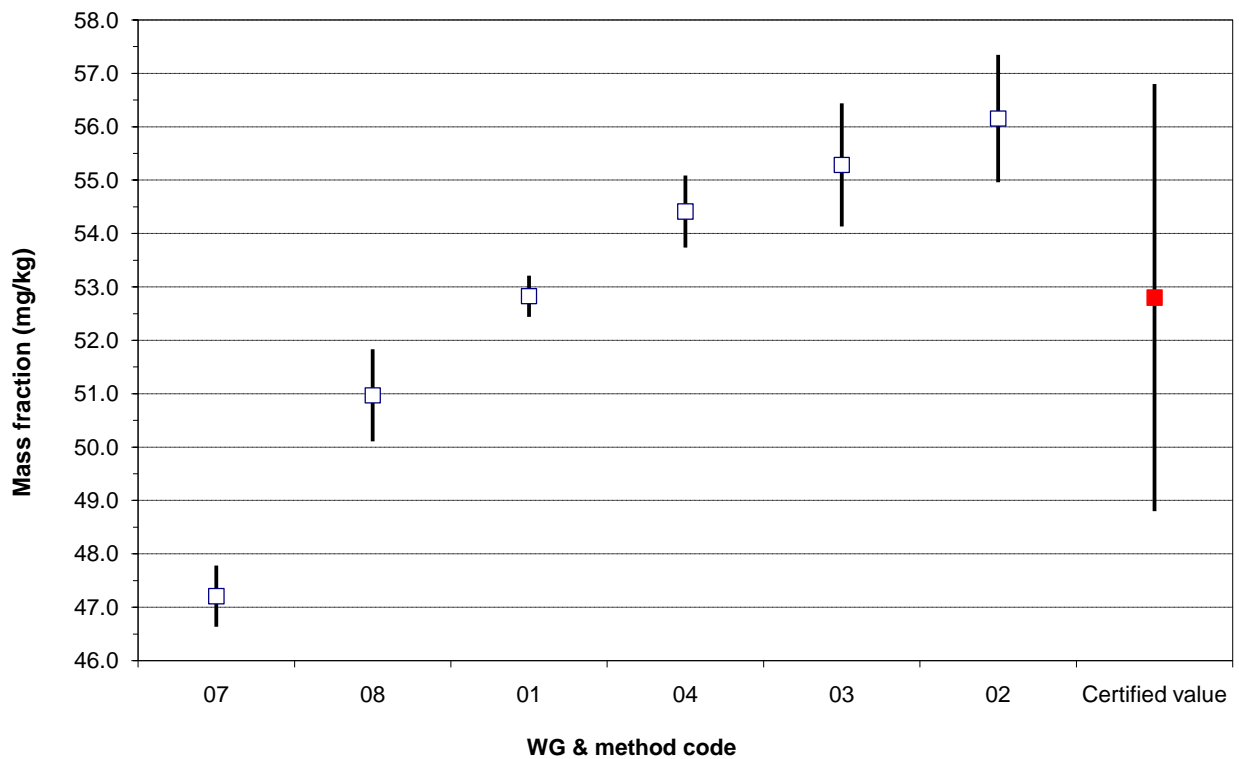


Certification study (measurement results of participants)

Vanadium

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
07	47.02	46.17	47.55	47.50	47.78	47.23	47.21	0.57	ET AAS
08	50.68	52.01	51.69	51.04	50.85	49.55	50.97	0.86	ET AAS
01	52.76	53.22	53.30	52.84	52.31	52.52	52.83	0.39	ICP OES
04	55.48	54.01	54.78	54.55	54.08	53.57	54.41	0.67	ICP OES
03	54.40	53.86	54.81	55.79	55.81	57.04	55.29	1.15	ICP OES
02	54.99	54.63	57.20	57.46	55.78	56.86	56.15	1.19	ICP-MS

M (mg/kg): 52.81
 SD_M (mg/kg): 3.31
 SD_M/√N (mg/kg): 1.35



Certification study (measurement results of participants)

Zinc

WG & method code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	#5 (mg/kg)	#6 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
04	2006	1980	2005	2018	2016	2003	2005	14	ICP OES
06	2001	2013	2020	2026	2007	2030	2016	11	F AAS
01	2001	2022	2040	2040	2022	2032	2026	15	ICP OES
05	2048	2024	2020	2060	2091	2063	2051	27	F AAS
02	2033	2050	2113	2110	2071	2048	2071	34	ICP-MS

M (mg/kg): 2034
 SD_M (mg/kg): 27
 SD_M/√N (mg/kg): 12

