Certification Report

Certified Reference Material

BAM-U115

Aqua Regia Extractable Trace Elements in Soil

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BAM holds an accreditation as a reference material producer according to ISO Guide 34 in combination with ISO/IEC 17025. This accreditation is valid only for the scope as specified in the certificate D-RM-11075-01-00. DAkkS is a signatory of the multilateral agreement (MLA) between EA, ILAC and IAF for mutual acceptance.	DAkkS Deutsche Akkreditierungsstelle D-RM-11075-01-00

Summary

This report describes the certification of a soil reference material for the determination of aqua regia extractable mass fractions of As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn.
The certified reference material (CRM) BAM-U115 is intended for the verification of measurement results obtained by standardized analytical protocols. As any reference material, it can also be used for routine performance checks (quality control charts) or validation studies.

The following mass fractions were certified:

Element	Extraction according to **EN 16174, Method A** *) (open vessel, reflux conditions)		Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)	
	Mass fraction[1] in mg/kg	**Uncertainty** U[2] in mg/kg	**Mass fraction**[1] in mg/kg	**Uncertainty** U[2] in mg/kg
As	27.7	0.9	27.9	1.1
Cd	4.52	0.17	4.65	0.16
Co	7.35	0.28	7.3	0.4
Cr	96.9	2.7	99.6	2.9
Cu	167	5	171	6
Hg	4.00	0.17	4.07	0.14
Ni	29.3	1.1	29.9	1.0
Pb	164	6	169	5
V	22.4	1.1	23.5	1.1
Zn	342	9	349	12

[1] Unweighted mean value of the means of accepted datasets obtained by at least 11 different laboratories and/or different methods of measurement. The certified values are corrected to the dry mass content of the material determined according to ISO 11465. They are operationally defined by the analytical protocols given in EN 16174.

[2] Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008).

*) Extraction procedure according to EN 16174, Method A, is identical to the analytical protocol given in ISO 11466.

CRM BAM-U115 is provided as a powder with particle sizes below 63 µm in a 100 mL screw-capped brown glass bottle containing (53 ± 1) g. The minimum amount of sample to be used for the determination of aqua regia extractable mass fractions of elements is 3 g when applying extraction according to Method A, and 0.5 g when applying extraction according to Method B (as prescribed by European Standard EN 16174).

The certified values are valid for a period of 36 months beginning with the dispatch of the reference material from BAM.

Contents

		Page
1	Introduction	1
2	Candidate material	1
3	Homogeneity study	1
4	Stability study	2
5	Inter-laboratory comparison (ILC)	4
5.1	Design of the certification study	4
5.2	Participants and used analytical methods	5
5.3	Statistical evaluation of ILC-results	6
6	Certified values and uncertainties	6
7	Metrological traceability	8
8	Additional material information	8
9	Information on the proper use of CRM BAM-U115	8
9.1	Recommended use	8
9.2	Transport, storage and handling	8
9.3	Shelf life	9
9.4	Safety information	9
9.5	Legal notice	9
10	References	10
11	Annexes	11
	List of used abbreviations	11
	Annex A: Measurement results of ILC-participants	12
	Annex B: Outcome of statistical tests on ILC-results	42
	Annex C: Homogeneity study (measurement results)	59
	Annex D: Stability study (measurement results)	69
	Annex E: Extraction procedures according to EN 16174	74

1 Introduction

The determination of trace element contents of soils after extraction with aqua regia is a very common analytical task in the daily practice of testing laboratories involved in the assessment and monitoring 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 this purpose 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.

The intention of the project described in this report was to certify aqua regia extractable mass fractions of the environmentally most relevant elements As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn. Because these mass fractions are operationally defined, strict adherence to an agreed extraction procedure is requested as the basic prerequisite for obtaining comparable analytical results.
For this reason, in the course of the current certification project the two extraction protocols given in EN 16174 [1] as Method A and Method B were followed (see Annex E). Method A is based on thermal heating in an open apparatus under reflux conditions in analogy to the extraction procedure prescribed by ISO 11466 [2], whereas Method B is performed as a pressurised microwave-assisted extraction in a closed vessel at (175 ± 5) °C.

The certification of reference material BAM-U115 was carried out according to the "Guidelines for the Development and Production of BAM Reference Materials" [3] and in full compliance with the relevant ISO Guides [4 - 6].

2 Candidate material

The starting material for preparing CRM BAM-U115 was a mixture of sandy and loamy soils collected at different industrially contaminated sites 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. Homogenization and bottling of the ground material were performed using a spinning riffler according to the so-called "cross-riffling scheme" [7]. A total of 400 bottles each containing (53 ± 1) g were produced in November 2015 and stored at (20 ± 3) °C.

3 Homogeneity study

A total of 12 bottled units of the candidate material were selected using a systematic sample picking scheme following the sequence of bottling to give complete coverage of the production batch.

From each selected unit four sub-samples were analyzed applying the extraction procedure according to EN 16174, Method B, and using sample intakes of 0.5 g. Each one sub-sample per unit was analyzed together under repeatability conditions in one run with one calibration. To minimize the risk of a possible calibration bias between the four sub-sample runs, each time two additional control samples were analyzed. The results obtained for these control samples were used to normalize the calibration status of the subsequent measurement series.
All measurement results and used analytical methods are given in Annex C.

The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budgets were calculated according to ISO Guide 35 [6] using Eq. (1) and Eq. (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} are given in the following Table 1.

Table 1: Relative uncertainty contributions due to possible sample inhomogeneity

Element	$s_{bb,r}$ (%)	$u_{bb,r}^{*}$ (%)	$u_{bb,r}$ (%)
As	$MS_{among} < MS_{within}$	0.56	0.56
Cd	0.41	0.33	0.41
Co	0.61	0.28	0.61
Cr	$MS_{among} < MS_{within}$	0.35	0.35
Cu	0.45	0.33	0.45
Hg	$MS_{among} < MS_{within}$	0.88	0.88
Ni	0.28	0.44	0.44
Pb	0.39	0.37	0.39
V	$MS_{among} < MS_{within}$	0.41	0.41
Zn	0.44	0.25	0.44

NOTE: Although the minimum sample intake required for extraction according to Method A is much larger than for Method B (3 g vs. 0.5 g) and therefore less impact of possible sample inhomogeneity on measurement results is to be expected, the same relative uncertainty contributions $u_{bb,r}$ were taken into account when calculating the combined uncertainties of certified values referring to extraction according to Method A and Method B, respectively.

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. Nevertheless, a stability check of the bottled material was performed.

Therefore, immediately after bottling selected units were stored at a temperature of -20 °C, +20 °C, +40 °C and +60 °C, respectively (the indicated temperature values imply a tolerance of ±3 °C).

After a storage time of 2, 4 and 6 months, respectively, two bottles per temperature level were analyzed in duplicate for aqua regia extractable mass fractions applying extraction according to

EN 16174, Method A. This procedure was chosen because of the larger sample intake compared to Method B in view to minimize the impact of possible sample inhomogeneity.
The extraction solutions were analyzed under repeatability conditions in one run with one calibration. The measurement results (see Annex D) were evaluated for each analyte calculating the ratios R_t and their uncertainties u_t using Eq. (3) and Eq. (4), respectively:

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

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

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

Table 2: Results of the stability test after storage times of 2, 4 and 6 months, respectively

Element	Storage time	$R_t \pm u_t$		
		Storage at 20 °C	Storage at 40 °C	Storage at 60 °C
As	2 months	1.0144 ± 0.0202	0.9967 ± 0.0228	1.0019 ± 0.0220
	4 months	0.9951 ± 0.0267	0.9981 ± 0.0260	1.0013 ± 0.0254
	6 months	0.9963 ± 0.0133	1.0055 ± 0.0132	1.0009 ± 0.0166
Cd	2 months	1.0063 ± 0.0148	1.0001 ± 0.0211	0.9994 ± 0.0155
	4 months	1.0070 ± 0.0287	1.0118 ± 0.0282	1.0128 ± 0.0282
	6 months	1.0043 ± 0.0169	1.0052 ± 0.0152	1.0048 ± 0.0159
Co	2 months	1.0042 ± 0.0207	0.9974 ± 0.0199	0.9996 ± 0.0215
	4 months	1.0083 ± 0.0241	1.0126 ± 0.0242	1.0168 ± 0.0230
	6 months	1.0025 ± 0.0126	1.0049 ± 0.0145	1.0044 ± 0.0107
Cr	2 months	1.0009 ± 0.0102	1.0019 ± 0.0062	0.9995 ± 0.0072
	4 months	1.0030 ± 0.0172	1.0115 ± 0.0252	1.0091 ± 0.0167
	6 months	0.9984 ± 0.0031	1.0009 ± 0.0035	1.0007 ± 0.0066
Cu	2 months	1.0045 ± 0.0087	1.0012 ± 0.0103	0.9974 ± 0.0063
	4 months	0.9972 ± 0.0129	0.9990 ± 0.0126	1.0016 ± 0.0177
	6 months	0.9981 ± 0.0064	1.0046 ± 0.0063	1.0038 ± 0.0094
Hg	2 months	1.0010 ± 0.0179	1.0001 ± 0.0268	0.9921 ± 0.0184
	4 months	0.9938 ± 0.0261	1.0070 ± 0.0268	1.0117 ± 0.0249
	6 months	0.9964 ± 0.0126	1.0033 ± 0.0151	1.0045 ± 0.0131
Ni	2 months	1.0085 ± 0.0233	0.9990 ± 0.0257	0.9991 ± 0.0191
	4 months	0.9960 ± 0.0100	1.0026 ± 0.0182	1.0079 ± 0.0101
	6 months	0.9964 ± 0.0119	1.0076 ± 0.0178	1.0113 ± 0.0146

Table 2 (continued): Results of the stability test after storage times of 2, 4 and 6 months, respectively

Element	Storage time	$R_t \pm u_t$		
		Storage at 20 °C	Storage at 40 °C	Storage at 60 °C
Pb	2 months	1.0047 ± 0.0111	0.9910 ± 0.0098	0.9879 ± 0.0138
	4 months	1.0077 ± 0.0287	1.0052 ± 0.0270	1.0075 ± 0.0280
	6 months	0.9925 ± 0.0092	0.9965 ± 0.0071	0.9948 ± 0.0078
V	2 months	1.0057 ± 0.0125	1.0047 ± 0.0118	0.9961 ± 0.0067
	4 months	1.0119 ± 0.0209	1.0060 ± 0.0156	1.0028 ± 0.0193
	6 months	0.9983 ± 0.0096	1.0073 ± 0.0138	1.0069 ± 0.0091
Zn	2 months	1.0016 ± 0.0080	0.9949 ± 0.0070	0.9932 ± 0.0113
	4 months	1.0045 ± 0.0194	1.0048 ± 0.0190	1.0041 ± 0.0189
	6 months	1.0017 ± 0.0085	1.0040 ± 0.0086	1.0008 ± 0.0088

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 as well as sample inhomogeneity 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.

Measurement results obtained in the course of the stability study were evaluated using software SoftCRM, version 1.2.2 [8]. A significant impact of storage conditions on the stability of the certified properties could not be detected, neither of storage time nor of temperature (up to +60 °C). In all cases the slope of the linear regression did not differ significantly from zero. For this reason, taking into account an expansion of the total uncertainty of the certified values by an 'instability component' 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 36 months after dispatch given in the certificate is maintained by post-certification measurements performed at BAM.

5 Inter-laboratory comparison (ILC)

5.1 Design of the certification study

The certification study was organized as an inter-laboratory comparison (ILC). Laboratories invited to participate were selected on the basis of their expertise demonstrated in the course of preceding proficiency tests or validation projects organized by BAM in the field of inorganic soil analysis.
Finally, a total of 17 laboratories took part in the ILC carried out in May/June 2016. All of them declared to operate an internal quality management system accredited to ISO/IEC 17025 [9] and covering the determination of aqua regia extractable trace elements in soils.
The strict observance of the requirements of EN 16174 concerning the extraction procedures to be applied as well as additional instructions given by BAM had been assured by all laboratories in advance. For analysis of the extraction solutions, participants were free to use the method of their choice.

Each participating laboratory received one unit of the bottled candidate material and had to analyze four independent sub-samples. In addition, the dry mass content of the soil material had to be determined on separate sub-samples by drying to constant mass at (105 ± 2) °C according to

ISO 11465 [10]. All reported aqua regia extractable mass fractions were corrected to the dry mass content of the soil sample.

5.2 Participants and used analytical methods

Participating laboratories in alphabetical order (*not identical with the order of laboratory code numbers given in Annex A*):

AGROLAB Agrar und Umwelt GmbH, Sarstedt (Germany)

ALcontrol Laboratories BV, Rotterdam (The Netherlands)

ALS Analytik Labor Schirmacher GmbH, Hamburg (Germany)

ALS Scandinavia AB, Luleå (Sweden)

AZBA – Analytisches Zentrum Berlin-Adlershof GmbH, Berlin (Germany)

Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin (Germany)

Central Institute for Supervising and Testing in Agriculture (UKZUZ), Brno (Czech Republic)

Central Mining Institute, Laboratory of Waste Analyses, Katowice (Poland)

Eurofins Umwelt Ost GmbH, Niederlassung Freiberg, Bobritzsch-Hilbersdorf (Germany)

Eurofins Umwelt West GmbH, Wesseling (Germany)

Fraunhofer Institut für Molekularbiologie und Angewandte Oekologie (IME), Umweltprobenbank und Elementanalytik, Schmallenberg (Germany)

ICA – Institut für Chemische Analytik GmbH, Leipzig (Germany)

UCL Umwelt Control Labor GmbH, Kiel (Germany)

UCL Umwelt Control Labor GmbH, Lünen (Germany)

SGS INSTITUT FRESENIUS GmbH, Herten (Germany)

SPECTRO Analytical Instruments GmbH, Kleve (Germany)

WESSLING GmbH, Labor Hannover, Hannover (Germany)

BAM delivered two independent datasets. Participant with code number 07 applied two different analytical methods for the determination of Hg in the extraction solutions. These results are indicated in the respective tables and graphs of Annex A as 7a (ICP-OES) and 7b (CV-AAS or CV-AFS, respectively).

Not all of the participants did apply both extraction methods under investigation; some of them did also not determine the full range of relevant elements.

For determination of element concentrations in the aqua regia extraction solutions the following analytical methods were used by the participants:

- Automatic mercury analyzer (AMA)
- Cold-vapour atomic absorption spectrometry (CV-AAS)
- Cold-vapour atomic fluorescence spectrometry (CV-AFS)
- Inductively coupled plasma mass spectrometry (ICP-MS)
- Inductively coupled plasma optical emission spectrometry (ICP-OES)

5.3 Statistical evaluation of ILC-results

The measurement results obtained by participating laboratories are compiled in Annex A. 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 [8]. The following tests were carried out:

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

Grubbs test, Dixon test and Nalimov test: Outlying means?

Cochran test: Outlying variances?

Bartlett test: Variances homogeneous?

Snedecor F-test: Differences between datasets statistically significant?

Kolmogorov-Smirnov-Lilliefors test and Skewness & Kurtosis test: Normal distribution of the means?

The results of these tests are summarized in Annex B in Tables B.1a to B.20 (with indication of the respective level of significance, $\alpha = 0.05$ or $\alpha = 0.01$).

An individual dataset was excluded from further data processing only in case that it had been identified as Nalimov- or Cochran-outlier at a level of significance $\alpha = 0.01$.

6 Certified values and uncertainties

The unweighted means of accepted dataset means were taken as the best estimates $w_{element}$ 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 dataset means ($SD_M/\sqrt{N}$; see Annex A) were taken as uncertainty contributions u_{ILC} resulting from the inter-laboratory comparison.

Additionally, the following uncertainty components were taken into account:

u_{bb} uncertainty due to potentially hidden inhomogeneity of the material (see Clause 3),

u_{prec} uncertainty reflecting the average precision of accepted laboratory means and being calculated according to Eq. (5):

$$u_{prec} = \sqrt{\sum_{i=1}^{N} SD_i^2 / nN} \qquad (5)$$

where SD_i is the standard deviation of the results of an individual participant, N is the number of accepted individual datasets, and n is the number of replicate sub-samples analyzed by each participant.

The different contributions to the overall uncertainties of the certified mass fractions were combined using the following Eq. (6):

$$u_{CRM} = \sqrt{u_{ILC}^2 + u_{bb}^2 + u_{prec}^2} \qquad (6)$$

Calculated aqua regia extractable mass fractions $w_{element}$ and absolute values of the different uncertainty components referring to extraction according to EN 16174, Method A and Method B, are given in Table 3 and Table 4, respectively.

Table 3: Mass fractions and uncertainty components for the relevant analytes in CRM BAM-U115; extraction according to EN 16174, Method A (before rounding)

Element	$w_{element}$ in mg/kg	u_{ILC} in mg/kg	u_{prec} in mg/kg	u_{bb} in mg/kg	u_{CRM} in mg/kg
As	27.68	0.376	0.186	0.155	0.447
Cd	4.521	0.0690	0.0392	0.0185	0.0815
Co	7.346	0.1059	0.0772	0.0448	0.1385
Cr	96.85	0.954	0.888	0.339	1.347
Cu	166.6	1.45	1.69	0.75	2.35
Hg	4.004	0.0660	0.0327	0.0352	0.0816
Ni	29.32	0.345	0.373	0.129	0.524
Pb	164.1	2.33	0.93	0.64	2.59
V	22.36	0.449	0.280	0.092	0.537
Zn	342.4	3.23	2.34	1.51	4.26

Table 4: Mass fractions and uncertainty components for the relevant analytes in CRM BAM-U115; extraction according to EN 16174, Method B (before rounding)

Element	$W_{element}$ in mg/kg	u_{ILC} in mg/kg	u_{prec} in mg/kg	u_{bb} in mg/kg	u_{CRM} in mg/kg
As	27.85	0.319	0.417	0.156	0.548
Cd	4.646	0.0579	0.0499	0.0191	0.0788
Co	7.321	0.1588	0.0703	0.0447	0.1793
Cr	99.58	0.975	1.006	0.349	1.444
Cu	171.4	1.96	1.83	0.77	2.79
Hg	4.066	0.0311	0.0488	0.0358	0.0680
Ni	29.85	0.400	0.243	0.131	0.486
Pb	168.6	1.36	1.77	0.66	2.33
V	23.52	0.422	0.314	0.096	0.535
Zn	348.6	4.43	3.02	1.53	5.58

The expanded uncertainty U was obtained by multiplying the combined uncertainty u_{CRM} by a coverage factor $k = 2$, giving a level of confidence of approximately 95 % to be associated with the interval $\pm U$ around the certified mass fraction [11].

The certified aqua regia extractable mass fractions of trace elements in CRM BAM-U115 and their corresponding expanded uncertainties after rounding are summarized on Page II of this report.

7 Metrological traceability

The certified aqua regia extractable mass fractions of trace elements in CRM BAM-U115 are operationally defined referring to the analytical protocols prescribed by EN 16174, Method A and Method B.

8 Additional material information

The main matrix constituents of CRM BAM-U115 were determined by semi-quantitative X-ray fluorescence (XRF) analysis. Obtained non-certified results are given in Table 5.

Table 5: Matrix composition of CRM BAM-U115 (informative values)

Element	Si	Al	Ca	Fe	K
Mass fraction in %	34.7	3.2	3.5	2.2	1.4

Mass fraction of any other element detectable with XRF was determined to be less than 0.2 %

Additional informative analytical results obtained in the course of sample characterization are summarized in Table 6.

Table 6: Informative secondary parameters characterizing CRM-BAM-U115

Parameter	Mass fraction in %	Analytical method
Dry mass content at 105 °C	98.6	ISO 11465 [10]
Loss on ignition at 550 °C	8.3	EN 15935 [12]
Organic carbon (TOC)	2.5	ISO 10694 [13]
Inorganic carbon (TIC)	1.1	ISO 10694 [13]

9 Information on the proper use of CRM BAM-U115

9.1 Recommended use

The intended purpose of CRM BAM-U115 is the verification of analytical results obtained for aqua regia extractable mass fractions of trace elements in soils applying the standardized procedures prescribed by EN 16174 (Method A and Method B, respectively). In this context it is noted that the extraction procedure according to EN 16174, Method A, is identical to the analytical protocol given in ISO 11466 [2].

As any reference material, CRM BAM-U115 can also be used for routine performance checks (quality control charts) or validation studies.

Please note that it cannot be expected that the two extraction methods specified in EN 16174 provide compatible measurement results for all types of soil samples. Depending on the origin of the material to be analyzed, extraction with aqua regia using the microwave-assisted closed vessel procedure might be prone to result in higher mass fractions for certain elements, in particular for Cr, Pb and V.

9.2 Transport, storage and handling

CRM BAM-U115 can be shipped at ambient temperature. Upon receipt the material should be stored at a temperature below 25 °C in its original tightly closed bottle. When handling the sample, the bottle shall be left unclosed as briefly as possible. Care should be taken to avoid moisture pick-up once the bottle is opened.

BAM cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

The material should be used as it is from the bottle. However, before taking a sub-sample a re-homogenisation by manual shaking of the closed bottle is strongly recommended.

It should be kept in mind that aqua regia extractable mass fractions of elements in soil are operationally defined. When performing analyses, the analytical protocols given in EN 16174 (Method A and Method B) must strictly be followed.

All analytical results have to be corrected for dry mass content of the material which has to be determined according to ISO 11465 using a separate sub-sample. The value given in the table above (98.6 %) should be regarded as being informative only.

9.3 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 36 months. Post-certification measurements will be conducted in appropriate periods to keep this information up to date.

9.4 Safety information

The usual laboratory safety precautions have to be applied. No hazardous effects are to be expected when the material is used under conditions commonly adopted for the analysis of environmental samples. 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.

9.5 Legal notice

Neither BAM, its contractors nor any person acting on their behalf:

(a) 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

(b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document.

10 References

[1] EN 16174 (2012): Sludge, treated biowaste and soil – Digestion of aqua regia soluble fractions of elements

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

[3] Guidelines for the Development and Production of BAM Reference Materials (February 2016) (available on request)

[4] ISO Guide 31 (2000): Reference materials – Contents of certificates and labels

[5] ISO Guide 34 (2009): General requirements for the competence of reference material producers

[6] ISO Guide 35 (2006): Reference materials – General and statistical principles for certification

[7] 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

[8] SoftCRM, version 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

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

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

[11] ISO/IEC Guide 98-3 (2008): Uncertainty of measurement – Part 3: Guide to the Expression of Uncertainty in Measurement (GUM)

[12] EN 15935 (2012): Sludge, treated biowaste, soil and waste – Determination of loss on ignition

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

11 Annexes

Annex A: Measurement results of ILC-participants

Annex B: Outcome of statistical tests on ILC-results

Annex C: Homogeneity study (measurement results)

Annex D: Stability study (measurement results)

Annex E: Extraction procedures according to EN 16174

List of used abbreviations

(if not explained elsewhere in the report)

M	arithmetic mean of means
N	number of accepted datasets
SD_i	standard deviation of an individual dataset
SD_M	standard deviation of the mean of dataset means

Table A.1a: Measurement results of ILC-participants **As (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
12	25.2	25.7	26.2	25.4	25.63	0.43	ICP-MS
10	25.73	25.96	25.98	26.01	25.92	0.13	ICP-MS
02	26.9	26.9	27.0	26.9	26.93	0.05	ICP-OES
08	26.76	27.83	26.70	27.19	27.12	0.52	ICP-MS
09	27.7	27.5	27.8	27.5	27.63	0.15	ICP.MS
17	28.72	28.21	26.29	27.39	27.65	1.06	ICP-MS
11	27.76	27.18	28.40	27.5	27.71	0.52	ICP-OES
06	27.6	28.5	28.3	28.1	28.13	0.39	ICP-MS
04	28.67	28.11	28.24	28.09	28.28	0.27	ICP-OES
07	28.44	28.47	28.18	28.61	28.43	0.18	ICP-OES
01	28.7	28.8	28.9	29.0	28.85	0.13	ICP-OES
05	30.01	28.88	30.27	30.41	29.89	0.70	ICP-OES

M (mg/kg): **27.68**

SD_M (mg/kg): 1.248

$SD_M/\sqrt{N}$ (mg/kg): 0.376

Dataset of Lab 17 was rejected as an outlier (see Annex B). It is not displayed in Figure A.1a.

Table A.1b: Measurement results of ILC-participants **As (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
15	24.5	24.7	24.7	25.6	24.88	0.49	ICP-MS
18	25.51	26.16	26.49	26.55	26.18	0.48	ICP-OES
12	26.6	26.9	26.4	26.1	26.50	0.34	ICP-MS
02	27.4	26.9	26.4	27.3	27.00	0.45	ICP-OES
17	27.75	26.91	26.60	27.41	27.17	0.51	ICP-MS
06	26.7	26.3	27.5	28.5	27.25	0.97	ICP-MS
04	28.16	28.01	28.56	27.38	28.03	0.49	ICP-OES
03	26.7	29.2	27.8	28.6	28.08	1.08	ICP-MS
16	26.3	28.4	29.4	29.4	28.38	1.46	ICP-MS
08	28.93	28.34	27.86	28.54	28.42	0.45	ICP-MS
07	28.84	27.97	28.43	28.43	28.42	0.36	ICP-OES
09	27.1	27.2	30.0	29.9	28.55	1.62	ICP-MS
10	28.87	28.81	28.43	28.61	28.68	0.20	ICP-MS
01	28.5	28.6	29.2	29.6	28.98	0.52	ICP-OES
13	29.1	29.8	30.5	28.0	29.35	1.07	ICP-OES
05	30.40	31.01	29.02	28.69	29.78	1.10	ICP-OES

M (mg/kg): **27.85**

SD_M (mg/kg): 1.276

$SD_M/\sqrt{N}$ (mg/kg): 0.319

Measurement results of ILC-participants

(graphical presentation)

Arsenic

Aqua regia extractable mass fraction

Figure A.1a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

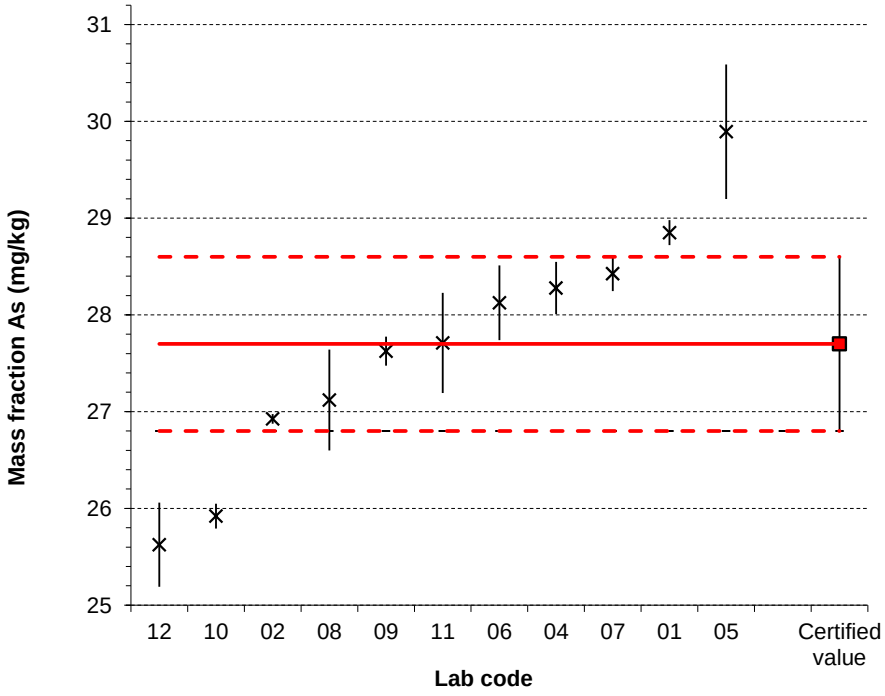


Figure A.1b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

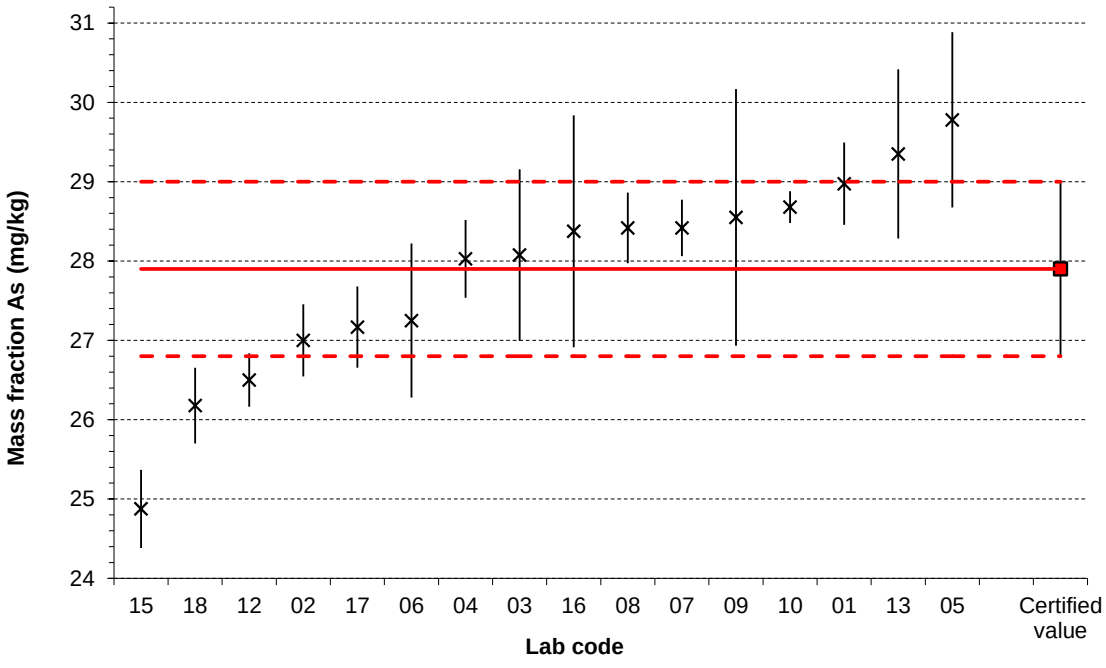


Table A.2a: Measurement results of ILC-participants **Cd (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
17	4.060	4.082	3.922	3.961	4.006	0.077	ICP-MS
12	4.13	4.21	4.25	4.26	4.213	0.059	ICP-MS
10	4.482	4.451	4.382	4.461	4.444	0.043	ICP-MS
11	4.513	4.411	4.522	4.355	4.450	0.081	ICP-OES
02	4.51	4.53	4.55	4.42	4.503	0.057	ICP-OES
07	4.533	4.602	4.545	4.430	4.528	0.072	ICP-OES
06	4.57	4.67	4.37	4.57	4.545	0.126	ICP-MS
01	4.5	4.5	4.6	4.6	4.550	0.058	ICP-OES
08	4.587	4.724	4.575	4.514	4.600	0.089	ICP-MS
09	4.87	4.82	4.62	4.69	4.750	0.115	ICP-MS
14	4.88	4.89	4.78	4.72	4.818	0.082	ICP-OES
04	4.840	4.863	4.831	4.867	4.850	0.018	ICP-OES
05	5.64	5.44	5.58	5.59	5.563	0.086	ICP-OES

M (mg/kg): **4.521**

SD_M (mg/kg): 0.2389

$SD_M/\sqrt{N}$ (mg/kg): 0.0690

Dataset of Lab 05 was rejected as an outlier (see Annex B). It is not displayed in Figure A.2a.

Table A.2b: Measurement results of ILC-participants **Cd (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
17	2.394	2.334	2.258	2.165	2.288	0.099	ICP-MS
18	4.205	4.305	4.287	4.305	4.276	0.048	ICP-OES
12	4.37	4.38	4.26	4.25	4.315	0.070	ICP-MS
15	4.34	4.56	4.18	4.30	4.345	0.159	ICP-MS
03	4.46	4.43	4.32	4.39	4.400	0.061	ICP-MS
09	4.63	4.59	4.47	4.60	4.573	0.070	ICP-MS
02	4.6	4.6	4.6	4.6	4.600	0.000	ICP-OES
10	4.579	4.616	4.609	4.688	4.623	0.046	ICP-MS
13	4.71	4.82	4.69	4.61	4.708	0.087	ICP-OES
07	4.676	4.847	4.606	4.719	4.712	0.101	ICP-OES
04	4.712	4.772	4.830	4.759	4.768	0.049	ICP-OES
01	4.8	4.8	4.8	4.9	4.825	0.050	ICP-OES
16	4.86	4.66	4.96	4.86	4.835	0.126	ICP-MS
08	5.007	5.003	4.740	4.671	4.855	0.175	ICP-MS
06	4.87	4.67	4.87	5.07	4.870	0.163	ICP-MS
14	5.04	5.07	4.84	4.98	4.983	0.102	ICP-OES
05	5.11	5.84	5.01	4.88	5.210	0.430	ICP-OES

M (mg/kg): **4.646**

SD_M (mg/kg): 0.2243

$SD_M/\sqrt{N}$ (mg/kg): 0.0579

Datasets of Lab 05 and Lab 17 were rejected as outliers (see Annex B). They are not displayed in Figure A.2b.

Measurement results of ILC-participants
(graphical presentation)

Cadmium
Aqua regia extractable mass fraction

Figure A.2a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

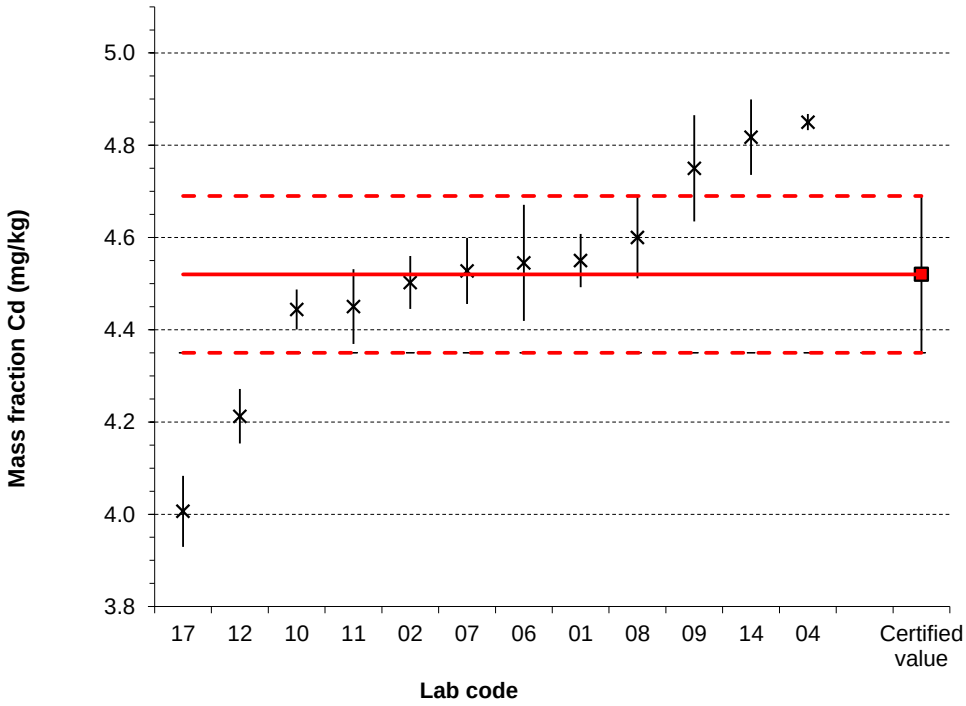


Figure A.2b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

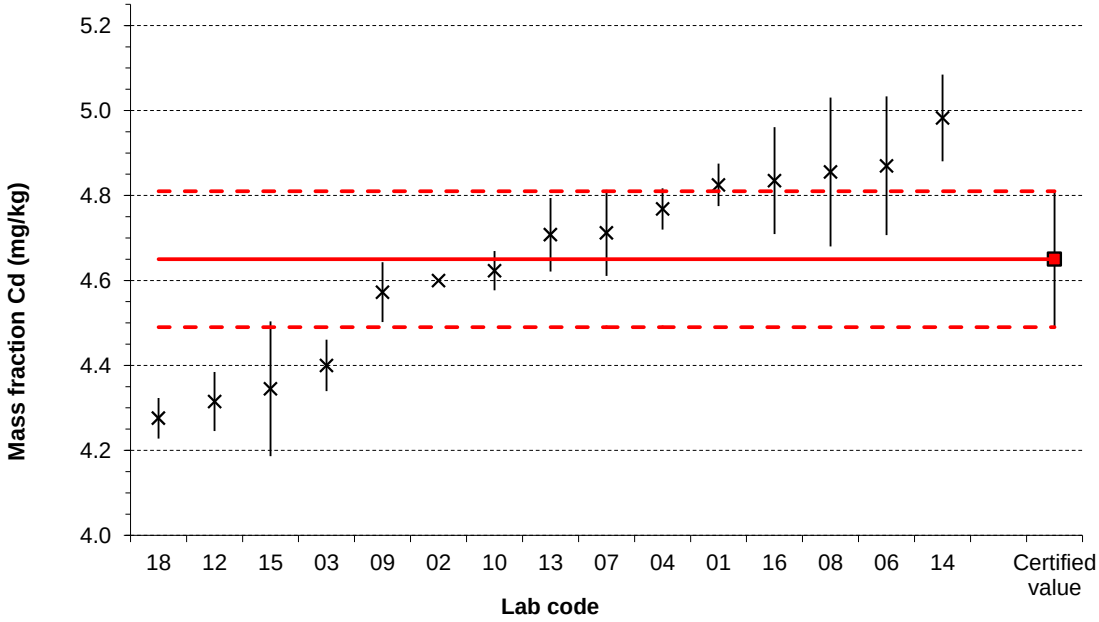


Table A.3a: Measurement results of ILC-participants **Co (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
12	5.990	6.010	5.890	5.720	5.903	0.133	ICP-OES
11	6.68	6.56	6.61	6.45	6.575	0.097	ICP-MS
08	6.699	6.880	7.116	7.089	6.946	0.196	ICP-MS
17	7.35	7.1	6.75	7.39	7.148	0.294	ICP-OES
14	7.22	7.39	7.2	7.22	7.258	0.089	ICP-OES
06	7.210	7.310	7.110	7.410	7.260	0.129	ICP-OES
10	7.296	7.285	7.352	7.383	7.329	0.046	ICP-MS
01	7.4	7.4	7.5	7.5	7.450	0.058	ICP-OES
04	7.443	7.451	7.461	7.481	7.459	0.016	ICP-MS
02	7.53	7.46	7.47	7.5	7.490	0.032	ICP-MS
07	7.381	7.629	7.712	7.62	7.586	0.142	ICP-OES
09	7.480	7.350	7.900	7.680	7.603	0.240	ICP-OES
05	8.24	7.77	8.05	8.16	8.055	0.205	ICP-OES

M (mg/kg): **7.346**

SD_M (mg/kg): 0.3667

$SD_M/\sqrt{N}$ (mg/kg): 0.1059

Dataset of Lab 12 was rejected as an outlier (see Annex B). It is not displayed in Figure A.3a.

Table A.3b: Measurement results of ILC-participants **Co (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
13	5.900	6.090	5.890	5.890	5.943	0.098	ICP-MS
15	6.260	6.610	6.220	6.300	6.348	0.178	ICP-OES
18	6.74	6.72	6.69	6.72	6.718	0.022	ICP-MS
03	6.89	6.97	6.89	6.97	6.930	0.046	ICP-MS
16	6.69	7.09	7.11	7.19	7.020	0.224	ICP-MS
12	7.14	7.14	7.03	7.00	7.078	0.073	ICP-MS
08	7.0	7.0	7.2	7.2	7.092	0.148	ICP-OES
17	7.394	7.211	7.244	7.338	7.297	0.084	ICP-MS
09	7.32	7.15	7.35	7.60	7.355	0.186	ICP-OES
02	7.340	7.480	7.540	7.070	7.358	0.209	ICP-OES
10	7.471	7.402	7.316	7.449	7.410	0.069	ICP-OES
14	7.5	7.5	7.6	7.4	7.500	0.062	ICP-OES
06	7.81	7.71	7.61	7.71	7.710	0.082	ICP-MS
04	7.784	7.869	7.836	7.841	7.833	0.035	ICP-MS
01	8.00	8.10	8.20	8.40	8.175	0.171	ICP-MS
07	8.04	8.42	8.49	8.42	8.341	0.206	ICP-OES
05	8.40	8.36	8.08	8.57	8.353	0.203	ICP-OES

M (mg/kg): **7.321**

SD_M (mg/kg): 0.6546

$SD_M/\sqrt{N}$ (mg/kg): 0.1588

Measurement results of ILC-participants **Cobalt**

(graphical presentation) Aqua regia extractable mass fraction

Figure A.3a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

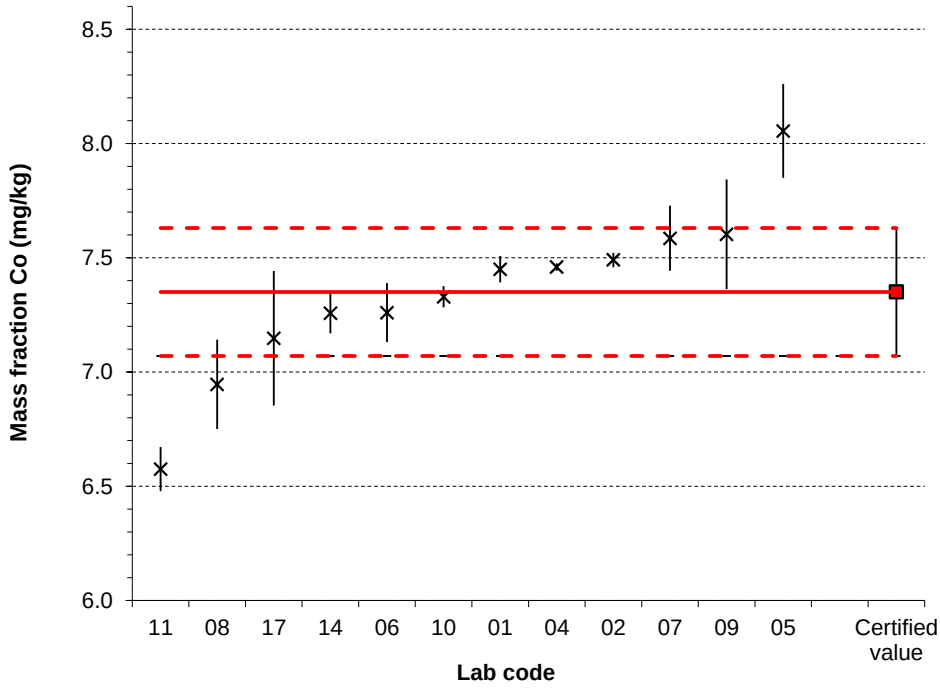


Figure A.3b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

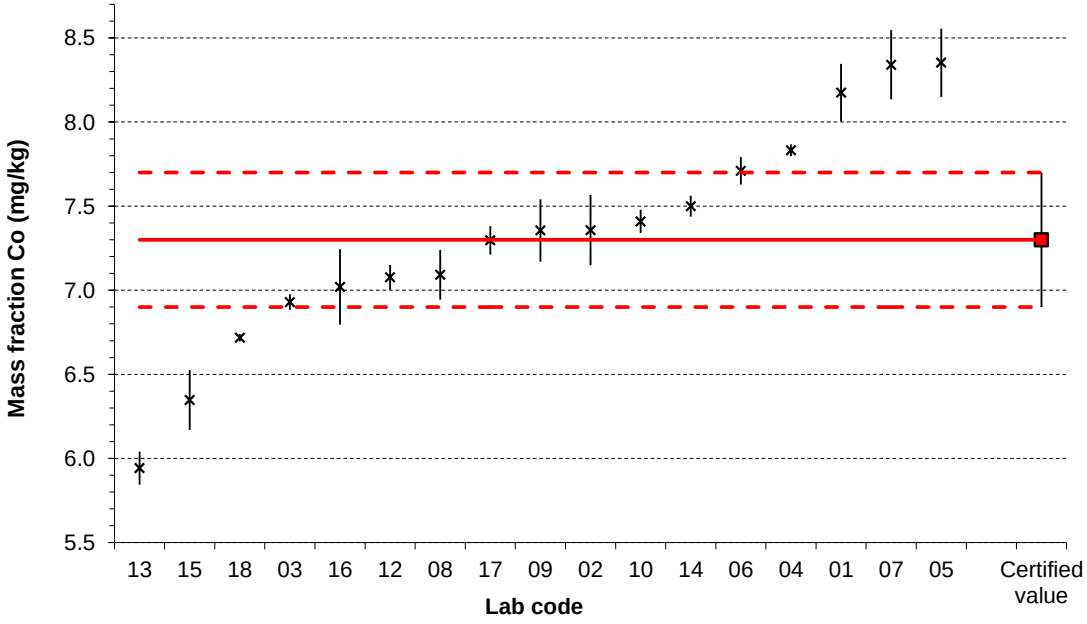


Table A.4a: Measurement results of ILC-participants **Cr (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
11	92.62	89.98	92.74	89.73	91.27	1.63	ICP-OES
04	91.58	91.25	91.58	92.15	91.64	0.37	ICP-OES
05	95.48	90.90	94.38	94.74	93.88	2.04	ICP-OES
12	92.8	94.2	97.2	96.1	95.08	1.96	ICP-MS
07	96.58	96.63	96.53	96.43	96.54	0.09	ICP-OES
02	97.9	97.9	96.8	96.8	97.35	0.64	ICP-OES
08	94.49	97.72	98.10	99.95	97.57	2.27	ICP-MS
10	96.10	98.87	97.47	98.62	97.77	1.27	ICP-MS
09	102	101	98.9	97.1	99.75	2.19	ICP-MS
14	100	101	101	98.7	100.18	1.09	ICP-OES
01	99	100	101	101	100.25	0.96	ICP-OES
17	105.2	100.3	93.38	103.5	100.60	5.22	ICP-MS
06	104	103	95.9	101	100.98	3.61	ICP-MS

M (mg/kg): **96.85**

SD_M (mg/kg): 3.303

$SD_M/\sqrt{N}$ (mg/kg): 0.954

Dataset of Lab 17 was rejected as an outlier (see Annex B). It is not displayed in Figure A.4a.

Table A.4b: Measurement results of ILC-participants **Cr (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
18	91.60	88.78	89.73	89.83	89.99	1.18	ICP-OES
15	90.9	94.5	91.2	95.5	93.03	2.32	ICP-MS
05	91.73	96.86	95.04	92.47	94.03	2.36	ICP-OES
16	90.2	93.2	97.3	96.3	94.25	3.22	ICP-MS
04	94.73	95.14	94.93	94.55	94.84	0.25	ICP-OES
08	93.56	93.42	97.61	96.33	95.23	2.08	ICP-MS
02	102	99.9	99.9	98.7	100.13	1.37	ICP-OES
13	100	103	100	98.9	100.48	1.76	ICP-OES
07	101.90	101.80	100.40	100.50	101.15	0.81	ICP-OES
03	100	102	101	102	101.25	0.96	ICP-MS
10	101.4	103.6	99.92	101.0	101.48	1.55	ICP-MS
17	102.8	98.17	99.59	106.3	101.72	3.62	ICP-MS
09	100	98.7	103	106	101.93	3.26	ICP-MS
12	103	103	101	102	102.25	0.96	ICP-MS
14	102	104	102	103	102.75	0.96	ICP-OES
06	102	105	103	104	103.50	1.29	ICP-MS
01	103	105	106	107	105.25	1.71	ICP-OES

M (mg/kg): **99.58**

SD_M (mg/kg): 3.902

$SD_M/\sqrt{N}$ (mg/kg): 0.975

Dataset of Lab 18 was rejected as an outlier (see Annex B). It is not displayed in Figure A.4b.

Measurement results of ILC-participants
(graphical presentation)

Chromium
Aqua regia extractable mass fraction

Figure A.4a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

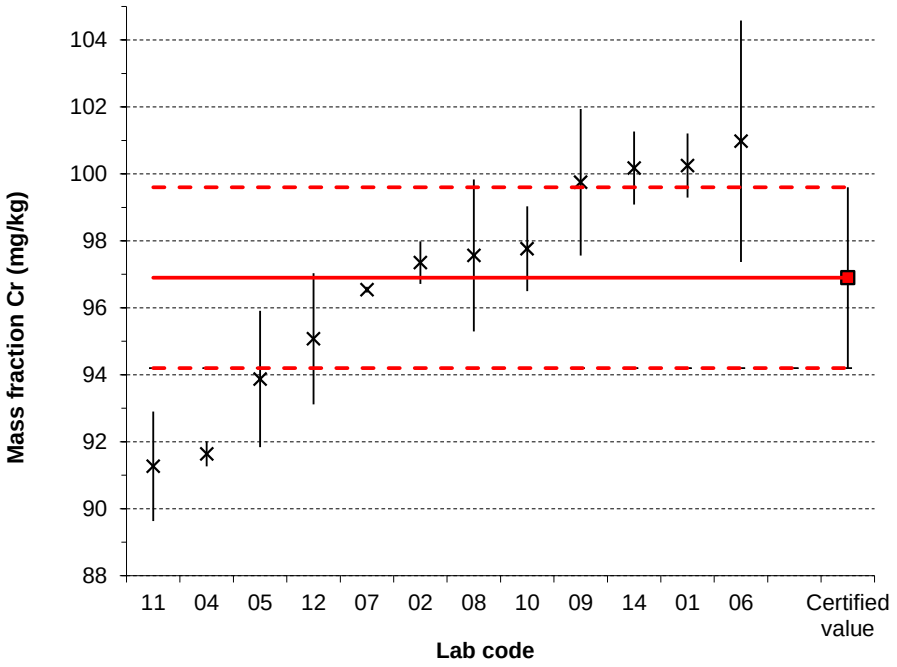


Figure A.4b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

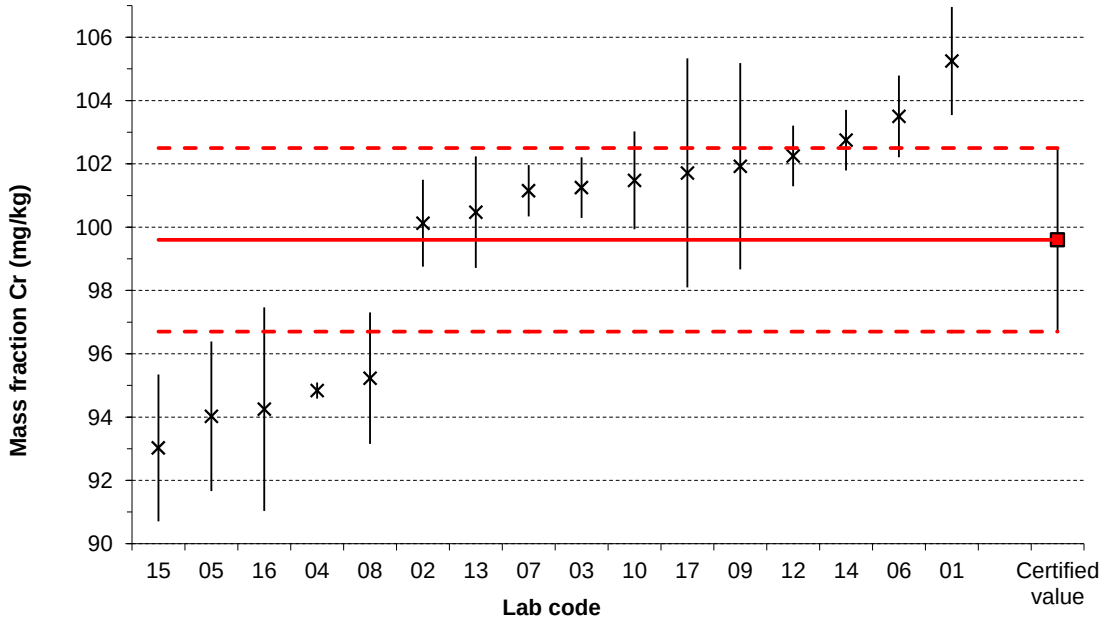


Table A.5a: Measurement results of ILC-participants **Cu (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_I (mg/kg)	Analytical method
12	157	160	160	158	158.8	1.5	ICP-MS
11	163.3	158.4	165.1	160.0	161.7	3.0	ICP-OES
09	159	159	167	164	162.3	3.9	ICP-MS
08	159.4	161.3	167.3	164.1	163.0	3.4	ICP-MS
10	165.2	163.0	164.1	164.2	164.1	0.9	ICP-MS
06	162	161	165	166	163.5	2.4	ICP-MS
04	167.3	167.5	167.2	167.3	167.3	0.1	ICP-OES
01	170	171	171	169	170.3	1.0	ICP-OES
02	172	171	170	169	170.5	1.3	ICP-OES
05	173.9	170.6	165.7	169.8	170.0	3.4	ICP-OES
07	171.7	172.8	173.1	171.5	172.3	0.8	ICP-OES
17	178.9	177.6	162.1	181.4	175.0	8.7	ICP-MS

M (mg/kg): **166.6**

SD_M (mg/kg): 5.01

$SD_M/\sqrt{N}$ (mg/kg): 1.45

Table A.5b: Measurement results of ILC-participants **Cu (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
16	152	162	162	162	159.5	5.0	ICP-MS
03	163	163	162	163	162.8	0.5	ICP-MS
18	162.2	163.4	163.4	164.0	163.3	0.8	ICP-OES
15	160	163	166	171	165.0	4.7	ICP-MS
08	161.8	159.2	168.5	172.6	165.5	6.1	ICP-MS
06	166	169	165	167	166.8	1.7	ICP-MS
04	169.2	170.8	170.6	169.4	170.0	0.8	ICP-OES
05	174.6	166.5	172.7	170.3	171.0	3.5	ICP-OES
09	159.0	160.0	178.0	193.0	172.5	16.2	ICP-MS
10	175.1	176.6	174.4	170.5	174.2	2.6	ICP-MS
14	176	176	173	172	174.3	2.1	ICP-OES
07	174.8	171.7	176.8	174.6	174.5	2.1	ICP-OES
12	173.0	168.0	196.0	163.0	175.0	14.6	ICP-MS
01	178	178	178	182	179.0	2.0	ICP-OES
02	180	180	179	182	180.3	1.3	ICP-OES
17	176.6	192.7	184.4	176.6	182.6	7.7	ICP-MS
13	187	183	185	177	183.0	4.3	ICP-OES

M (mg/kg): **171.4**

SD_M (mg/kg): 7.57

$SD_M/\sqrt{N}$ (mg/kg): 1.96

Datasets of Lab 09 and Lab 12 were rejected as outliers (see Annex B). They are not displayed in Figure A.5b.

Measurement results of ILC-participants (graphical presentation)

Copper

Aqua regia extractable mass fraction

Figure A.5a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

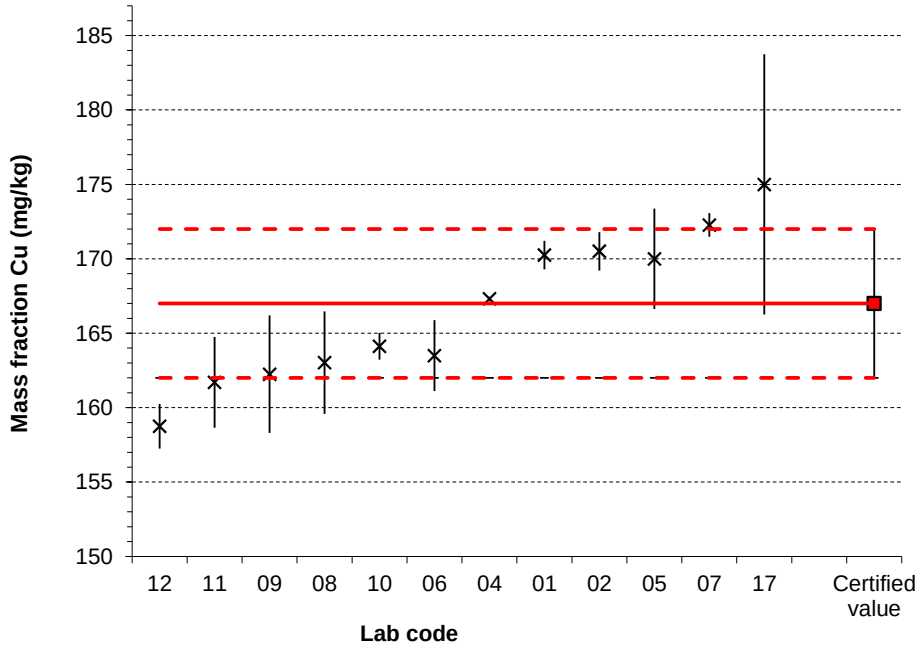


Figure A.5b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

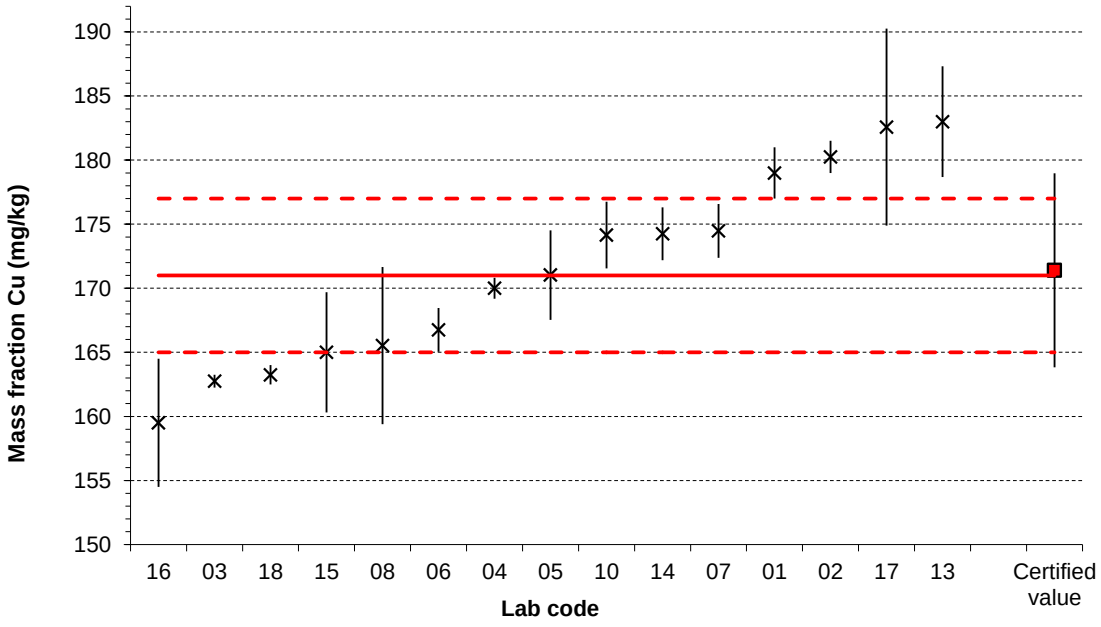


Table A.6a: Measurement results of ILC-participants **Hg (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
02	3.55	3.58	3.66	3.61	3.600	0.047	CV-AAS
12	3.67	3.73	3.80	3.65	3.713	0.068	CV-AAS
06	3.66	3.86	3.86	3.76	3.785	0.096	CV-AAS
10	3.838	3.943	3.883	3.932	3.899	0.048	ICP-MS
07a	4.042	3.893	4.055	3.905	3.974	0.087	ICP-OES
01	3.92	4.04	4.01	3.97	3.985	0.052	ICP-OES
08	4.024	4.170	3.988	4.060	4.061	0.079	ICP-MS
11	4.113	4.048	4.108	4.030	4.075	0.042	CV-AAS
07b	4.160	4.129	4.152	4.170	4.153	0.017	CV-AAS
14	4.12	4.24	4.23	4.08	4.168	0.080	CV-AFS
17	4.333	4.320	3.940	4.135	4.182	0.185	CV-AAS
04	4.286	4.233	4.303	4.195	4.254	0.049	AMA
09	4.46	4.29	4.37	4.43	4.388	0.075	ICP-MS
05	5.72	5.69	5.79	5.56	5.690	0.096	CV-AAS

M (mg/kg): **4.004**

SD_M (mg/kg): 0.2287

$SD_M/\sqrt{N}$ (mg/kg): 0.0660

Datasets of Lab 05 and Lab 17 were rejected as outliers (see Annex B). They are not displayed in Figure A.6a.

Table A.6b: Measurement results of ILC-participants **Hg (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)	Analytical method
09	3.83	3.61	3.62	3.74	3.700	0.105	ICP-MS
12	4.00	3.90	3.86	3.91	3.918	0.059	CV-AAS
02	4.00	3.94	3.84	3.96	3.935	0.068	CV-AAS
15	3.87	4.00	3.91	4.15	3.983	0.124	CV-AAS
17	4.032	3.784	4.012	4.107	3.984	0.139	CV-AAS
07a	4.043	4.039	3.949	4.002	4.008	0.044	ICP-OES
01	4.0	4.0	4.0	4.1	4.025	0.050	ICP-OES
14	4.10	3.86	4.06	4.15	4.043	0.127	CV-AFS
10	4.042	4.056	4.102	4.026	4.057	0.033	ICP-MS
06	4.06	4.16	3.96	4.16	4.085	0.096	CV-AAS
04	4.194	4.104	4.203	4.031	4.133	0.081	AMA
08	4.119	4.395	4.098	4.075	4.172	0.150	ICP-MS
07b	4.164	4.285	4.274	4.261	4.246	0.056	CV-AFS
16	4.44	4.14	4.20	4.32	4.275	0.133	ICP-MS
03	3.86	4.73	4.32	4.46	4.343	0.364	ICP-MS
13	4.49	4.61	4.65	4.57	4.580	0.068	CV-AAS
05	5.66	5.48	5.61	5.75	5.625	0.113	CV-AAS

M (mg/kg): **4.066**

SD_M (mg/kg): 0.1121

$SD_M/\sqrt{N}$ (mg/kg): 0.0311

Datasets of Lab 03, Lab 05, Lab 09 and Lab 13 were rejected as outliers (see Annex B).
They are not displayed in Figure A.6b.

Measurement results of ILC-participants
(graphical presentation)

Mercury
Aqua regia extractable mass fraction

Figure A.6a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

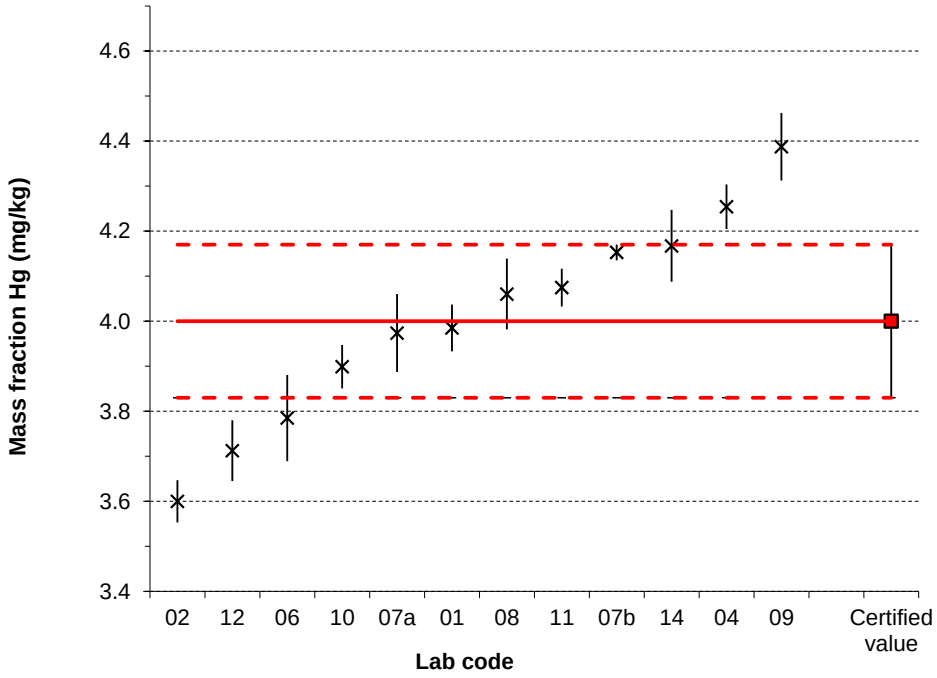


Figure A.6b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

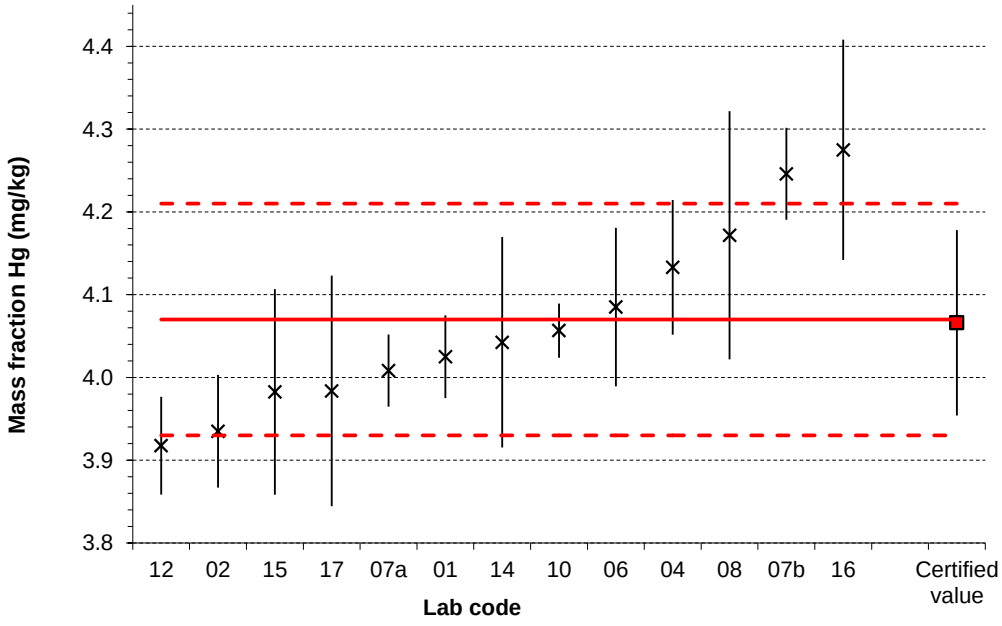


Table A.7a: Measurement results of ILC-participants **Ni (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
11	27.56	26.80	27.71	26.78	27.21	0.49	ICP-OES
04	28.31	28.23	28.26	28.41	28.30	0.08	ICP-OES
10	29.44	28.16	27.72	27.95	28.32	0.77	ICP-MS
12	27.7	28.0	29.1	29.0	28.45	0.70	ICP-MS
07	28.39	28.90	28.28	28.27	28.46	0.30	ICP-OES
14	28.3	28.2	28.1	30.2	28.70	1.00	ICP-OES
09	28.6	29.7	28.7	29.3	29.08	0.52	ICP-MS
08	28.68	29.71	29.95	29.99	29.58	0.61	ICP-MS
05	31.50	28.24	29.30	29.47	29.63	1.36	ICP-OES
02	30.5	30.6	30.6	30.6	30.58	0.05	ICP-OES
06	30.6	30.3	31.4	30.5	30.70	0.48	ICP-MS
17	31.98	31.19	28.70	31.03	30.73	1.41	ICP-MS
01	31.2	31.3	31.6	31.7	31.45	0.24	ICP-OES

M (mg/kg): **29.32**

SD_M (mg/kg): 1.244

$SD_M/\sqrt{N}$ (mg/kg): 0.345

Table A.7b: Measurement results of ILC-participants **Ni (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
05	26.10	27.02	27.83	26.26	26.80	0.79	ICP-OES
15	27.8	28.4	27.8	29.0	28.25	0.57	ICP-MS
07	28.32	28.41	28.44	28.40	28.39	0.05	ICP-OES
18	28.68	28.56	29.05	28.47	28.69	0.25	ICP-OES
14	29.1	29.0	28.6	28.8	28.88	0.22	ICP-OES
08	28.82	28.91	29.78	30.04	29.39	0.61	ICP-MS
10	29.82	29.52	29.64	29.29	29.57	0.22	ICP-MS
09	29.2	28.6	30.1	30.9	29.70	1.01	ICP-MS
12	29.8	30.0	29.6	29.6	29.75	0.19	ICP-MS
13	29.6	30.6	29.8	29.2	29.80	0.59	ICP-OES
03	30.5	30.1	29.5	29.5	29.90	0.49	ICP-MS
16	29.4	29.4	30.4	30.4	29.90	0.58	ICP-MS
04	30.01	30.13	29.99	29.85	30.00	0.11	ICP-OES
02	30.5	30.6	30.6	30.6	30.58	0.05	ICP-OES
17	31.38	30.87	31.65		31.30	0.40	ICP-MS
06	32.6	33.2	32.5	33.5	32.95	0.48	ICP-MS
01	33.5	33.5	33.5	34.2	33.68	0.35	ICP-OES

M (mg/kg): **29.85**

SD_M (mg/kg): 1.649

$SD_M/\sqrt{N}$ (mg/kg): 0.400

Measurement results of ILC-participants **Nickel**

(graphical presentation) Aqua regia extractable mass fraction

Figure A.7a: Extractionaccording to **EN 16174, Method A** (open vessel, reflux conditions)

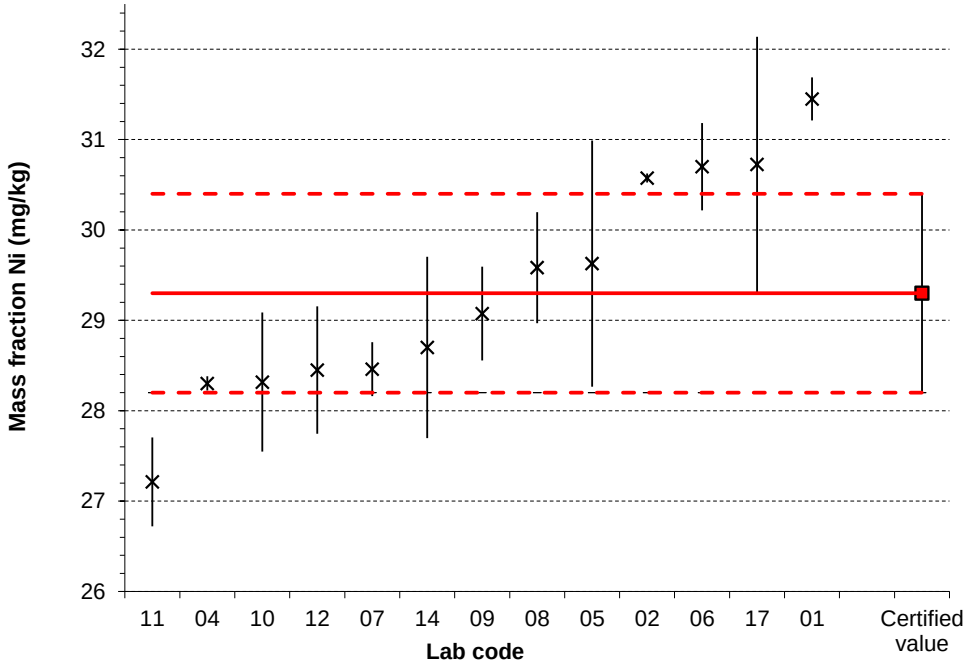


Figure A.7b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

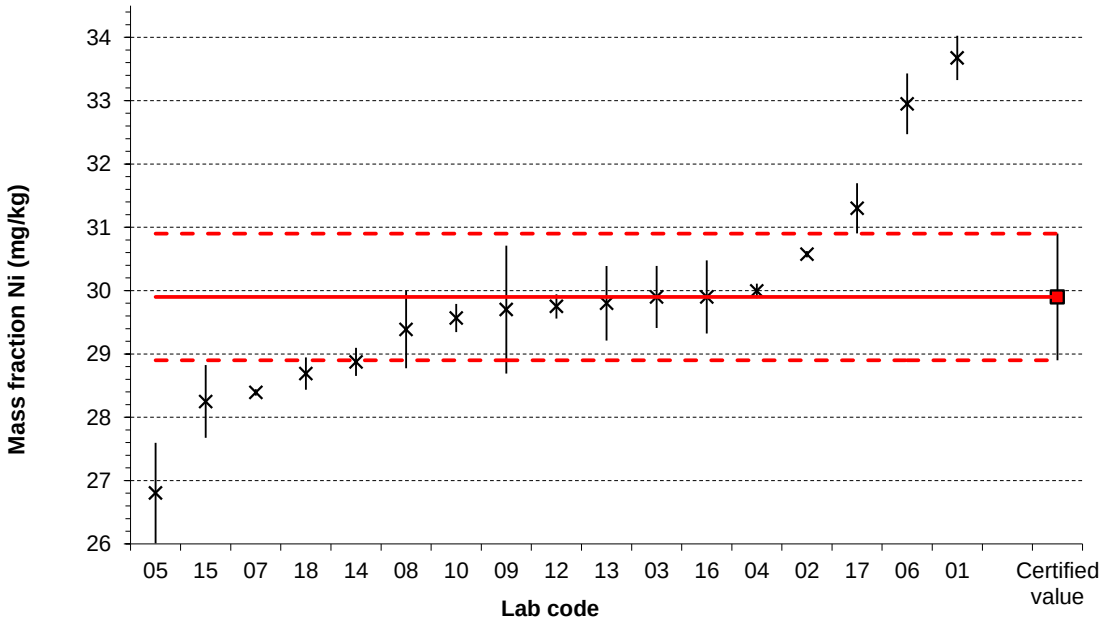


Table A.8a: Measurement results of ILC-participants **Pb (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
11	152.8	147.9	153.9	149.2	151.0	2.9	ICP-OES
12	151	153	156	151	152.8	2.4	ICP-MS
06	161	160	158	160	159.8	1.3	ICP-MS
05	164.1	155.3	161.6	161.9	160.7	3.8	ICP-OES
08	162.1	164.0	159.7	160.5	161.6	1.9	ICP-MS
09	155	157	170	171	163.3	8.4	ICP-MS
02	165	165	164	165	164.8	0.5	ICP-OES
10	166.0	167.2	166.6	168.3	167.0	1.0	ICP-MS
07	169.0	169.7	170.9	169.8	169.9	0.8	ICP-OES
17	174.9	173.2	160.6	171.3	170.0	6.4	ICP-MS
04	171.9	171.4	170.9	171.2	171.4	0.4	ICP-OES
14	172	173	173	170	172.0	1.4	ICP-OES
01	173	174	175	175	174.3	1.0	ICP-OES

M (mg/kg): **164.1**

SD_M (mg/kg): 7.74

$SD_M/\sqrt{N}$ (mg/kg): 2.33

Datasets of Lab 09 and Lab 17 were rejected as outliers (see Annex B). They are not displayed in Figure A.8a.

Table A.8b: Measurement results of ILC-participants **Pb (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
12	162	163	158	159	160.5	2.4	ICP-MS
18	160.9	157.1	164.5	159.9	160.6	3.1	ICP-OES
06	162	163	160	161	161.5	1.3	ICP-MS
03	166	160	162	166	163.5	3.0	ICP-MS
16	162	152	172	172	164.5	9.6	ICP-MS
05	167.0	167.9	160.9	162.5	164.6	3.4	ICP-OES
15	163	163	167	173	166.5	4.7	ICP-MS
09	165	169	164	174	168.0	4.5	ICP-MS
17	175.2	164.0	175.3	166.9	170.4	5.8	ICP-MS
14	172	171	181	165	172.3	6.6	ICP-OES
02	172	170	174	174	172.5	1.9	ICP-OES
10	174.8	173.1	173.6	170.8	173.1	1.7	ICP-MS
04	172.9	173.7	173.9	173.5	173.5	0.4	ICP-OES
08	176.6	172.4	172.7	173.4	173.8	1.9	ICP-MS
07	176.8	175.3	172.4	171.1	173.9	2.6	ICP-OES
13	174	177	176	169	174.0	3.6	ICP-OES
01	186	186	187	191	187.5	2.4	ICP-OES

M (mg/kg): **168.6**

SD_M (mg/kg): 5.26

$SD_M/\sqrt{N}$ (mg/kg): 1.36

Datasets of Lab 01 and Lab 16 were rejected as outliers (see Annex B). They are not displayed in Figure A.8b.

Measurement results of ILC-participants **Lead**

(graphical presentation) Aqua regia extractable mass fraction

Figure A.8a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

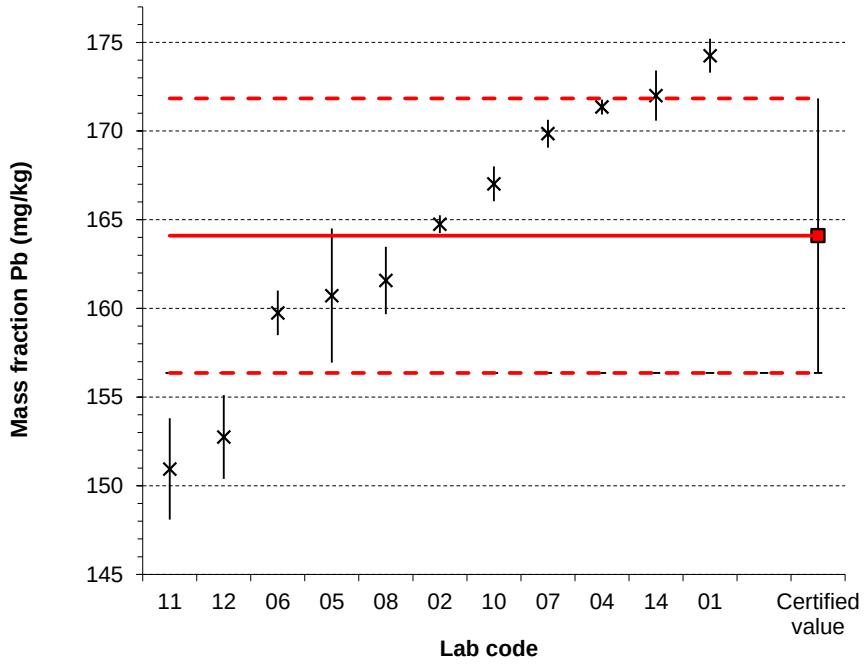


Figure A.8b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

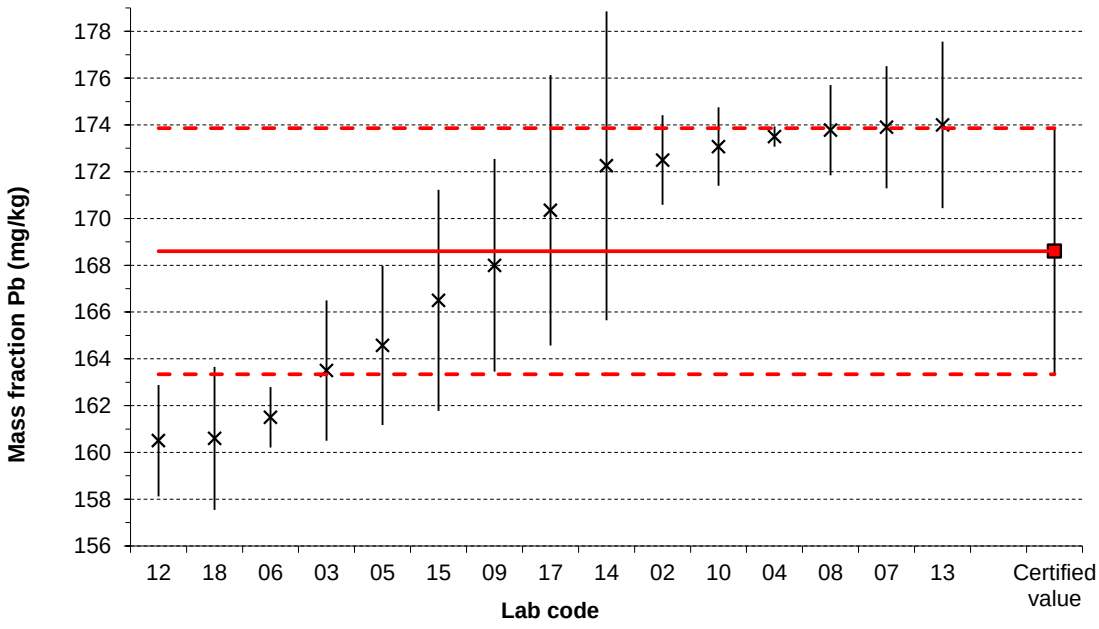


Table A.9a: Measurement results of ILC-participants V (A)

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
04	19.97	20.19	19.99	20.06	20.05	0.10	ICP-OES
17	20.71	19.77	18.83	21.22	20.13	1.06	ICP-MS
11	20.92	20.21	20.77	20.20	20.53	0.37	ICP-OES
06	21.5	20.4	20.2	21.4	20.88	0.67	ICP-MS
08	20.86	22.66	22.13	23.17	22.21	0.99	ICP-MS
02	22.2	22.2	22.3	22.3	22.25	0.06	ICP-OES
01	22.0	22.2	22.4	22.6	22.30	0.26	ICP-OES
10	22.44	22.41	22.83	23.01	22.67	0.30	ICP-MS
07	22.61	22.99	22.73	22.87	22.80	0.17	ICP-OES
05	24.02	22.84	22.87	23.41	23.29	0.56	ICP-OES
14	23.8	23.9	24.6	23.6	23.98	0.43	ICP-OES
12	24.9	24.9	24.2	24.6	24.65	0.33	ICP-MS
09	24.5	24.1	25.8	25.3	24.93	0.77	ICP-MS

M (mg/kg): **22.36**

SD_M (mg/kg): 1.620

$SD_M/\sqrt{N}$ (mg/kg): 0.449

Table A.9b: Measurement results of ILC-participants **V (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
15	17.8	18.0	18.1	17.6	17.88	0.22	ICP-MS
02	21.5	21.7	21.9	20.0	21.28	0.87	ICP-OES
08	21.22	20.81	22.16	21.28	21.37	0.57	ICP-MS
18	20.80	22.18	21.53	22.59	21.78	0.78	ICP-OES
04	22.20	22.14	21.39	21.90	21.91	0.37	ICP-OES
06	21.9	21.3	22.4	22.3	21.98	0.50	ICP-MS
01	20.6	22.8	22.8	23.0	22.30	1.14	ICP-OES
17	23.64	24.61	22.56	23.34	23.54	0.85	ICP-MS
16	23.3	23.3	24.3	23.3	23.55	0.50	ICP-MS
10	23.80	23.67	23.76	23.15	23.60	0.30	ICP-MS
03	24.6	25.1	24.5	25.0	24.80	0.29	ICP-MS
14	25.2	24.8	25.5	24.7	25.05	0.37	ICP-OES
12	25.7	25.6	24.6	25.4	25.33	0.50	ICP-MS
07	25.47	25.17	25.16	25.74	25.39	0.28	ICP-OES
05	24.90	26.23	25.51	25.18	25.46	0.57	ICP-OES
09	25.1	24.6	25.8	26.4	25.48	0.79	ICP-MS

M (mg/kg): **23.52**

SD_M (mg/kg): 1.636

$SD_M/\sqrt{N}$ (mg/kg): 0.422

Dataset of Lab 15 was rejected as outlier (see Annex B). It is not displayed in Figure A9b.

Measurement results of ILC-participants
(graphical presentation)

Vanadium
Aqua regia extractable mass fraction

Figure A.9a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

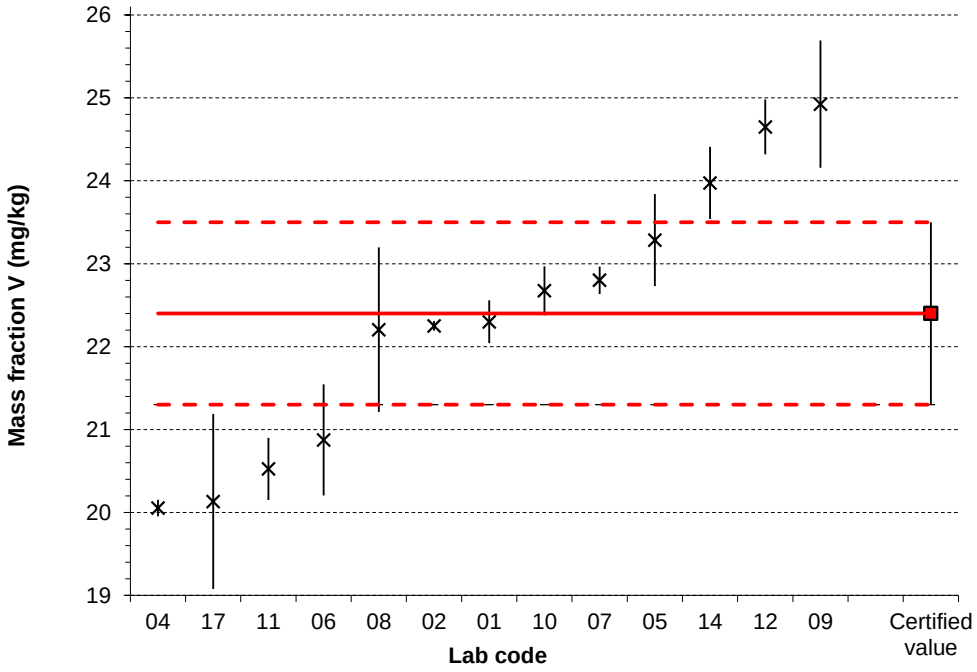


Figure A.9b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

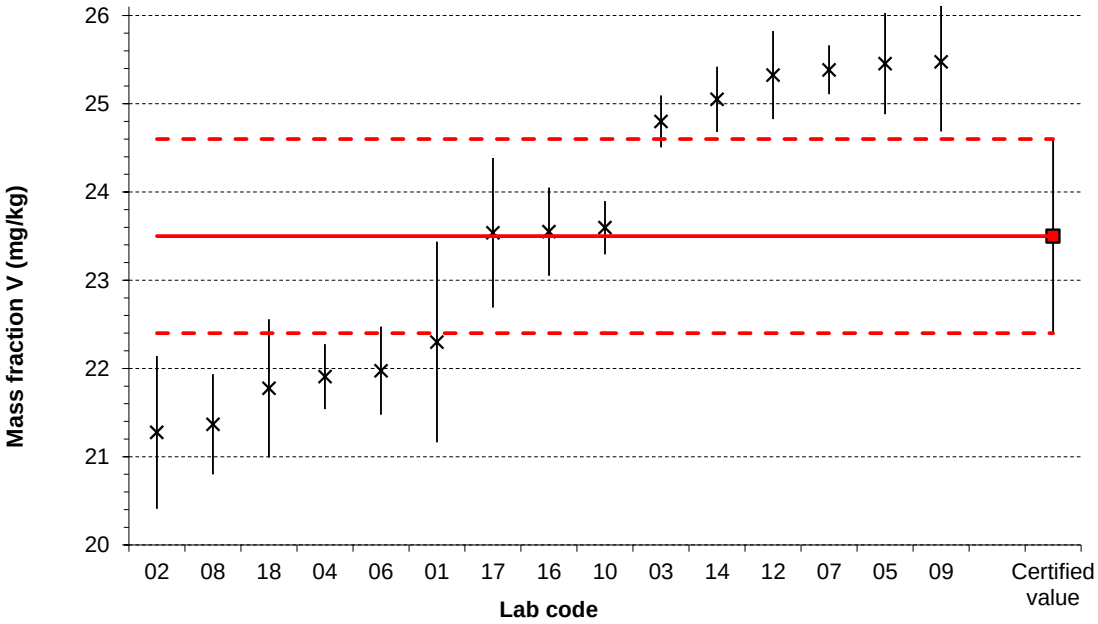


Table A.10a: Measurement results of ILC-participants **Zn (A)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method A** (open vessel, reflux conditions)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
11	332.4	323.4	329.8	319.1	326.2	6.0	ICP-OES
12	322	325	332		326.3	5.1	ICP-MS
10	330.4	327.7	331.2	334.3	330.9	2.7	ICP-MS
02	334	334	335	337	335.0	1.4	ICP-OES
08	343.9	336.5	333.6	329.6	335.9	6.0	ICP-MS
05	341.4	338.8	333.7	336.5	337.6	3.3	ICP-OES
17	346.0	348.8	330.6	351.9	344.3	9.5	ICP-MS
07	344.4	344.9	344.6	344.9	344.7	0.2	ICP-OES
14	349	348	345	348	347.5	1.7	ICP-OES
01	348	350	351	352	350.3	1.7	ICP-OES
09	353	343	362	350	352.0	7.9	ICP-MS
06	358	357	361	362	359.5	2.4	ICP-MS
04	361.5	360.3	362.1	362.6	361.6	1.0	ICP-OES

M (mg/kg): **342.4**

SD_M (mg/kg): 11.63

$SD_M/\sqrt{N}$ (mg/kg): 3.23

Table A.10b: Measurement results of ILC-participants **Zn (B)**

Aqua regia extractable mass fraction

Extraction method: **EN 16174, Method B** (microwave-assisted, 175 °C)

Lab Code	Sub-sample 1 (mg/kg)	Sub-sample 2 (mg/kg)	Sub-sample 3 (mg/kg)	Sub-sample 4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)	Analytical method
16	304	314	324	324	316.5	9.6	ICP-MS
15	310	318	316	335	319.8	10.7	ICP-MS
08	327.3	326.2	335.7	335.8	331.3	5.2	ICP-MS
17	342.8	331.5	339.5	340.8	338.7	5.0	ICP-MS
18	337.2	334.9	344.5		338.9	5.0	ICP-OES
03	333	333	344	350	340.0	8.4	ICP-MS
12	343	346	339	337	341.3	4.0	ICP-MS
10	346.0	340.9	344.2	341.2	343.1	2.5	ICP-MS
14	348	352	343	347	347.5	3.7	ICP-OES
07	351.7	353.4	352.4	349.1	351.7	1.8	ICP-OES
05	354.8	346.1	353.2	356.6	352.7	4.6	ICP-OES
09	347	342	357	370	354.0	12.4	ICP-MS
02	358	359	356	354	356.8	2.2	ICP-OES
04	360.5	362.3	359.1	361.6	360.9	1.4	ICP-OES
06	379	375	375	376	376.3	1.9	ICP-MS
13	375	381	381	371	377.0	4.9	ICP-OES
01	376	377	381	385	379.8	4.1	ICP-OES

M (mg/kg): **348.6**

SD_M (mg/kg): 18.25

$SD_M/\sqrt{N}$ (mg/kg): 4.43

Measurement results of ILC-participants **Zinc**

(graphical presentation) Aqua regia extractable mass fraction

Figure A.10a: Extraction according to **EN 16174, Method A** (open vessel, reflux conditions)

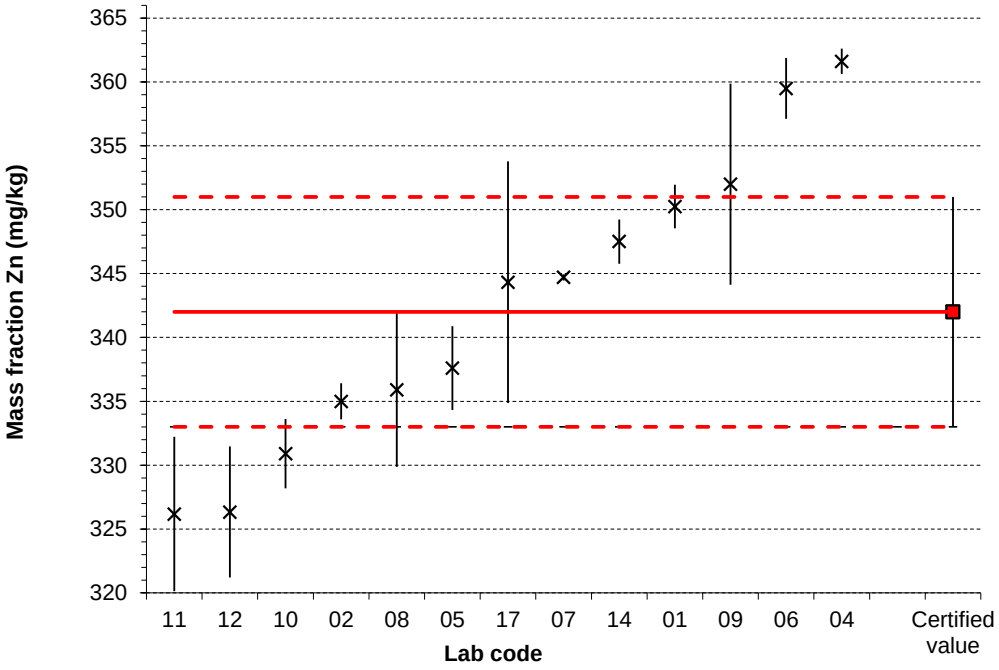


Figure A.10b: Extraction according to **EN 16174, Method B** (microwave-assisted, 175 °C)

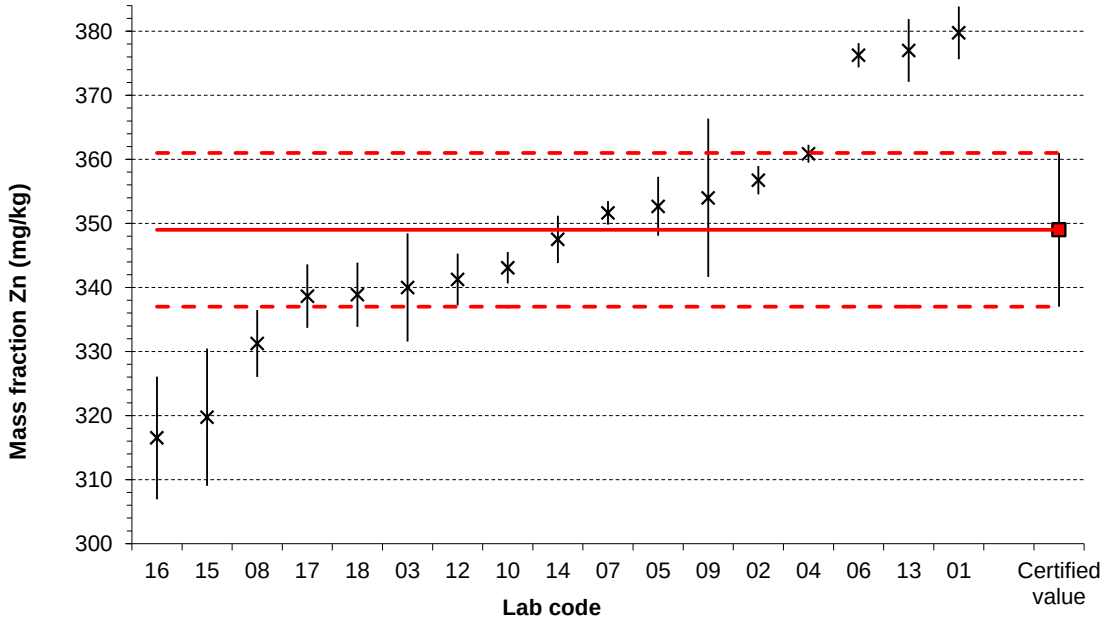


Table B.1a: Outcome of statistical tests on results obtained for **As** (Extraction **Method A**)

Number of evaluated datasets: 12	Outcome of the statistical test
Scheffé's multiple t-test	Datasets are not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 05 is an outlier
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Lab 17 is an outlier
Cochran test (α = 0.01)	Lab 17 is an outlier
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 17 was rejected as Cochran-outlier (α = 0.01).

Table B.1b: Outcome of statistical tests on results obtained for **As** (Extraction **Method A**) after removal of Lab 17

Number of evaluated datasets: 11	Outcome of the statistical test
Scheffé's multiple t-test	Datasets are not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.2: Outcome of statistical tests on results obtained for **As** (Extraction **Method B**)

Number of evaluated datasets: 16	Outcome of the statistical test
Scheffé's multiple t-test	Datasets are not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 15 is an outlier
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.3a: Outcome of statistical tests on results obtained for **Cd** (Extraction **Method A**)

Number of evaluated datasets: 13	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 05 is an outlier
Grubbs test (α = 0.01)	Lab 05 is an outlier
Dixon test (α = 0.05)	Labs 05 and 17 are outliers
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 05 is an outlier
Nalimov test (α = 0.01)	Lab 05 is an outlier
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 05 was rejected as Nalimov-outlier (α = 0.01).

Table B.3b: Outcome of statistical tests on results obtained for **Cd** (Extraction **Method A**) after removal of Lab 05

Number of evaluated datasets: 12	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	Lab 17 is an outlier
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 17 is an outlier
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.4a: Outcome of statistical tests on results obtained for **Cd** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 17 is an outlier
Grubbs test (α = 0.01)	Lab 17 is an outlier
Dixon test (α = 0.05)	Lab 17 is an outlier
Dixon test (α = 0.01)	Lab 17 is an outlier
Nalimov test (α = 0.05)	Lab 17 is an outlier
Nalimov test (α = 0.01)	Lab 17 is an outlier
Cochran test (α = 0.05)	Lab 05 is an outlier
Cochran test (α = 0.01)	Lab 05 is an outlier
Bartlett test (α = 0.05)	Out of test range
Bartlett test (α = 0.01)	Out of test range
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Not normal distribution of datasets

Dataset of Lab 17 was rejected as Nalimov-outlier (α = 0.01), dataset of Lab 05 was rejected as Cochran-outlier (α = 0.01).

Table B.4b: Outcome of statistical tests on results obtained for **Cd** (Extraction **Method B**) after removal of Lab 05 and Lab 17

Number of evaluated datasets: 15	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.5a: Outcome of statistical tests on results obtained for **Co** (Extraction **Method A**)

Number of evaluated datasets: 13	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 12 is an outlier
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	Lab 12 is an outlier
Dixon test (α = 0.01)	Lab 12 is an outlier
Nalimov test (α = 0.05)	Lab 12 is an outlier
Nalimov test (α = 0.01)	Lab 12 is an outlier
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 12 was rejected as Nalimov-outlier (α = 0.01).

Table B.5b: Outcome of statistical tests on results obtained for **Co** (Extraction **Method A**) after removal of Lab 12

Number of evaluated datasets: 12	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	Lab 11 is an outlier
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Labs 05 and 11 are outliers
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.6: Outcome of statistical tests on results obtained for **Co** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 13 is an outlier
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.7a: Outcome of statistical tests on results obtained for **Cr** (Extraction **Method A**)

Number of evaluated datasets: 13	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Labs 06 and 17 are outliers
Cochran test (α = 0.01)	Lab 17 is an outlier
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 17 was rejected as Cochran-outlier (α = 0.01).

Table B.7b: Outcome of statistical tests of results obtained for **Cr** (Extraction **Method A**) after removal of Lab 17

Number of evaluated datasets: 12	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Lab 06 is an outlier
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.8a: Outcome of statistical tests on results obtained for **Cr** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 18 is an outlier
Nalimov test (α = 0.01)	Lab 18 is an outlier
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 18 was rejected as Nalimov-outlier (α = 0.01).

Table B.8b: Outcome of statistical tests of results obtained for **Cr** (Extraction **Method B**) after removal of Lab 18

Number of evaluated datasets: 16	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.9: Outcome of statistical tests on results obtained for **Cu** (Extraction **Method A**)

Number of evaluated datasets: 12	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.10a: Outcome of statistical tests on results obtained for **Cu** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Labs 09, 12 and 17 are outliers
Cochran test (α = 0.01)	Labs 09 and 12 are outliers
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Datasets of Lab 09 and Lab 12 were rejected as Cochran-outliers (α = 0.01).

Table B.10a: Outcome of statistical tests on results obtained for **Cu** (Extraction **Method B**) after removal of Lab 09 and Lab 12

Number of evaluated datasets: 15	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Lab 17 is an outlier
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.11a: Outcome of statistical tests on results obtained for **Hg** (Extraction **Method A**)

Number of evaluated datasets: 14	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 05 is an outlier
Grubbs test (α = 0.01)	Lab 05 is an outlier
Dixon test (α = 0.05)	Lab 05 is an outlier
Dixon test (α = 0.01)	Lab 05 is an outlier
Nalimov test (α = 0.05)	Lab 05 is an outlier
Nalimov test (α = 0.01)	Lab 05 is an outlier
Cochran test (α = 0.05)	Lab 17 is an outlier
Cochran test (α = 0.01)	Lab 17 is an outlier
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Not normal distribution of datasets

Dataset of Lab 05 was rejected as Nalimov-outlier (α = 0.01), dataset of Lab 17 was rejected as Cochran-outlier (α = 0.01).

Table B.11b: Outcome of statistical tests on results obtained for **Hg** (Extraction **Method A**) after removal of Lab 05 and Lab 17

Number of evaluated datasets: 12	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.12a: Outcome of statistical tests on results obtained for **Hg** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 05 is an outlier
Grubbs test (α = 0.01)	Lab 05 is an outlier
Dixon test (α = 0.05)	Lab 05 is an outlier
Dixon test (α = 0.01)	Lab 05 is an outlier
Nalimov test (α = 0.05)	Lab 05 is an outlier
Nalimov test (α = 0.01)	Lab 05 is an outlier
Cochran test (α = 0.05)	Lab 03 is an outlier
Cochran test (α = 0.01)	Lab 03 is an outlier
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Not normal distribution of datasets

Dataset of Lab 05 was rejected as Nalimov-outlier (α = 0.01), dataset of Lab 03 was rejected as Cochran-outlier (α = 0.001).

Table B.12b: Outcome of statistical tests of results obtained for **Hg** (Extraction **Method B**) after removal of Lab 03 and Lab 05

Number of evaluated datasets: 15	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 13 is an outlier
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	Lab 13 is an outlier
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Labs 09 and 13 are outliers
Nalimov test (α = 0.01)	Labs 09 and 13 are outliers
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Not normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Datasets of Lab 09 and Lab 13 were rejected as Nalimov-outliers (α = 0.01)

Table B.12c: Outcome of statistical tests of results obtained for **Hg** (Extraction **Method B**) after removal of Lab 03, Lab 05, Lab 09 and Lab 13

Number of evaluated datasets: 13	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.13: Outcome of statistical tests on results obtained for **Ni** (Extraction **Method A**)

Number of evaluated datasets: 18	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.14: Outcome of statistical tests on results obtained for **Ni** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Labs 01 and 06 are outliers
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Lab 09 is an outlier
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.15a: Outcome of statistical tests on results obtained for **Pb** (Extraction **Method A**)

Number of evaluated datasets: 13	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 11 is an outlier
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Labs 05, 09 and 17 are outliers
Cochran test (α = 0.01)	Labs 09 and 17 are outliers
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Datasets of Lab 09 and Lab 17 were rejected as Cochran-outliers (α = 0.01).

Table B.15b: Outcome of statistical tests of results obtained for **Pb** (Extraction **Method A**) after removal of Lab 09 and Lab 17

Number of evaluated datasets: 11	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Lab 05 is an outlier
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.16a: Outcome of statistical tests on results obtained for **Pb** (Extraction **Method B**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 01 is an outlier
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 01 is an outlier
Nalimov test (α = 0.01)	Lab 01 is an outlier
Cochran test (α = 0.05)	Lab 16 is an outlier
Cochran test (α = 0.01)	Lab 16 is an outlier
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 01 was rejected as Nalimov-outlier (α = 0.01), dataset of Lab 16 was rejected as Cochran-outlier (α = 0.01).

Table B.16b: Outcome of statistical tests of results obtained for **Pb** (Extraction **Method B**) after removal of Lab 01 and Lab 16

Number of evaluated datasets: 15	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Not normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.17: Outcome of statistical tests on results obtained for V (Extraction **Method A**)

Number of evaluated datasets: 17	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of dat sets

Table B.18a: Outcome of statistical tests on results obtained for V (Extraction **Method B**)

Number of evaluated datasets: 16	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	Lab 15 is an outlier
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	Lab 15 is an outlier
Nalimov test (α = 0.01)	Lab 15 is an outlier
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Dataset of Lab 15 was rejected as Nalimov-outlier (α = 0.01).

Table B.18b: Outcome of statistical tests of results obtained for V (Extraction Method B) after removal of Lab 15

Number of evaluated datasets: 15	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.19: Outcome of statistical tests on results obtained for Zn (Extraction Method A)

Number of evaluated datasets: 13	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	Lab 17 is an outlier
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances not homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table B.20: Outcome of statistical tests on results obtained for **Zn** (Extraction **Method B**)

Number of evaluated datasets: 18	Outcome of the statistical test
Scheffé's multiple t-test	Datasets not compatible two-by-two
Grubbs test (α = 0.05)	No outlier detected
Grubbs test (α = 0.01)	No outlier detected
Dixon test (α = 0.05)	No outlier detected
Dixon test (α = 0.01)	No outlier detected
Nalimov test (α = 0.05)	No outlier detected
Nalimov test (α = 0.01)	No outlier detected
Cochran test (α = 0.05)	No outlier detected
Cochran test (α = 0.01)	No outlier detected
Bartlett test (α = 0.05)	Variances not homogeneous
Bartlett test (α = 0.01)	Variances homogeneous
Snedecor F-test (α = 0.05)	Significant differences between datasets
Snedecor F-test (α = 0.01)	Significant differences between datasets
Summary of Bartlett test and Snedecor F-test	Pooling of individual data not allowed
Kolmogorov-Smirnov-Lilliefors test (α = 0.05)	Normal distribution of datasets
Kolmogorov-Smirnov-Lilliefors test (α = 0.01)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.05)	Normal distribution of datasets
Skewness & Kurtosis test (α = 0.01)	Normal distribution of datasets

Table C.1: Homogeneity study; results for **As** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	27.62	27.31	26.95	28.61	27.62	0.71
038	27.49	26.92	27.66	28.55	27.66	0.67
074	28.34	27.50	28.00	28.46	28.07	0.43
110	28.39	26.93	27.63	27.88	27.71	0.61
146	28.07	27.13	27.32	28.63	27.79	0.69
182	29.01	27.05	27.58	27.88	27.88	0.82
218	28.70	27.32	28.98	28.01	28.25	0.74
254	28.46	26.89	27.76	28.56	27.92	0.77
290	28.30	27.76	27.91	29.29	28.31	0.69
326	28.27	27.33	27.83	27.79	27.80	0.38
362	27.70	27.41	27.97	27.56	27.66	0.24
398	28.95	28.47	27.37	28.07	28.22	0.67

M (mg/kg): **27.91**

SD_M (mg/kg): 0.248

u_{bb} (% rel.): 0.56
(acc. to ISO Guide 35)

Table C.2: Homogeneity study; results for **Cd** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-MS

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	4.589	4.546	4.570	4.682	4.597	0.059
038	4.550	4.582	4.489	4.582	4.551	0.044
074	4.520	4.472	4.570	4.597	4.540	0.055
110	4.582	4.590	4.586	4.622	4.595	0.018
146	4.499	4.520	4.523	4.530	4.518	0.013
182	4.747	4.535	4.554	4.523	4.590	0.106
218	4.609	4.561	4.629	4.592	4.598	0.029
254	4.478	4.513	4.531	4.542	4.516	0.028
290	4.465	4.651	4.672	4.578	4.592	0.093
326	4.484	4.606	4.582	4.470	4.535	0.068
362	4.517	4.598	4.671	4.581	4.592	0.063
398	4.509	4.649	4.678	4.655	4.623	0.077

M (mg/kg):	**4.570**
SD_M (mg/kg):	0.0360
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.41

Table C.3: Homogeneity study; results for **Co** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-MS

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	7.551	7.464	7.402	7.557	7.494	0.074
038	7.684	7.610	7.502	7.472	7.567	0.098
074	7.537	7.380	7.375	7.486	7.444	0.080
110	7.546	7.463	7.480	7.578	7.517	0.055
146	7.440	7.482	7.306	7.407	7.409	0.075
182	7.420	7.329	7.263	7.404	7.354	0.072
218	7.422	7.307	7.431	7.455	7.404	0.066
254	7.513	7.254	7.348	7.396	7.378	0.108
290	7.389	7.446	7.399	7.521	7.439	0.060
326	7.436	7.446	7.575	7.304	7.440	0.111
362	7.460	7.411	7.426	7.363	7.415	0.040
398	7.333	7.522	7.513	7.660	7.507	0.134

M (mg/kg):	**7.447**
SD_M (mg/kg):	0.0624
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.61

Table C.4: Homogeneity study; results for **Cr** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	100.6	101.5	100.9	103.4	101.6	1.3
038	101.3	102.2	100.1	103.1	101.7	1.3
074	101.9	100.3	100.7	103.8	101.7	1.6
110	101.0	100.2	101.1	103.9	101.5	1.6
146	101.4	99.6	100.0	103.1	101.0	1.6
182	103.2	99.1	100.9	102.3	101.4	1.8
218	104.5	101.2	101.2	102.3	102.3	1.6
254	102.4	99.9	99.3	103.1	101.2	1.9
290	102.3	101.2	100.1	102.5	101.5	1.1
326	102.1	100.4	101.6	100.7	101.2	0.8
362	102.9	100.5	101.2	101.3	101.5	1.0
398	103.5	100.8	101.3	103.8	102.3	1.5

M (mg/kg):	**101.6**
SD_M (mg/kg):	0.40
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.35

Table C.5: Homogeneity study; results for **Cu** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	163.1	167.0	166.2	171.6	167.0	3.5
038	164.0	165.7	168.1	166.8	166.2	1.7
074	166.1	168.2	167.4	168.7	167.6	1.2
110	165.7	166.8	168.6	168.2	167.3	1.3
146	166.0	166.8	163.9	164.9	165.4	1.3
182	170.3	162.6	167.0	165.2	166.3	3.3
218	167.8	166.8	167.9	167.4	167.5	0.5
254	162.9	168.3	169.0	166.4	166.6	2.7
290	168.0	166.0	165.1	169.6	167.2	2.0
326	167.2	170.9	169.5	163.4	167.8	3.3
362	165.3	167.1	164.5	166.0	165.7	1.1
398	171.8	173.2	166.5	171.5	170.8	3.0

M (mg/kg):	**167.1**
SD_M (mg/kg):	1.38
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.45

Table C.6: Homogeneity study; results for **Hg** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-MS

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	3.916	3.794	4.003	4.145	3.965	0.148
038	3.936	3.865	3.865	3.943	3.902	0.043
074	3.890	3.862	3.806	4.442	4.000	0.297
110	3.964	3.847	3.997	3.966	3.944	0.066
146	3.894	3.772	3.807	4.000	3.868	0.102
182	3.825	3.796	3.891	4.015	3.882	0.097
218	3.933	3.755	3.977	3.901	3.892	0.096
254	3.807	3.661	3.873	3.925	3.817	0.114
290	4.042	3.798	4.117	4.041	4.000	0.139
326	3.832	3.915	3.958	3.894	3.900	0.052
362	3.809	3.888	4.209	4.021	3.982	0.175
398	3.879	3.859	3.950	4.246	3.984	0.179

M (mg/kg):	**3.928**
SD_M (mg/kg):	0.059
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.88

Table C.7: Homogeneity study; results for **Ni** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-MS

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	29.29	29.14	29.24	29.11	29.20	0.08
038	29.60	29.82	29.55	28.44	29.35	0.62
074	29.02	28.95	28.99	28.91	28.97	0.05
110	29.27	30.09	29.58	28.94	29.47	0.49
146	28.88	28.83	28.64	28.73	28.77	0.11
182	28.80	28.62	28.96	30.17	29.14	0.70
218	29.92	28.90	29.35	29.44	29.40	0.42
254	30.22	28.07	28.52	28.58	28.85	0.94
290	28.29	28.76	29.07	29.10	28.80	0.38
326	28.77	28.74	29.74	28.63	28.97	0.52
362	28.57	29.05	29.11	28.58	28.83	0.29
398	28.73	29.05	29.69	30.58	29.51	0.82

M (mg/kg):	**29.10**
SD_M (mg/kg):	0.277
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.44

Table C.8: Homogeneity study; results for **Pb** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	174.1	182.7	172.1	174.4	175.8	4.7
038	174.2	175.6	174.9	173.3	174.5	1.0
074	172.3	172.2	172.4	171.0	172.0	0.7
110	172.4	168.5	176.0	172.6	172.4	3.0
146	173.8	169.0	175.1	177.3	173.8	3.5
182	173.8	173.5	170.8	167.9	171.5	2.8
218	176.5	175.3	177.4	172.8	175.5	2.0
254	170.3	169.2	171.5	173.6	171.2	1.9
290	170.5	170.5	174.0	176.8	172.9	3.1
326	173.3	177.0	173.5	171.1	173.7	2.5
362	173.1	175.0	175.1	170.3	173.3	2.3
398	175.1	175.5	174.7	171.7	174.2	1.7

M (mg/kg):	**173.4**
SD_M (mg/kg):	1.48
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.39

Table C.9: Homogeneity study; results for V (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	26.94	26.89	27.29	27.48	27.15	0.28
038	27.07	26.60	27.04	27.19	26.97	0.26
074	27.45	26.43	26.78	27.51	27.04	0.53
110	26.48	26.25	26.84	27.36	26.73	0.48
146	27.07	26.14	26.25	26.85	26.58	0.45
182	26.95	26.09	26.60	27.32	26.74	0.52
218	27.10	26.69	26.77	27.25	26.95	0.26
254	27.13	25.96	26.71	27.37	26.79	0.62
290	27.31	26.40	26.65	27.55	26.98	0.54
326	27.00	26.54	27.15	26.96	26.92	0.26
362	27.52	26.53	26.51	26.83	26.85	0.47
398	27.37	26.27	26.88	27.45	26.99	0.54

M (mg/kg): **26.89**

SD_M (mg/kg): 0.159

u_{bb} (% rel.): 0.41
(acc. to ISO Guide 35)

Table C.10: Homogeneity study; results for **Zn** (Extraction Method B)

Sample intake: approx. 500 mg Analytical method: ICP-OES

Sample I.D.	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
002	353.7	351.9	360.4	359.1	356.3	4.1
038	355.2	356.7	353.8	357.3	355.7	1.6
074	353.9	352.9	347.2	356.8	352.7	4.0
110	355.5	352.4	352.2	356.5	354.2	2.2
146	356.2	347.9	345.9	356.5	351.6	5.5
182	354.2	346.3	347.9	354.8	350.8	4.3
218	359.8	353.0	354.8	353.5	355.3	3.1
254	353.0	344.4	347.5	356.1	350.2	5.3
290	353.3	353.8	357.1	355.7	355.0	1.7
326	355.8	352.9	357.8	350.2	354.2	3.3
362	354.7	350.6	355.3	352.0	353.2	2.2
398	358.0	353.1	363.4	359.7	358.6	4.3

M (mg/kg):	**354.0**
SD_M (mg/kg):	2.42
u_{bb} (% rel.): (acc. to ISO Guide 35)	0.44

Table D.1: Stability study; results for **As** (Extraction Method A)

Analytical method: ICP-OES

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	28.33	29.25	28.69	29.25	28.88	0.45
	+20 °C	29.53	28.78	29.55	29.32	29.30	0.36
	+40 °C	29.17	28.08	28.95	28.94	28.79	0.48
	+60 °C	29.37	28.94	29.11	28.32	28.94	0.45
4 months	-20 °C	28.02	27.37	29.03	28.29	28.18	0.69
	+20 °C	27.61	28.06	28.12	28.37	28.04	0.32
	+40 °C	28.42	27.81	28.04	28.22	28.12	0.26
	+60 °C	28.40	28.09	28.36	28.01	28.22	0.19
6 months	-20 °C	29.06	28.77	29.39	29.46	29.17	0.32
	+20 °C	29.23	28.74	29.20	29.08	29.06	0.22
	+40 °C	29.52	29.44	29.03	29.33	29.33	0.21
	+60 °C	29.44	29.15	28.70	29.50	29.20	0.37

Table D.2: Stability study; results for **Cd** (Extraction Method A)

Analytical method: ICP-MS

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	4.703	4.542	4.610	4.626	4.620	0.066
	+20 °C	4.648	4.665	4.656	4.629	4.650	0.015
	+40 °C	4.614	4.622	4.711	4.536	4.621	0.072
	+60 °C	4.645	4.585	4.634	4.605	4.617	0.027
4 months	-20 °C	4.410	4.655	4.589	4.693	4.587	0.125
	+20 °C	4.587	4.668	4.629	4.592	4.619	0.038
	+40 °C	4.666	4.632	4.657	4.609	4.641	0.026
	+60 °C	4.615	4.671	4.639	4.657	4.646	0.024
6 months	-20 °C	4.681	4.701	4.617	4.548	4.637	0.069
	+20 °C	4.660	4.698	4.660	4.609	4.657	0.037
	+40 °C	4.669	4.654	4.647	4.674	4.661	0.013
	+60 °C	4.631	4.691	4.663	4.651	4.659	0.025

Table D.3: Stability study; results for **Co** (Extraction Method A)

Analytical method: ICP-MS

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	7.477	7.136	7.307	7.299	7.305	0.139
	+20 °C	7.349	7.357	7.382	7.253	7.335	0.057
	+40 °C	7.291	7.295	7.329	7.228	7.286	0.042
	+60 °C	7.264	7.228	7.317	7.397	7.302	0.073
4 months	-20 °C	7.034	7.355	7.272	7.385	7.262	0.159
	+20 °C	7.227	7.312	7.377	7.372	7.322	0.070
	+40 °C	7.294	7.412	7.416	7.290	7.353	0.070
	+60 °C	7.360	7.444	7.373	7.356	7.383	0.041
6 months	-20 °C	7.354	7.270	7.229	7.187	7.260	0.071
	+20 °C	7.321	7.259	7.326	7.206	7.278	0.057
	+40 °C	7.223	7.237	7.377	7.344	7.295	0.077
	+60 °C	7.324	7.312	7.269	7.264	7.292	0.030

Table D.4: Stability study; results for **Cr** (Extraction Method A)

Analytical method: ICP-OES

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	98.46	98.42	97.65	98.64	98.29	0.44
	+20 °C	97.87	97.41	99.34	98.92	98.39	0.90
	+40 °C	98.63	97.86	98.60	98.83	98.48	0.43
	+60 °C	97.70	98.62	97.86	98.81	98.25	0.55
4 months	-20 °C	96.81	99.57	98.31	96.36	97.76	1.47
	+20 °C	98.92	97.05	97.79	98.46	98.06	0.81
	+40 °C	101.29	97.55	97.03	99.67	98.89	1.97
	+60 °C	98.30	98.02	99.62	98.68	98.66	0.70
6 months	-20 °C	98.52	98.85	98.98	99.00	98.84	0.22
	+20 °C	98.98	98.53	98.52	98.69	98.68	0.21
	+40 °C	98.61	98.93	98.93	99.25	98.93	0.26
	+60 °C	98.69	99.70	98.23	99.01	98.91	0.62

Table D.5: Stability study; results for **Cu** (Extraction Method A)

Analytical method: ICP-OES

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	169.1	170.4	172.0	170.4	170.5	1.2
	+20 °C	175.2	173.5	175.4	174.5	174.7	0.9
	+40 °C	169.6	170.0	170.6	172.5	170.7	1.3
	+60 °C	170.0	169.6	171.1	169.4	170.0	0.8
4 months	-20 °C	172.9	172.0	173.3	169.7	172.0	1.6
	+20 °C	173.5	169.8	171.2	171.5	171.5	1.5
	+40 °C	173.6	170.2	171.2	172.2	171.8	1.5
	+60 °C	174.2	170.9	174.6	169.3	172.3	2.6
6 months	-20 °C	172.4	172.1	173.7	173.7	173.0	0.8
	+20 °C	173.2	171.6	172.8	173.0	172.7	0.7
	+40 °C	173.5	173.8	174.7	173.1	173.8	0.7
	+60 °C	174.1	172.1	175.3	173.0	173.6	1.4

Table D.6: Stability study; results for **Hg** (Extraction Method A)

Analytical method: ICP-MS

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	4.154	3.982	4.061	4.046	4.061	0.071
	+20 °C	4.044	4.066	4.083	4.066	4.065	0.016
	+40 °C	4.108	4.032	4.145	3.959	4.061	0.083
	+60 °C	4.019	4.065	4.017	4.013	4.029	0.024
4 months	-20 °C	3.871	4.067	3.966	4.060	3.991	0.092
	+20 °C	3.953	3.904	4.019	3.989	3.966	0.050
	+40 °C	4.026	4.061	4.046	3.943	4.019	0.053
	+60 °C	3.999	4.072	4.061	4.019	4.038	0.034
6 months	-20 °C	4.064	3.986	3.960	4.020	4.008	0.045
	+20 °C	4.002	3.985	4.020	3.965	3.993	0.024
	+40 °C	3.963	4.036	4.057	4.027	4.021	0.041
	+60 °C	4.052	4.041	4.016	3.993	4.026	0.026

Table D.7: Stability study; results for Ni (Extraction Method A)

Analytical method: ICP-MS

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	29.13	27.88	28.54	28.66	28.55	0.52
	+20 °C	28.60	28.71	29.40	28.47	28.80	0.42
	+40 °C	28.73	28.36	29.11	27.86	28.52	0.53
	+60 °C	28.55	28.28	28.69	28.59	28.53	0.18
4 months	-20 °C	28.11	28.64	28.31	28.61	28.42	0.25
	+20 °C	28.15	28.25	28.42	28.40	28.31	0.13
	+40 °C	28.16	29.11	28.55	28.15	28.49	0.45
	+60 °C	28.50	28.80	28.69	28.58	28.64	0.13
6 months	-20 °C	28.50	28.10	28.07	28.75	28.36	0.33
	+20 °C	28.14	28.27	28.34	28.26	28.25	0.08
	+40 °C	28.19	28.30	28.83	28.96	28.57	0.38
	+60 °C	28.65	29.03	28.47	28.55	28.68	0.25

Table D.8: Stability study; results for Pb (Extraction Method A)

Analytical method: ICP-OES

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	174.6	176.2	174.6	177.2	175.7	1.3
	+20 °C	176.2	174.5	177.5	177.7	176.5	1.5
	+40 °C	173.2	173.7	173.6	175.8	174.1	1.2
	+60 °C	173.5	173.3	174.2	169.6	172.7	2.1
4 months	-20 °C	175.1	169.8	176.5	168.9	172.6	3.8
	+20 °C	176.0	170.0	176.9	172.7	173.9	3.2
	+40 °C	176.6	170.2	172.8	174.3	173.5	2.7
	+60 °C	177.2	170.9	175.5	171.9	173.9	3.0
6 months	-20 °C	173.9	172.9	174.2	174.5	173.9	0.7
	+20 °C	172.1	173.3	174.2	170.9	172.6	1.4
	+40 °C	173.5	172.9	174.6	172.2	173.3	1.0
	+60 °C	173.9	172.2	174.1	171.8	173.0	1.2

Table D.9: Stability study; results for V (Extraction Method A)

Analytical method: ICP-OES

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	22.98	23.11	23.04	22.93	23.02	0.08
	+20 °C	23.08	22.80	23.24	23.46	23.15	0.28
	+40 °C	22.82	23.00	23.28	23.39	23.12	0.26
	+60 °C	22.82	23.04	23.04	22.80	22.93	0.13
4 months	-20 °C	22.84	22.76	22.93	22.51	22.76	0.18
	+20 °C	23.66	22.67	22.99	22.80	23.03	0.44
	+40 °C	22.91	22.63	22.73	23.32	22.90	0.30
	+60 °C	23.09	22.72	23.18	22.30	22.82	0.40
6 months	-20 °C	23.21	23.47	23.06	23.31	23.26	0.17
	+20 °C	23.15	23.24	23.08	23.41	23.22	0.14
	+40 °C	23.59	23.51	23.59	23.03	23.43	0.27
	+60 °C	23.34	23.44	23.32	23.59	23.42	0.12

Table D.10: Stability study; results for Zn (Extraction Method A)

Analytical method: ICP-OES

Storage time	Storage temperature	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD_i (mg/kg)
2 months	-20 °C	351.9	354.1	352.5	356.3	353.7	2.0
	+20 °C	354.1	351.5	355.2	356.2	354.3	2.0
	+40 °C	352.3	349.7	352.7	350.1	351.2	1.5
	+60 °C	349.4	348.7	350.7	356.4	351.3	3.5
4 months	-20 °C	349.8	347.9	358.3	348.9	351.2	4.8
	+20 °C	358.7	347.4	354.3	350.8	352.8	4.8
	+40 °C	358.7	348.1	350.5	354.3	352.9	4.6
	+60 °C	355.8	346.9	356.8	351.1	352.7	4.6
6 months	-20 °C	354.0	355.1	353.1	355.2	354.4	1.0
	+20 °C	351.3	357.0	354.3	357.5	355.0	2.9
	+40 °C	358.7	357.8	353.8	352.9	355.8	2.9
	+60 °C	359.1	353.0	353.9	352.9	354.7	3.0

Extraction according to EN 16174, Method A:

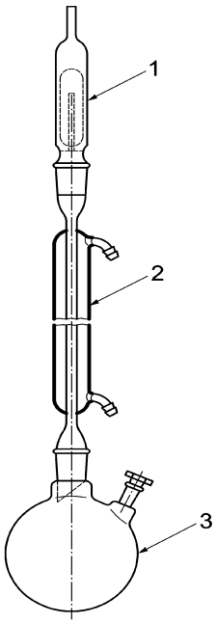
(*procedure almost identical to ISO 11466*)

Weigh approximately 3 g, to the nearest 0,01 g, of the soil sample and transfer it to the 250 mL reaction vessel of the apparatus shown in the figure below. Similar equipment can also be used.

Add some acid-washed glass beads (diameter ~ 3 mm) as boiling aids.
In case of dry samples moisten the test portion with about 0.5 mL of water and add, with mixing, 21 mL of concentrated hydrochloric acid followed by 7 mL of concentrated nitric acid.
Connect the reflux condenser to the reaction vessel. Fill the absorption vessel with approx. 15 mL of 0.5 mol/L nitric acid.
Connect the absorption vessel to the reflux condenser, and let stand at room temperature until any effervescence almost ceases to allow for slow oxidation of the organic matter in the sample.

NOTE: The time of standing at room temperature can influence the extraction efficiency of aqua regia. For comparison reasons of the method it is advised to start heating as soon as possible after the first strong reaction has ceased.

Connect the reaction vessel to the heating device and raise the temperature of the reaction mixture to reflux conditions and maintain for 2 h ensuring that the condensation zone is lower than 1/3 of the height of the reflux condenser, then allow to cool. Add the content of the absorption vessel to the reaction vessel via the reflux condenser, rinsing both the absorption vessel and condenser with further 10 mL of 0.5 mol/L nitric acid.



1 Absorption vessel
2 Reflux condenser
3 Reaction vessel

Add about 20 mL of water, filter the sample through an acid-resistant membrane filter (preferably with a pore size of 0.45 µm) into a 100 mL volumetric flask, wash the filter residue with 0.5 mol/L nitric acid and fill up to volume with water.
The measurement solution is now ready for analysis for elements of interest using appropriate elemental analysis techniques.

Extraction according to EN 16174, Method B:

(*microwave-assisted extraction*)

Operate the microwave equipment according to the instructions of the manufacturer!
Weigh an amount of 0.5 g to 1 g of the soil sample with an accuracy of 0,001 g and transfer it into the extraction vessel. Referring to the manufacturer's instructions, the upper limits of mass of the test portion shall be taken into account.

Moisten the sample with a few drops of water. Add separately 6 mL of concentrated hydrochloric acid and 2 mL of concentrated nitric acid and mix well. If a vigorous reaction occurs, allow the reaction cease before capping the vessel.

Cap the extraction vessel according to the manufacturer's instructions. Weigh the extraction vessel before starting the heating program. The carrousel of the microwave system must be filled with the number of extraction vessels prescribed by the manufacturer. If a lower number of samples should be processed, place extraction vessels filled with the same amount of aqua regia without sample.

The temperature of the extraction mixture in each vessel shall be raised with a heating rate of approx. 10 °C/min to 15 °C/min to (175 ± 5) °C and remain at this temperature for (10 ± 1) min.
At the end of the microwave heating program, allow the vessels to cool before removing them from the microwave system.

Cooling of the vessels may be accelerated by internal or external cooling devices.

After reaching room temperature, check if the microwave vessels maintained their seal throughout the extraction procedure. Weigh the vessels to evaluate seal integrity. If the weight loss of the sample exceeds 10 % of the weight of the added test portion and reagents before the start of the extraction procedure, the respective sample is considered compromised.

Carefully uncap and vent each vessel in a well-ventilated fume hood. Add about 20 mL of water, filter the sample through an acid-resistant membrane filter (preferably with a pore size of 0.45 µm) into a volumetric flask (typically 50 mL or 100 mL), wash the residue with 0.5 mol/L nitric acid and fill up to volume with water.
The measurement solution is now ready for analysis for elements of interest using appropriate elemental analysis techniques.