Bundesanstalt für Materialforschung und -prüfung (BAM)

The certification of trace elements in wood

BAM-U130

Certification report

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Abstract

This report describes the preparation and certification of reference material BAM-U130, trace elements in wood. The certified mass fractions are listed below.

Parameter	Mass fraction [3]	
	Certified Value [1] in mg/kg	Uncertainty [2] in mg/kg
As	4.0	0.4
Cd	2.52	0.30
Cr	39.3	2.7
Cu	30.0	2.7
Hg	0.66	0.06
Pb	41	5

[1] Unweighted mean value of the means of accepted sets of data (consisting of 4 single results), each set being obtained by a different laboratory and/or a different method of measurement.
[2] Estimated expanded uncertainty *U* with a coverage factor of $k = 2$, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).
[3] All results are corrected to the dry mass content of the wood material determined after drying to constant mass at (103 ± 2) °C.

Contents

List of abbreviations

(if not explained elsewhere)

ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
CV-AAS	cold vapour atomic absorption spectrometry

p.a.	*per analysi*
M	mean of the laboratories' means
u_c	combined uncertainty of certified mass fraction
s_M	standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification
n	number of accepted laboratory mean values of interlaboratory comparison for certification

1 Introduction

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

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

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

Thus, for decision-making with respect to waste wood management reliable analytical data are needed and – due to their great economic and environmental impact – must be assured by appropriate quality control. One aspect of quality assurance of analytical measurement results is the application of suitable certified reference materials (CRM). In 2009 BAM produced ERM-CD100 for the determination of the heavy metals and pentachlorophenol (PCP) which were (and partly are) in use as wood preservatives. This CRM has been sold out and it was decided to close this gap with separate CRMs for heavy metals and PCP. As the respective analytical procedures require different extraction or digestion procedures a subsample of a wood material can only be used for either one of the analytes. In order to enable the use of the material efficiently BAM-U130 was certified for the heavy metals only.
The certification was carried out on the basis of ISO 17034 [2] and the relevant ISO-Guides [3,4].

2 Candidate material

The material was prepared at BAM using untreated German beech wood performing the following processing steps:
- milling of the wood sticks by means of a cutting mill with a bottom sieve of 10 mm mesh size,
- additional milling of the ground stock under with a centrifugal mill using a 1 mm mesh ring sieve,
- sieving of the material with a 1000-µm-sieve and a 250 µm-sieve. The particle fraction between 250 µm and 1000 µm was taken for BAM-U130.

A certain amount of mill charge was immersed in aqueous solutions of As, Cr, Cd, Cu, Hg, and Pb salts (chemicals and concentrations see Table 2) and thereafter slowly dried over several weeks to constant weight to yield fraction.

Tab. 2: Chemicals and concentrations of the solutions used for spiking untreated wood

Element	Concentration in mg/l	Chemicals (all p.a.)
As	90	As_2O_3
Cd	60	$Cd(NO_3)_2 \cdot 4H_2O$
Cr	900	$K_2Cr_2O_7$
Cu	800	$CuSO_4 \cdot 5H_2O$
Hg	20	$HgCl_2$
Pb	1000	$Pb(NO_3)_2$

To fit the mass fractions of the relevant analytes to legal threshold values, stepwise blending of the doped wood materials was performed by means of a 120-litre drum hoop mixer. Final homogenisation and bottling were carried out with a spinning riffler.
A total of 256 units containing (32 ± 1) g of homogenized wood material each were bottled in 125 ml amber glass containers with screw caps equipped with PE insert and sealed with shrinking foil. The bottles were stored at 4 °C in the dark.

3 Homogeneity study

Twelve bottles were selected equidistantly from the whole batch of 256 units following the sequence of bottling. The selected units were analysed three times each using sample intakes of 0.5 g and of 1.5 g.
For trace element determination the wood material was digested with aqua regia following the procedures given in EN 13657 [5]:
(1) boiling in an open reaction vessel under reflux for 2 h using a sample intake of 1.5 g,
(2) microwave digestion for 20 min in a closed vessel using a sample intake of 0.5 g.
All prepared solutions were analysed under repeatability conditions after randomisation in one run with one calibration. Results and used analytical methods are given in Annex 1.
The estimates of inhomogeneity contributions u_{bb} potentially hidden by the measurement uncertainty and to be included into the total uncertainty budget were estimated according to ISO Guide 35 [4] as the maximum of the values obtained from Eq. (1) and (2).

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

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

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}, which was true for As, Cd, and Hg. For Cu and Pb s_{bb} was used, for Cr u^*_{bb} was used.

To calculate the uncertainty contribution of possible inhomogeneity the u_{bb}.-values obtained for 1.5 g and 0.5 g sample intake were compared and the higher value was used (0.5 g for As, Cd, Cr, Cu, Hg; 1.5 g for Pb).

4 Stability study

Stability testing was carried out according to the so-called isochronous design [6]. Selected units of the candidate material were subjected to accelerated ageing at temperatures between 4 °C and 60 °C over periods of 4 weeks to 12 months (see Annex 3). After the respective periods of time the individual units were stored at -20 °C. All units were analysed in triplicate after digestion of 1.5 g using the open vessel (reflux) procedure as for homogeneity testing.
A total of six digests/extracts obtained from two reference samples which had been kept at -20 °C since bottling and being evenly distributed over the whole measurement sequence were analysed together with the exposed samples in one run under repeatability conditions.
All measurement results from the stability study are given in Annex 3. They were evaluated using software eCerto [7]. 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 uncertainty contribution of potential instability was negligible. Furthermore, published literature data and previous experience collated over substantial periods of time with similar materials used in large proficiency testing schemes and fomer CRM ERM-CD100 provide evidence of an extreme stability of all analytes in the material under consideration. A long-term uncertainty contribution u_{lts} was estimated representing the product of the relative standard uncertainty of the slope of the regression line for the recommended storage temperature +40 °C as temperature with the highest risk of instability. multiplied by a factor of 3 (taking into account a minimum shelf life of three years).
Stability testing will be continued by further measurements of units stored at 4 °C, 23 °C and 40 °C over the period of availability of the material. That way, information on the long term stability of units of BAM-U130 having been opened at least once for withdrawal of material is expected in the course of the post certification monitoring.

5 Certification study

5.1 Design of the study

The certification study was organised as an interlaboratory comparison. 14 laboratories invited to participate were selected on the basis of their expertise demonstrated in the course of a preceding proficiency test where a similar wood material was requested to be analysed for trace elements. All laboratories hold an accreditation according to ISO/ IEC 17025.
Each participant received one unit of bottled wood material and was asked to analyse four independent sub-samples for their contents of trace elements. The moisture content of the bottled wood material had to be determined in dublicate using separate sub-samples. Additionally, information on details of the applied analytical procedures was requested. Table 3 shows the analytical methods used by the participating laboratories.

Tab. 3: Sample digestion and element detection

Lab code	Sample intake (g)	Acid mixture	Apparatus	Detection method
202	1.985 – 2.163	HCl + HNO_3 acc. to EN 13657 [7]	Open vessel (reflux)	ICP-MS CV AAS (Hg)
203	0.504 – 0.533	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-OES CV AAS (Hg)
204	0.3	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-OES CV AAS (Hg)
205	1.0 – 1.5	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-OES CV AAS (Hg)
206	2.34 – 3.05	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-OES
207	1.5 – 3.0	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-MS CV AAS (Hg)
208	1.001 – 1.017	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-OES CV AAS (Hg)
209	0.5 – 1.5	HCl + HNO_3 acc. to EN 13657	2x Closed vessel (microwave) 2x Open vessel (reflux)	ICP-OES ICP-MS CV AAS (Hg)
210	2.0	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-OES CV AAS (Hg)
211	0.5	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-OES CV AAS (Hg)
212	1.93 – 2.09	HCl + HNO_3 acc. to EN 13346	Open glass tube	ICP-OES CV AAS (Hg)
213	3.0	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-MS CV AAS (Hg)
214	3.5	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-MS CV AAS (Hg)
215	1.5	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-MS
216	0.5	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-MS
217	1.5	HCl + HNO_3 acc. to EN 13657	Open vessel (reflux)	ICP-OES CV AAS (Hg)
218	0.5	HCl + HNO_3 acc. to EN 13657	Closed vessel (microwave)	ICP-OES CV AAS (Hg)

5.2 Participants

AKS Aqua-Kommunal-Service GmbH, Frankfurt (Oder)
Analysen Service GmbH, Privates Institut für Umweltanalytik, Penzlin
ArcelorMittal Eisenhüttenstadt, Forschungs- und Qualitätszentrum GmbH, Eisenhüttenstadt
AWV- Dr. Busse GmbH, Plauen
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin
BVU Bioverfahrenstechnik und Umweltanalytik GmbH, Markt Rettenbach
GBA Gesellschaft für Bioanalytik mbH, Pinneberg
GLU mbH, Gesellschaft für Lebensmittel und Umweltconsulting mbH, Hoppegarten
ICA - Institut für Chem. Analytik GmbH, Leipzig
Institut Dr. Lörcher, Ludwigsburg
nano GmbH, Weitnau
SGS Analytics Germany GmbH, Augsburg
SGS Institut Fresenius GmbH, Berlin
WESSLING GmbH Umweltanalytik Oppin, Landsberg OT Oppin

5.3 Analytical results and statistical evaluation

The measurement results submitted by the participants in the certification study are listed in Annex 1. They are corrected to dry mass content based on the respective moisture content of the sample determined by the individual participant. The bars in the graphic presentations indicate the standard deviation of individual results. The green line represents the certified value of each element (mean of laboratories' means), the dotted lines the single standard deviation of the laboratories' means.
The statistical evaluation of the data was performed using the software program eCerto [6]. The following results were obtained:

Tab. 4: Outcome of statistical tests on the results obtained for As

	1st run
Number of data sets	18
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	214, 217
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	218
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	218
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The outlying results were not removed.

Tab. 5: Outcome of statistical tests on the results obtained for Cd

	1st run
Number of data sets	18
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	211
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The outlying result was not removed.

Tab. 6: Outcome of statistical tests on the results obtained for Cr

	1st run	2nd run
Number of data sets	18	18
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	203	---
Dixon (α = 0.01)	203	---
Nalimov (α = 0.05)	203	204, 212
Nalimov (α = 0.01)	203	---
Grubbs (α = 0.05)	203	---
Grubbs (α = 0.01)	203	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying result (203, 1st run) was removed.

Tab. 7: Outcome of statistical tests on the results obtained for Cu

	1st run
Number of data sets	18
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

Tab. 8: Outcome of statistical tests on the results obtained for Hg

	1st run
Number of data sets	18
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

Tab. 9: Outcome of statistical tests on the results obtained for Pb

	1st run
Number of data sets	18
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	216
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The outlying result was not removed.

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

$$u_{char} = \frac{s_M}{\sqrt{n}} \qquad (3)$$

n : number of data sets used for calculating the certified mass fraction of each element

Additionally, the following uncertainty components were taken into account:

- u_{bb} uncertainty due to potentially hidden inhomogeneity of the material (see Paragraph 3)
- u_{dm} uncertainty of dry matter correction carried out by the participants in the certification study (thereby the standard deviation of the mean of 14 laboratory means for the moisture content – see Annex 1 – was attributed with equal value to the mean dry matter content of 92.85 % giving a relative uncertainty $u_{dm,r}$ of approximately 0.25 %)

u_{lts} uncertainty resulting from stability testing of the material (see Paragraph 4)

The different contributions to the overall uncertainties of the certified mass fractions were combined using the following Eq. (4):

$$u_c = \sqrt{u_{char}^2 + u_{bb}^2 + u_{dm}^2 + u_{lts}^2} \qquad (4)$$

Tab. 10: Mass fractions and uncertainty components for the analytes in BAM-U130 (before rounding)

Analyte	w_{char} (mg kg^{-1})	u_{char} (mg kg^{-1})	u_{bb} (mg kg^{-1})	u_{dm} (mg kg^{-1})	u_{lts*} (mg kg^{-1})	u_{com} (mg kg^{-1})
As	4.044	0.0937	0.1690	0.0102	< 0.0001	0.1935
Cd	2.516	0.0517	0.1366	0.0063	< 0.0001	0.1462
Cr	39.26	0.422	1.2287	0.0987	0.0003	1.3029
Cu	30.00	0.635	1.1782	0.0754	0.0001	1.3406
Hg	0.663	0.0131	0.0227	0.0017	< 0.0001	0.0263
Pb	40.52	0.961	1.8920	0.1017	0.0003	2.1245

*Uncertainty contribution from storage temperature 40 °C multiplied with a factor of 3.

The expanded uncertainties U are calculated by multiplication of u_c with a coverage factor of k = 2 using Equation 5.

$$U = k \cdot u_c \qquad (5)$$

The calculated mass fractions and their resp. expanded uncertainties are given in Table 9. Rounding was done according to DIN 1333 [8].

Tab. 11: Certified mass fractions and expanded uncertainties of analytes in BAM-U130 (after rounding)

Analyte	Mass fraction in mg/kg	Uncertainty in mg/kg
As	4.0	0.4
Cd	2.52	0.30
Cr	39.3	2.7
Cu	30.0	2.7
Hg	0.66	0.06
Pb	41	5

6 Information on the proper use of BAM-U130

6.1 Shelf life

The initial stability study after storage of selected units at different temperatures did not reveal any statistically significant deterioration of the certified properties. However, starting with dispatch of the material from BAM the validity of the certificate expires after 24 months. Post-certification measurements will be conducted in appropriate periods to keep this information up to date.

6.2 Recommendations for transport, storage and use

Transportation of the bottled sample does not require special precautions. The stability of the contents of the relevant analytes allows the dispatch of the material at ambient temperature. Short heating of the closed bottle up to +40 °C for a few days does not affect the quality of BAM-U130.
On receiving, bottled material has to be stored at (4 ± 2) °C. Before withdrawing a sub-sample, the bottle should be allowed to reach room temperature and mixed thoroughly. Thereafter, the bottle should be closed tightly and stored at (4 ± 2) °C.
The material should be used as it is provided. However, before taking a sub-sample a re-homogenisation by manual shaking of the closed bottle is highly recommended. The bottle shall be left unclosed as shortly as possible.
The minimum sample size for one trace element determination is 0.5 g.
Analytical results have to be corrected to the dry mass content of the material. In this context it should be noted that under appropriate storage and handling conditions no significant moisture exchange between the bottled material and the ambient atmosphere may occur. Thus, at least at the beginning of the use of the material the required dry mass correction can be made on the basis of the indicated moisture content at the time of certification being 7.15 %. Nevertheless, after repeated use of the material its moisture content should be determined (at least in duplicate) either by Karl Fischer titration method or by heating in an oven at a temperature of (103 ± 2) °C using separate sub-samples.

6.3 Safety instructions

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

7 Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

8 References

[1] Verordnung über Anforderungen an die Verwertung und Beseitigung von Altholz (Altholzverordnung – AltholzV) vom 15. August 2002, Bundesgesetzblatt, Teil I (2002) 59: 3302– 3317

[2] ISO 17034, General requirements for the competence of reference material producers, 2016

[3] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation, 2015

[4] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability, 2017

[5] EN 13657 (2002): Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements

[6] A. Lamberty, H. Schimmel, J. Pauwels: The study of the stability of reference materials by isochronous measurements. Fresenius J Anal Chem (1998) 360:359 - 361

[7] J. Lisec, eCerto Software, BAM 2021

[8] DIN 1333:1992-02 Zahlenangaben

9 Information on and purchase of the CRM

Certified reference material BAM-U130 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Fachbereich 1.6: Anorganische Referenzmaterialien
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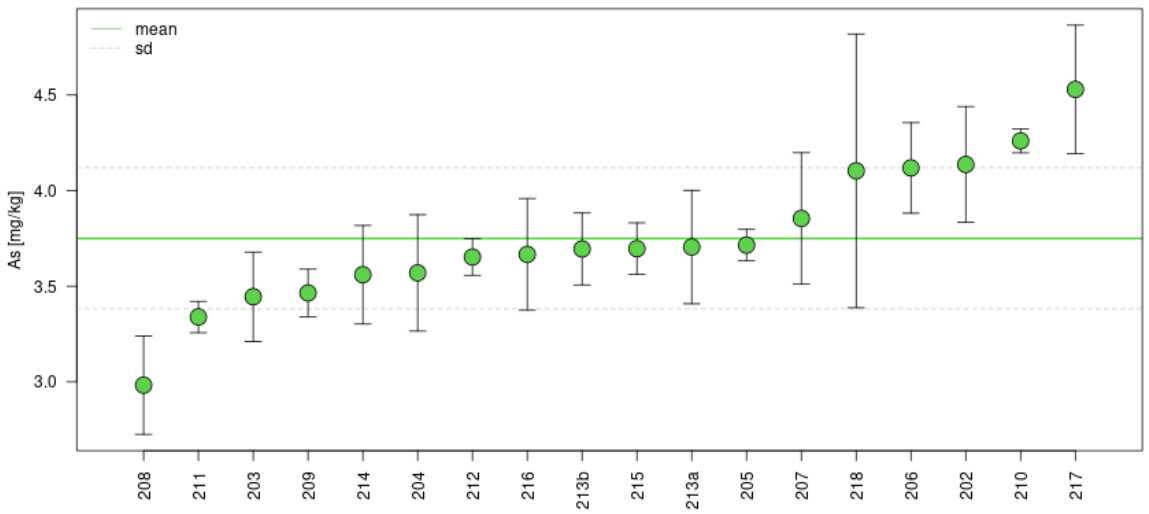
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 72061
Email: sales.crm@bam.de
https://www.webshop.bam.de

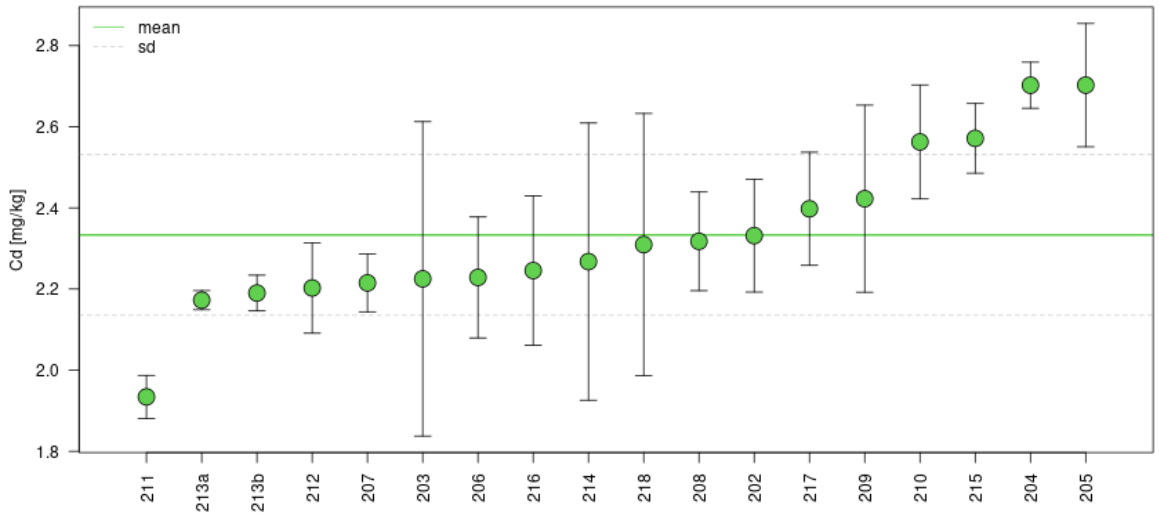
Each unit will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM, https://www.bam.de.

Appendix 1: Certification study

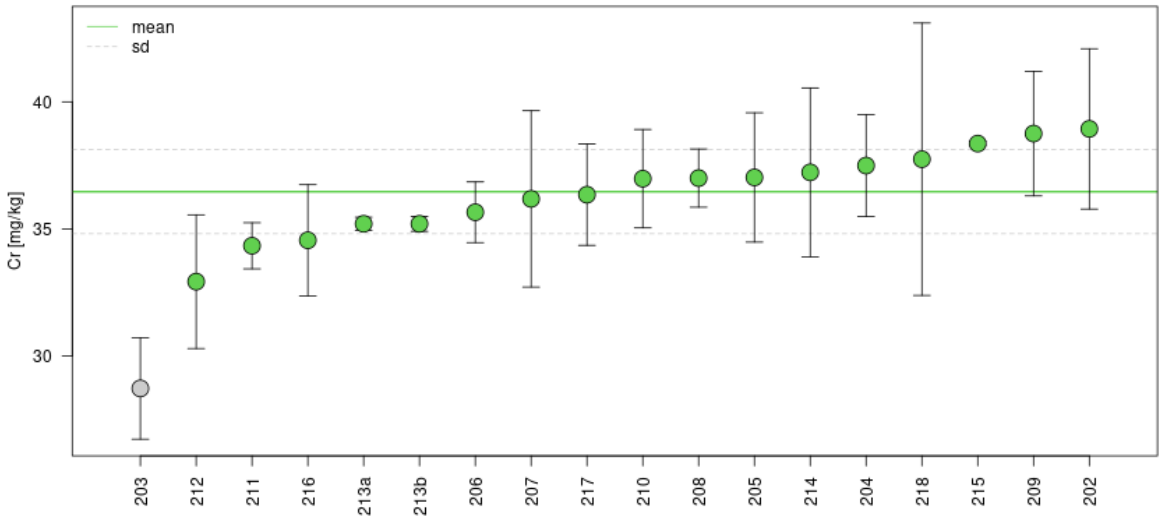
Certification study (measurement results of participating laboratories)							As
Lab code	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Lab mean** (mg/kg)	**SD** (mg/kg)	**Analytical method**
202	4.382	4.444	4.775	3.990	4.398	0.3222	ICP-MS
203	3.541	4.079	3.562	3.648	3.707	0.2519	ICP-OES
204	4.298	3.582	3.946	3.637	3.866	0.3298	ICP-OES
205	3.894	3.979	4.064	3.872	3.952	0.0875	ICP-OES
206	4.260	4.201	4.612	4.718	4.448	0.2558	ICP-OES
207	4.382	4.405	3.745	3.783	4.079	0.3640	ICP-MS
208	2.879	3.380	3.217	3.533	3.252	0.2805	ICP-OES
209	3.823	3.640	3.576	3.844	3.721	0.1331	ICP-OES/ ICP-MS
210	4.564	4.672	4.521	4.629	4.596	0.0671	ICP-OES
211	3.507	3.641	3.706	3.683	3.634	0.0891	ICP-OES
212	3.767	3.948	3.873	4.001	3.897	0.1017	ICP-OES
213a	3.854	3.757	4.470	3.919	4.000	0.3201	ICP-MS
213b	3.761	4.203	4.095	3.869	3.982	0.2027	ICP-MS
214	3.538	3.678	4.131	4.012	3.840	0.2781	ICP-MS
215	3.887	3.961	4.024	4.229	4.025	0.1471	ICP-MS
216	4.053	4.003	3.571	4.343	3.993	0.3186	ICP-MS
217	4.897	4.551	4.850	5.431	4.932	0.3661	ICP-OES
218	4.269	3.636	4.456	5.513	4.469	0.7798	ICP-OES
			M (mg/kg):		**4.044**		
			SD_M (mg/kg):		0.3977		
			$SD_M/\sqrt{N}$ (mg/kg):		0.0937		



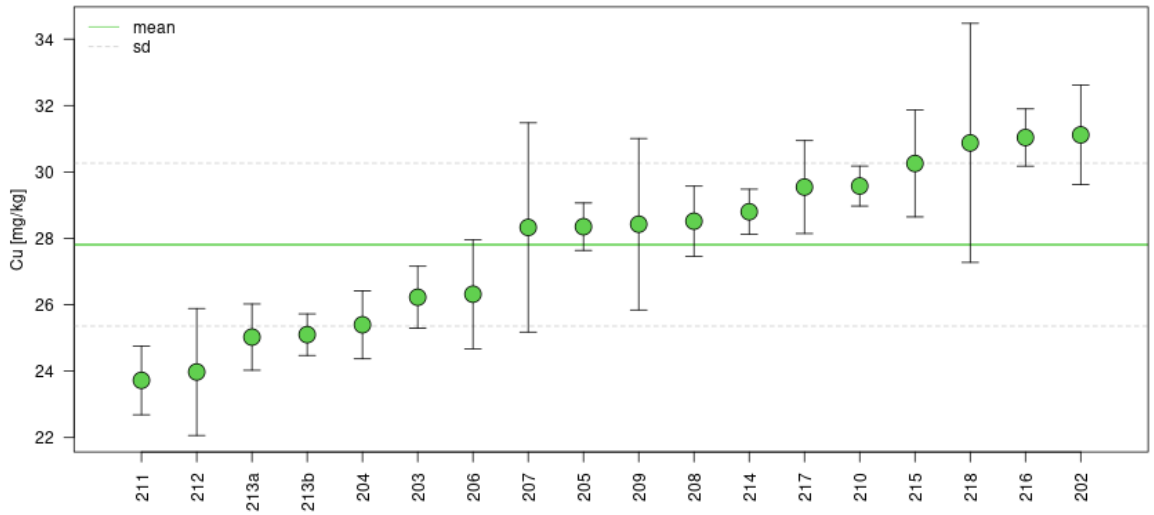
Certification study (measurement results of participating laboratories)							**Cd**
Lab code	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Lab mean** (mg/kg)	**SD** (mg/kg)	**Analytical method**
202	2.363	2.374	2.681	2.496	2.479	0.1479	ICP-MS
203	2.185	2.916	1.959	2.518	2.395	0.4170	ICP-OES
204	2.928	2.850	3.001	2.926	2.926	0.0615	ICP-OES
205	2.851	2.681	3.074	2.894	2.875	0.1617	ICP-OES
206	2.292	2.618	2.446	2.271	2.407	0.1610	ICP-OES
207	2.419	2.287	2.398	2.272	2.344	0.0753	ICP-MS
208	2.475	2.661	2.366	2.606	2.527	0.1325	ICP-OES
209	2.760	2.330	2.459	2.856	2.601	0.2476	ICP-OES/ ICP-MS
210	2.762	2.687	2.978	2.633	2.765	0.1517	ICP-OES
211	2.057	2.054	2.165	2.144	2.105	0.0578	ICP-OES
212	2.209	2.497	2.369	2.326	2.350	0.1189	ICP-OES
213a	2.343	2.364	2.310	2.364	2.345	0.0255	ICP-MS
213b	2.339	2.382	2.306	2.414	2.360	0.0474	ICP-MS
214	2.837	2.664	2.039	2.243	2.446	0.3684	ICP-MS
215	2.731	2.729	2.927	2.813	2.800	0.0936	ICP-MS
216	2.562	2.615	2.166	2.437	2.445	0.2003	ICP-MS
217	2.717	2.663	2.678	2.386	2.611	0.1518	ICP-OES
218	2.817	2.314	2.121	2.807	2.515	0.3520	ICP-OES
			M (mg/kg):		**2.516**		
			SD_M (mg/kg):		0.2134		
			$SD_M/\sqrt{N}$ (mg/kg):		0.0517		



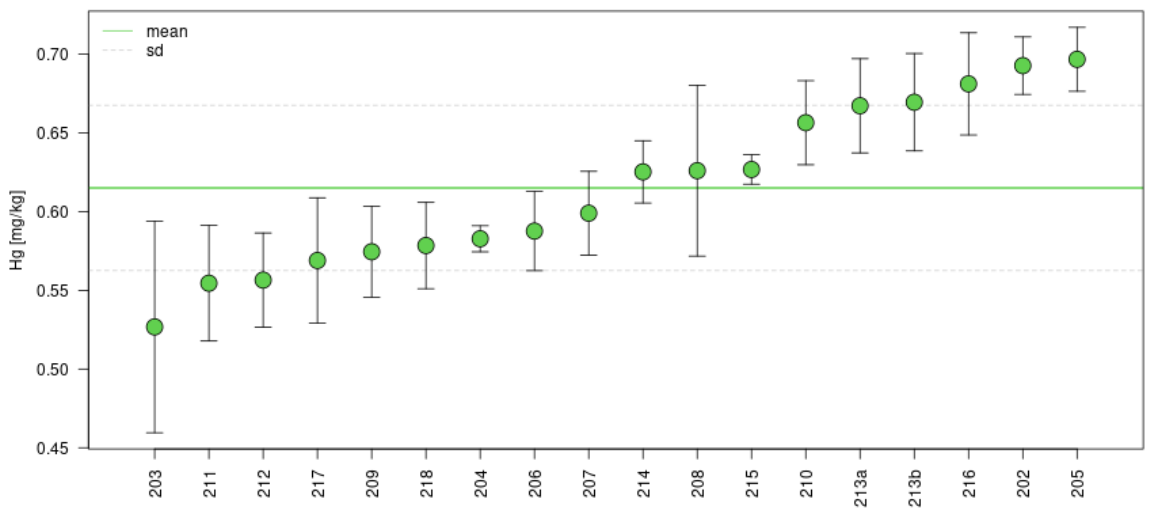
Certification study (measurement results of participating laboratories)							Cr
Lab code	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Lab mean** (mg/kg)	**SD** (mg/kg)	**Analytical method**
202	37.587	42.673			40.130	3.5962	ICP-MS
203	32.393	30.026	32.932	28.304	30.914	2.1495	ICP-OES
204	43.530	38.484	39.575	40.813	40.601	2.1726	ICP-OES
205	36.596	42.553	40.638	37.766	39.388	2.7086	ICP-OES
206	39.903	39.039	36.879	38.197	38.504	1.2881	ICP-OES
207	39.122	43.005	36.508	34.508	38.286	3.6699	ICP-MS
208	40.007	40.541	41.915	38.905	40.342	1.2503	ICP-OES
209	42.306	38.334	41.125	44.669	41.609	2.6338	ICP-OES/ ICP-MS
210	41.864	37.549	38.735	41.433	39.895	2.0892	ICP-OES
211	38.618	36.651	37.704	36.512	37.371	0.9868	ICP-OES
212	38.734	32.012	34.253	35.533	35.133	2.8075	ICP-OES
213a	37.895	38.327	37.679	38.111	38.003	0.2788	ICP-MS
213b	37.935	37.827	38.366	37.612	37.935	0.3173	ICP-MS
214	41.309	41.202	34.946	43.143	40.150	3.5820	ICP-MS
215	41.787	41.629	41.840	41.819	41.769	0.0955	ICP-MS
216	40.116	35.156	39.152	36.084	37.627	2.3812	ICP-MS
217	41.643	41.028	38.708	36.934	39.578	2.1689	ICP-OES
218	41.431	36.846	36.886	49.233	41.099	5.8338	ICP-OES
			M (mg/kg):		**39.260**	without 203	
			SD_M (mg/kg):		1.7384		
			$SD_M/\sqrt{N}$ (mg/kg):		0.4216		



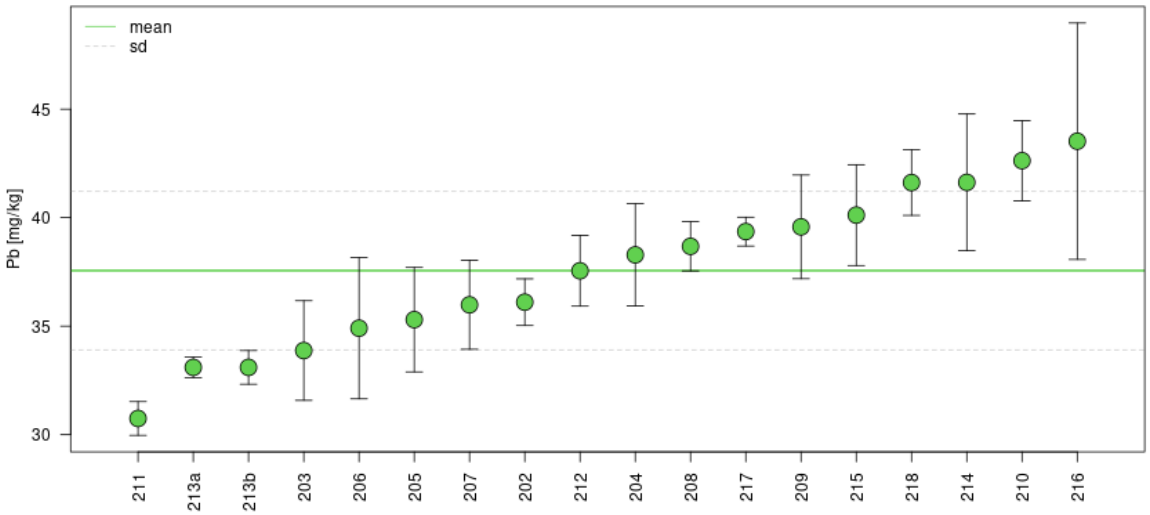
Certification study (measurement results of participating laboratories)							**Cu**
Lab code	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Lab mean** (mg/kg)	**SD** (mg/kg)	**Analytical method**
202	30.719	34.227	33.744	33.622	33.078	1.5942	ICP-MS
203	28.089	29.272	28.627	26.905	28.223	1.0033	ICP-OES
204	29.037	26.776	27.595	26.605	27.503	1.1102	ICP-OES
205	29.681	30.000	31.277	29.681	30.160	0.7597	ICP-OES
206	30.130	26.911	26.868	29.773	28.421	1.7737	ICP-OES
207	28.952	34.720	29.312	26.921	29.976	3.3329	ICP-MS
208	31.970	31.774	31.185	29.441	31.093	1.1507	ICP-OES
209	34.038	30.173	27.274	30.602	30.522	2.7716	ICP-OES/ ICP-MS
210	31.290	31.938	31.614	32.801	31.911	0.6496	ICP-OES
211	26.011	24.222	26.183	26.864	25.820	1.1274	ICP-OES
212	26.036	23.369	24.756	28.171	25.583	2.0403	ICP-OES
213a	27.314	28.178	26.991	25.587	27.018	1.0774	ICP-MS
213b	26.943	27.805	26.188	27.266	27.050	0.6759	ICP-MS
214	30.200	31.494	31.818	30.739	31.063	0.7315	ICP-MS
215	31.526	31.358	34.720	34.178	32.946	1.7517	ICP-MS
216	33.442	35.146	33.613	32.987	33.797	0.9371	ICP-MS
217	32.022	32.789	33.735	30.142	32.172	1.5240	ICP-OES
218	30.628	31.487	33.064	39.303	33.620	3.9202	ICP-OES
			M (mg/kg):		**29.997**		
			SD_M (mg/kg):		2.6913		
			$SD_M/\sqrt{N}$ (mg/kg):		0.6343		



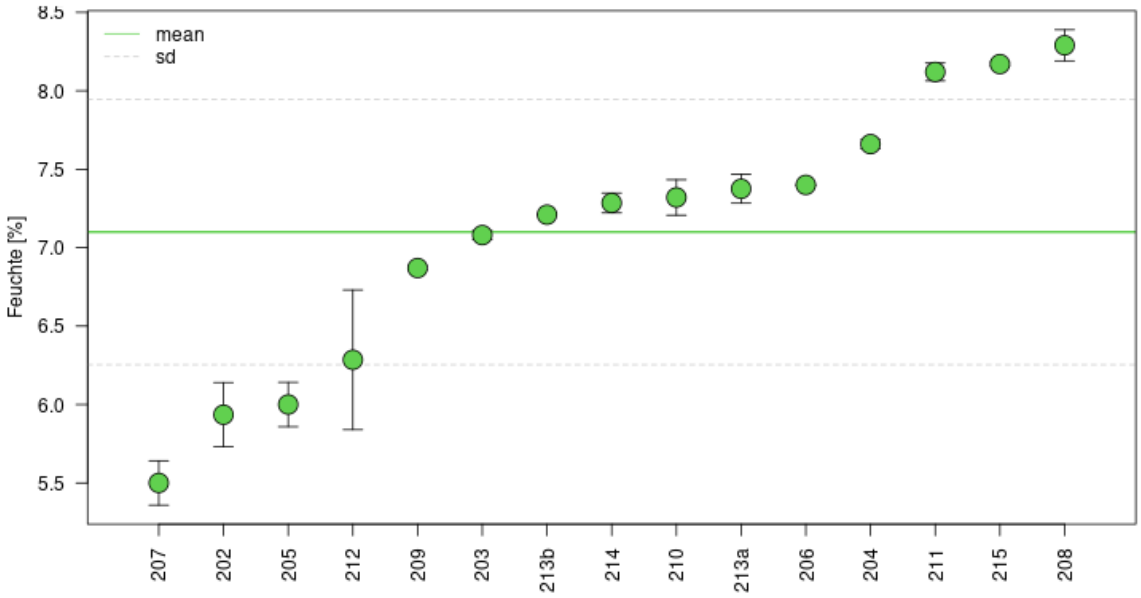
Certification study (measurement results of participating laboratories)							**Hg**
Lab code	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Lab mean** (mg/kg)	**SD** (mg/kg)	**Analytical method**
202	0.724	0.728	0.728	0.765	0.736	0.0194	CVAAS
203	0.577	0.470	0.646	0.575	0.567	0.0724	CVAAS
204	0.637	0.638	0.618	0.631	0.631	0.0089	CVAAS
205	0.734	0.730	0.773	0.728	0.741	0.0216	CVAAS
206	0.611	0.643	0.615	0.669	0.635	0.0271	ICP-OES
207	0.668	0.640	0.600	0.628	0.634	0.0281	CVAAS
208	0.639	0.627	0.749	0.715	0.683	0.0591	CVAAS
209	0.629	0.591	0.593	0.655	0.617	0.0310	CVAAS
210	0.683	0.729	0.684	0.737	0.708	0.0288	CVAAS
211	0.661	0.570	0.600	0.583	0.604	0.0399	CVAAS
212	0.618	0.611	0.599	0.547	0.594	0.0320	CVAAS
213a	0.687	0.727	0.762	0.706	0.720	0.0323	CVAAS
213b	0.718	0.737	0.754	0.677	0.722	0.0334	CVAAS
214	0.690	0.647	0.692	0.668	0.674	0.0213	CVAAS
215	0.668	0.691	0.687	0.684	0.683	0.0102	ICP-MS
216	0.733	0.784	0.699	0.751	0.742	0.0354	ICP-MS
217	0.619	0.615	0.675	0.569	0.620	0.0434	CVAAS
218	0.608	0.623	0.674	0.615	0.630	0.0299	CVAAS
			M (mg/kg):		**0.663**		
			SD_M (mg/kg):		0.0557		
			$SD_M/\sqrt{N}$ (mg/kg):		0.0131		



Certification study (measurement results of participating laboratories)							**Pb**
Lab code	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Lab mean** (mg/kg)	**SD** (mg/kg)	**Analytical method**
202	38.151	39.595	36.915	38.873	38.384	1.1428	ICP-MS
203	32.824	37.774	38.205	37.021	36.456	2.4704	ICP-OES
204	41.735	44.441	38.206	41.461	41.461	2.5531	ICP-OES
205	38.404	35.000	40.745	36.064	37.553	2.5591	ICP-OES
206	39.471	33.337	36.577	41.393	37.694	3.5153	ICP-OES
207	40.392	36.011	39.439	36.466	38.077	2.1663	ICP-MS
208	40.781	41.511	43.409	42.994	42.174	1.2352	ICP-OES
209	46.279	41.018	40.803	41.877	42.494	2.5656	ICP-OES/ ICP-MS
210	44.886	43.807	48.123	47.151	45.992	1.9903	ICP-OES
211	33.623	34.392	32.341	33.492	33.462	0.8461	ICP-OES
212	40.335	41.509	37.561	40.869	40.068	1.7392	ICP-OES
213a	35.951	35.628	35.088	36.275	35.735	0.5064	ICP-MS
213b	35.995	35.349	36.642	34.702	35.672	0.8348	ICP-MS
214	44.869	48.212	40.231	46.271	44.896	3.3986	ICP-MS
215	40.550	46.276	42.840	45.079	43.686	2.5299	ICP-MS
216	40.632	52.020	44.207	52.715	47.394	5.9327	ICP-MS
217	42.050	43.748	42.571	43.070	42.860	0.7240	ICP-OES
218	47.107	44.111	46.322	43.737	45.319	1.6496	ICP-OES
			M (mg/kg):		**40.521**		
			SD_M (mg/kg):		4.0775		
			$SD_M/\sqrt{N}$ (mg/kg):		0.9611		



Certification study (measurement results of participating laboratories					**Moisture**
Lab code	**#1** (%)	**#2** (%)	**Lab mean** (%)	**SD** (%)	**Analytical method**
202	5.79	6.08	5.935	0.2051	DIN EN 15934/ DIN EN 13183
203	7.06	7.10	7.080	0.0283	DIN EN 15934/ DIN EN 13183
204	7.64	7.68	7.660	0.0283	DIN EN 15934/ DIN EN 13183
205	6.10	5.90	6.000	0.1414	DIN EN 15934/ DIN EN 13183
206	7.40	7.40	7.400	0.0000	DIN EN 15934/ DIN EN 13183
207	5.40	5.60	5.500	0.1414	
208	8.22	8.36	8.290	0.0990	
209	6.86	6.88	6.870	0.0141	DIN EN 15934/ DIN EN 13183
210	7.40	7.24	7.320	0.1131	DIN EN 15934/ DIN EN 13183
211	8.16	8.08	8.120	0.0566	DIN EN 15934/ DIN EN 13183
212	6.60	5.97	6.285	0.4455	DIN EN 15934/ DIN EN 13183
213a	7.31	7.44	7.375	0.0919	DIN EN 15934/ DIN EN 13183
213b	7.21	7.21	7.210	0.0000	DIN EN 15934/ DIN EN 13183
214	7.33	7.24	7.285	0.0636	DIN EN 15934/ DIN EN 13183
215	8.18	8.16	8.170	0.0141	DIN EN 15934
216	8.18	8.16	8.170	0.0141	DIN EN 15934
217	8.18	8.16	8.170	0.0141	DIN EN 15934
218	8.18	8.16	8.170	0.0141	DIN EN 15934
		M (%):	**7.100**		
		SD_M (%):	0.8460		
		$SD_M/\sqrt{N}$ (%):	0.2184		



Appendix 2: Homogeneity study

Homogeneity study (measurement results)					**As**
(1) Sample intake: 1.5 g			Analytical method:		ICP-OES
Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	4.751	4.653	4.617	4.674	0.0690
042	5.236	4.726	4.206	4.723	0.5148
063	4.852	4.312	4.488	4.551	0.2753
084	4.799	4.589	4.181	4.523	0.3146
105	4.061	4.528	5.028	4.539	0.4834
126	4.284	4.636	4.525	4.482	0.0788
147	4.168	4.250	4.318	4.246	0.0482
168	4.662	4.465	5.171	4.766	0.4998
189	4.312	4.136	4.606	4.351	0.3323
210	4.363	4.917	4.775	4.685	0.1001
231	4.128	4.087	4.298	4.171	0.1493
252	4.082	4.674	4.373	4.377	0.2128
		M (mg/kg):		**4.507**	
		SD_M (mg/kg):		0.1905	
		$u_{bb, rel}$ (%):		2.073	
		(acc. to ISO Guide 35)			
(2) Sample intake: 0.5 g			Analytical method:		ICP-MS
Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	3.775	3.997	3.907	3.893	0.1116
028	4.430	3.512	3.246	3.729	0.6212
044	3.414	3.953	4.124	3.830	0.3708
060	3.888	4.318	3.062	3.756	0.6380
076	3.584	3.985	3.860	3.810	0.2054
092	3.403	5.107	4.600	4.370	0.3584
108	3.239	3.881	3.463	3.528	0.2956
124	3.900	3.850	3.670	3.807	0.1269
140	4.197	3.985	3.557	3.913	0.3025
156	4.244	4.169	4.178	4.197	0.0070
172	3.714	3.839	4.771	4.108	0.6591
188	4.824	3.025	3.238	3.695	0.1505
		M (mg/kg):		**3.886**	
		SD_M (mg/kg):		0.2340	
		$u_{bb, rel}$ (%):		4.172	
		(acc. to ISO Guide 35)			

Homogeneity study (measurement results)					**Cd**
(1) Sample intake: 1.5 g				Analytical method:	ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	2.570	2.945	2.658	2.724	0.1963
042	2.735	2.687	2.267	2.563	0.2574
063	2.731	2.741	2.529	2.667	0.1193
084	2.535	2.537	2.731	2.601	0.1124
105	2.966	2.470	2.460	2.632	0.2892
126	2.630	2.872	2.544	2.682	0.2320
147	2.678	2.549	2.330	2.519	0.1551
168	2.714	2.519	2.615	2.616	0.0677
189	2.576	2.576	2.972	2.708	0.2802
210	2.567	2.581	2.623	2.591	0.0301
231	2.745	2.586	2.803	2.711	0.1535
252	2.338	2.497	2.310	2.382	0.1322

		M (mg/kg):		**2.616**	
		SD_M (mg/kg):		0.0975	
		$u_{bb,\ rel}$ (%):		2.055	
		(acc. to ISO Guide 35)			

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

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	2.781	3.048	2.339	2.723	0.3581
028	2.266	2.677	2.973	2.639	0.3551
044	2.464	2.237	3.111	2.604	0.4535
060	1.938	2.871	2.990	2.600	0.5761
076	2.295	2.538	1.985	2.273	0.2772
092	2.835	2.336	2.527	2.566	0.1351
108	2.588	2.247	2.043	2.293	0.1442
124	2.781	2.855	1.914	2.517	0.6654
140	2.188	3.085	2.380	2.551	0.4985
156	2.545	3.089	1.789	2.474	0.9192
172	2.615	2.601	2.152	2.456	0.3175
188	2.653	2.418	1.568	2.213	0.6010

		M (mg/kg):		**2.492**	
		SD_M (mg/kg):		0.1583	
		$u_{bb,\ rel}$ (%):		5.480	
		(acc. to ISO Guide 35)			

Homogeneity study (measurement results)					**Cr**
(1) Sample intake: 1.5 g				Analytical method:	ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	42.661	42.572	37.888	41.040	2.7307
042	34.059	40.640	34.840	36.513	3.5954
063	37.663	42.434	41.854	40.650	2.6032
084	37.137	37.941	39.284	38.121	1.0845
105	38.454	35.911	36.116	36.827	1.4128
126	36.543	42.062	46.439	41.681	3.0946
147	39.601	42.160	38.706	40.156	2.4424
168	39.067	34.362	39.257	37.562	3.4617
189	45.686	35.054	38.010	39.583	2.0895
210	41.210	46.095	36.309	41.204	6.9200
231	40.006	35.799	37.754	37.853	1.3823
252	36.091	40.646	34.479	37.072	4.3608

M (mg/kg):	**39.022**	
SD_M (mg/kg):	1.8922	
$u_{bb, rel}$ (%):	2.662	
(acc. to ISO Guide 35)		

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

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	40.98	35.13	38.12	38.07	2.924
028	33.08	38.29	38.86	36.75	3.185
044	31.81	32.30	33.74	32.62	1.005
060	35.42	35.99	40.95	37.45	3.043
076	37.46	32.45	33.68	34.53	2.608
092	30.21	38.05	42.56	36.94	3.184
108	34.57	39.13	34.88	36.19	3.009
124	38.76	36.46	32.60	35.94	2.730
140	32.67	35.00	36.77	34.82	1.252
156	33.82	34.21	30.14	32.72	2.884
172	35.75	44.39	36.01	38.72	5.924
188	26.26	34.01	36.50	32.26	1.755

M (mg/kg):	**35.58**	
SD_M (mg/kg):	2.194	
$u_{bb, rel}$ (%):	3.112	
(acc. to ISO Guide 35)		

Homogeneity study (measurement results)					**Cu**
(1) Sample intake: 1.5 g				Analytical method:	ICP-OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	31.046	27.428	30.261	29.578	1.9032
042	29.065	30.195	26.782	28.681	1.7384
063	29.086	26.985	28.895	28.322	1.1621
084	29.337	30.925	31.102	30.454	0.9720
105	26.352	27.466	31.338	28.385	2.6171
126	33.094	30.348	33.500	32.314	2.2284
147	33.890	26.214	33.596	31.233	5.2202
168	27.404	32.527	29.429	29.787	2.1903
189	33.156	31.082	32.156	32.131	0.7591
210	30.822	29.410	29.739	29.990	0.2323
231	29.212	30.007	31.527	30.249	1.0744
252	29.674	30.413	31.059	30.382	0.4568

		M (mg/kg):		**30.125**	
		SD_M (mg/kg):		1.3153	
		$u_{bb,\ rel}$ (%):		2.106	
		(acc. to ISO Guide 35)			

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

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	32.56	29.43	29.33	30.44	1.836
028	28.26	27.71	32.26	29.41	2.486
044	24.22	24.71	30.86	26.59	3.698
060	26.03	37.38	23.83	29.08	7.273
076	32.97	32.25	32.74	32.66	0.368
092	29.68	34.78	26.95	30.47	5.534
108	23.97	27.78	27.63	26.46	0.105
124	31.70	29.11	22.91	27.91	4.378
140	23.80	27.25	24.87	25.31	1.682
156	25.72	28.64	22.74	25.70	4.170
172	25.60	27.21	27.85	26.89	0.454
188	26.60	26.04	30.12	27.59	2.884

		M (mg/kg):		**28.21**	
		SD_M (mg/kg):		2.229	
		$u_{bb,\ rel}$ (%):		3.909	
		(acc. to ISO Guide 35)			

Homogeneity study (measurement results) **Hg**

(1) Sample intake: 1.5 g Analytical method: ICP-MS

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	0.735	0.738	0.698	0.724	0.0219
042	0.659	0.684	0.619	0.654	0.0330
063	0.662	0.692	0.636	0.663	0.0280
084	0.683	0.641	0.660	0.661	0.0211
105	0.623	0.688	0.575	0.628	0.0571
126	0.640	0.659	0.651	0.650	0.0057
147	0.680	0.731	0.610	0.674	0.0861
168	0.634	0.652	0.667	0.651	0.0107
189	0.707	0.670	0.617	0.665	0.0380
210	0.704	0.628	0.734	0.689	0.0743
231	0.625	0.684	0.629	0.646	0.0393
252	0.640	0.626	0.669	0.645	0.0304

M (mg/kg):	**0.662**
SD_M (mg/kg):	0.0246
$u_{bb, rel}$ (%):	1.791
(acc. to ISO Guide 35)	

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

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	0.710	0.671	0.580	0.654	0.0667
028	0.632	0.605	0.672	0.636	0.0336
044	0.666	0.726	0.611	0.668	0.0579
060	0.563	0.738	0.645	0.649	0.0874
076	0.677	0.672	0.619	0.656	0.0320
092	0.818	0.641	0.596	0.685	0.0320
108	0.611	0.650	0.625	0.628	0.0176
124	0.627	0.627	0.715	0.657	0.0622
140	0.701	0.722	0.624	0.683	0.0691
156	0.557	0.796	0.600	0.651	0.1382
172	0.711	0.594	0.601	0.635	0.0052
188	0.632	0.655	0.533	0.606	0.0866

M (mg/kg):	**0.651**
SD_M (mg/kg):	0.0223
$u_{bb, rel}$ (%):	3.416
(acc. to ISO Guide 35)	

Homogeneity study (measurement results)					**Pb**
(1) Sample intake: 1.5 g				Analytical method:	ICP-OES

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	36.357	44.756	42.723	41.278	4.3818
042	43.165	41.699	43.921	42.928	1.1297
063	36.925	36.094	41.561	38.193	2.9458
084	41.394	38.242	39.107	39.581	1.6283
105	45.906	45.374	34.165	41.815	6.6303
126	40.784	41.886	43.380	42.017	1.0561
147	43.758	33.768	36.086	37.871	1.6391
168	43.039	40.457	39.934	41.143	0.3702
189	40.707	40.248	45.734	42.229	3.8788
210	35.621	37.455	32.647	35.241	3.3998
231	34.072	33.965	35.870	34.636	1.3467
252	37.772	38.758	47.883	41.471	6.4520

		M (mg/kg):		**39.867**	
		SD_M (mg/kg):		2.7830	
		$u_{bb,\ rel}$ (%):		4.653	
		(acc. to ISO Guide 35)			
(2) Sample intake: 0.5 g				Analytical method:	ICP-OES

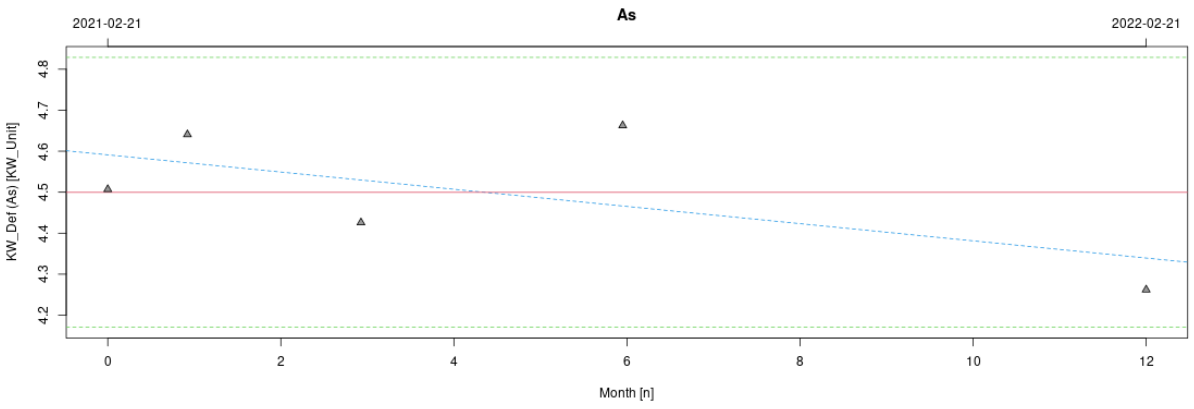
Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
012	40.04	41.15	40.42	40.54	0.564
028	48.43	36.59	46.02	43.68	6.256
044	38.95	36.51	31.76	35.74	3.659
060	36.32	36.55	51.71	41.52	8.818
076	35.74	43.52	34.49	37.92	4.891
092	45.57	42.21	39.23	42.34	2.108
108	32.30	33.86	49.38	38.51	10.972
124	44.40	32.51	42.99	39.97	7.408
140	37.33	38.81	50.55	42.23	8.299
156	37.24	37.84	38.20	37.76	0.257
172	33.99	39.50	28.07	33.85	8.083
188	42.66	35.64	39.75	39.35	2.907

		M (mg/kg):		**39.45**	
		SD_M (mg/kg):		2.874	
		$u_{bb,\ rel}$ (%):		4.504	
		(acc. to ISO Guide 35)			

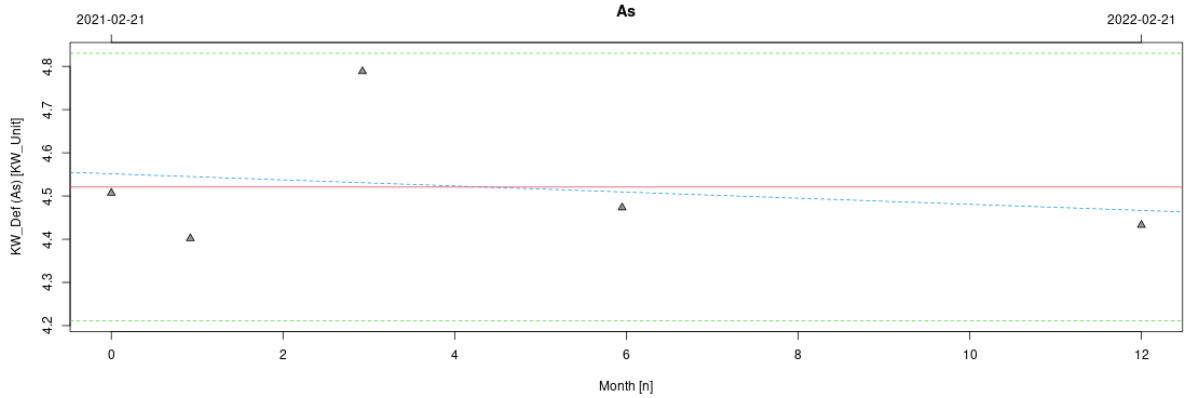
Appendix 3: Stability study

Stability study						**ICP-OES**	**As**
Mass fraction in mg/kg							
Sample No.	storage temperature	#**1**	#**2**	#**3**	Mean	SD	$RSD_{\%}$
170/171	-20°C	4.465	4.579	4.878	4.641	0.213	4.59
170/171	-20°C	4.036	4.229	5.012	4.426	0.517	11.68
172/173	-20°C	4.917	4.790	4.281	4.663	0.336	7.22
172/173	-20°C	4.378	4.327	4.081	4.262	0.159	3.73
176/177	4°C; 1 month	4.364	4.471	4.370	4.402	0.060	1.37
176/177	4°C; 3 months	4.824	4.895	4.646	4.788	0.129	2.69
178/179	4°C; 6 months	4.503	4.554	4.362	4.473	0.099	2.22
178/179	4°C; 12 months	4.476	4.441	4.382	4.433	0.048	1.07
182/183	23°C; 1 month	4.709	4.312	4.660	4.560	0.217	4.75
182/183	23°C; 3 months	4.918	4.959	4.977	4.951	0.030	0.61
184/185	23°C; 6 months	4.287	4.660	4.333	4.427	0.203	4.59
184/185	23°C; 12 months	4.540	4.629	4.451	4.540	0.089	1.97
188/191	40°C; 1 month	4.187	4.106	4.405	4.233	0.155	3.65
188/191	40°C; 3 months	4.154	4.660	4.230	4.348	0.273	6.28
192/193	40°C; 6 months	4.629	4.316	4.804	4.583	0.247	5.39
192/193	40°C; 12 months	4.882	4.586	4.677	4.715	0.152	3.21
194/195	60°C; 1 month	4.327	4.402	4.860	4.530	0.289	6.38
194/195	60°C; 3 months	4.542	4.899	4.739	4.727	0.179	3.79

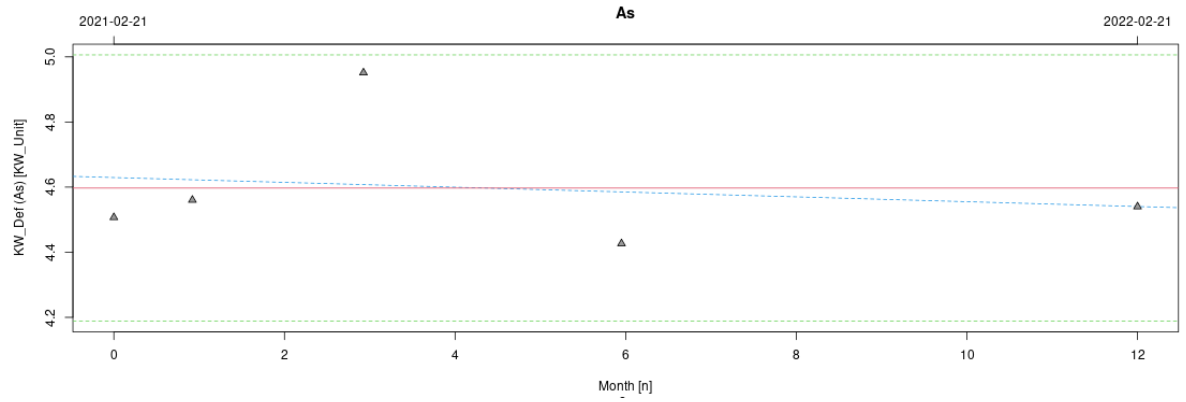
-20 °C:



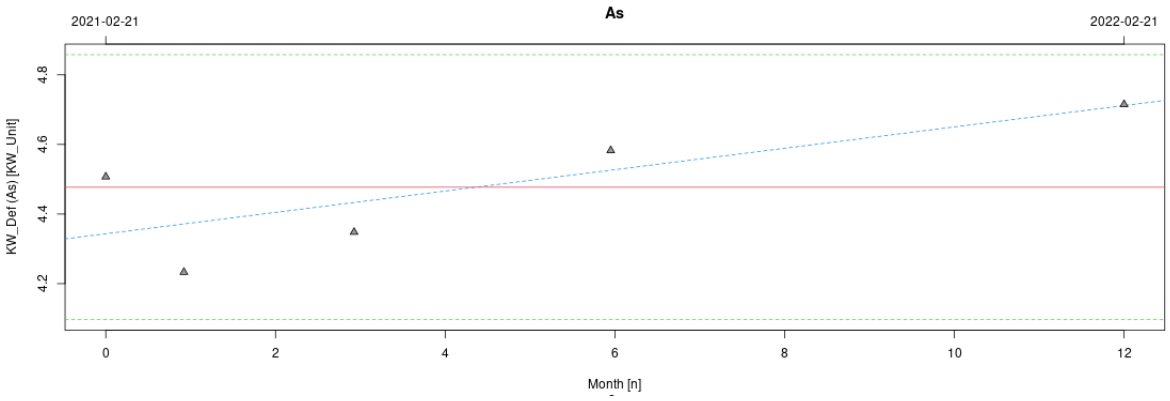
4 °C:


As
2021-02-21
2022-02-21
KW_Def (As) [KW_Unit]
4.2
4.3
4.4
4.5
4.6
4.7
4.8
0
2
4
6
8
10
12
Month [n]

23 °C:

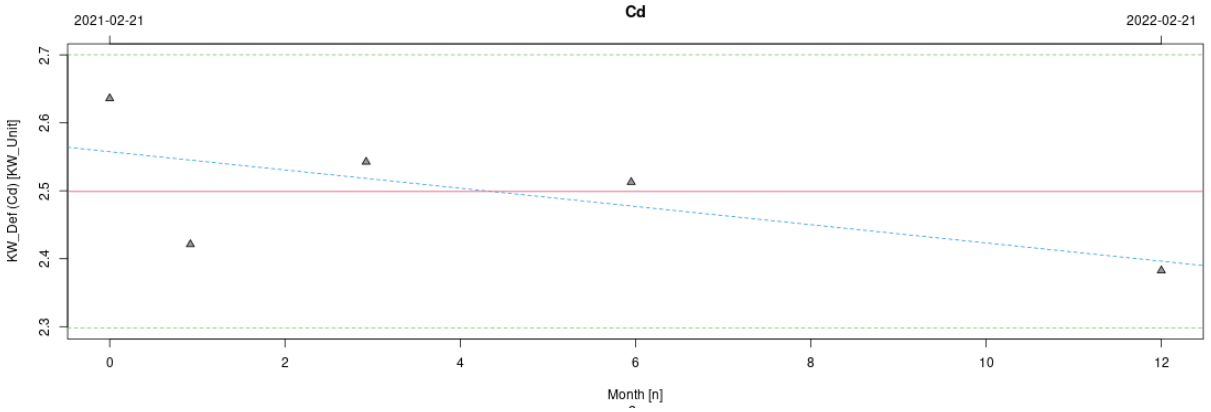

As
2021-02-21
2022-02-21
KW_Def (As) [KW_Unit]
4.2
4.4
4.6
4.8
5.0
0
2
4
6
8
10
12
Month [n]

40 °C:

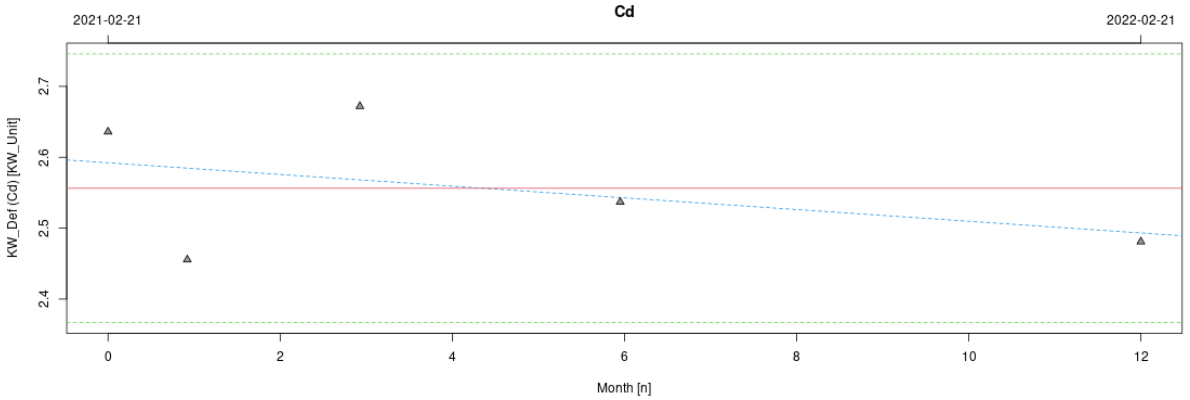

As
2021-02-21
2022-02-21
KW_Def (As) [KW_Unit]
4.2
4.4
4.6
4.8
0
2
4
6
8
10
12
Month [n]

Stability study						**ICP-OES**	**Cd**
Mass fraction in mg/kg							
Sample No.	storage temperature	#**1**	#**2**	#3	Mean	SD	$RSD_{\%}$
170/171	-20°C	2.463	2.296	2.504	2.421	0.110	4.54
170/171	-20°C	2.338	3.021	2.269	2.543	0.416	16.35
172/173	-20°C	2.588	2.488	2.462	2.513	0.067	2.65
172/173	-20°C	2.247	2.645	2.255	2.383	0.228	9.55
176/177	4°C; 1 month	2.696	2.318	2.353	2.456	0.209	8.50
176/177	4°C; 3 months	2.843	2.283	2.890	2.672	0.338	12.64
178/179	4°C; 6 months	2.754	2.496	2.361	2.537	0.200	7.86
178/179	4°C; 12 months	2.298	2.661	2.483	2.481	0.181	7.31
182/183	23°C; 1 month	2.637	2.421	2.740	2.599	0.162	6.25
182/183	23°C; 3 months	2.358	2.642	2.836	2.612	0.241	9.21
184/185	23°C; 6 months	2.647	2.672	2.628	2.649	0.022	0.83
184/185	23°C; 12 months	2.396	2.422	2.523	2.447	0.067	2.74
188/191	40°C; 1 month	2.301	2.172	2.427	2.300	0.127	5.54
188/191	40°C; 3 months	2.957	2.721	3.048	2.909	0.169	5.80
192/193	40°C; 6 months	2.279	2.462	3.050	2.597	0.403	15.52
192/193	40°C; 12 months	2.555	2.130	2.476	2.387	0.226	9.45
194/195	60°C; 1 month	2.275	2.530	2.401	2.402	0.128	5.31
194/195	60°C; 3 months	2.693	2.925	2.683	2.767	0.137	4.94

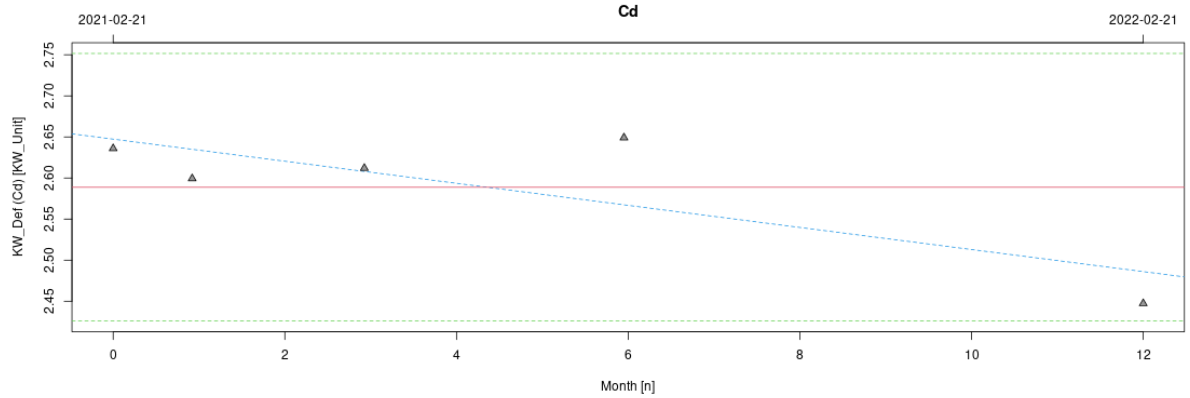
-20 °C:



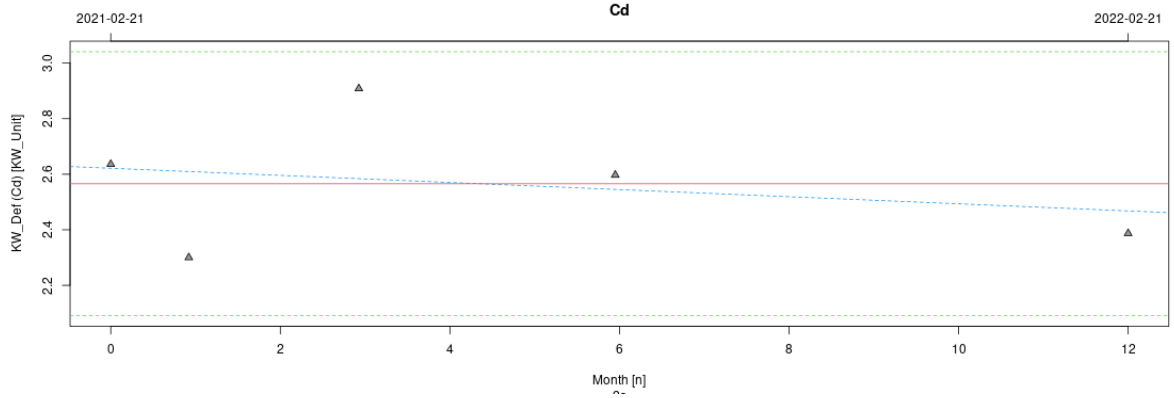
4 °C:


Cd
2021-02-21
2022-02-21
KW_Def (Cd) [KW_Unit]
2.4
2.5
2.6
2.7
0
2
4
6
8
10
12
Month [n]

23 °C:

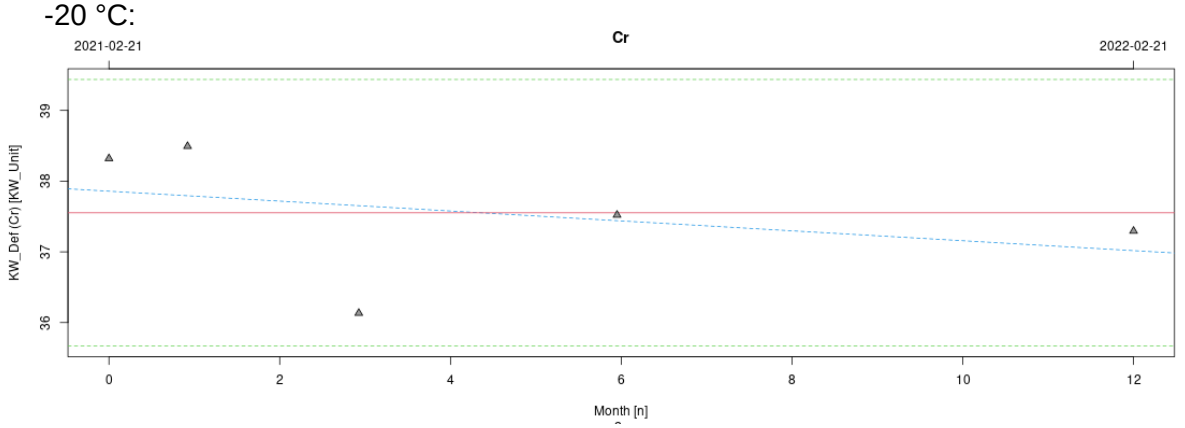

Cd
2021-02-21
2022-02-21
KW_Def (Cd) [KW_Unit]
2.45
2.50
2.55
2.60
2.65
2.70
2.75
0
2
4
6
8
10
12
Month [n]

40 °C:

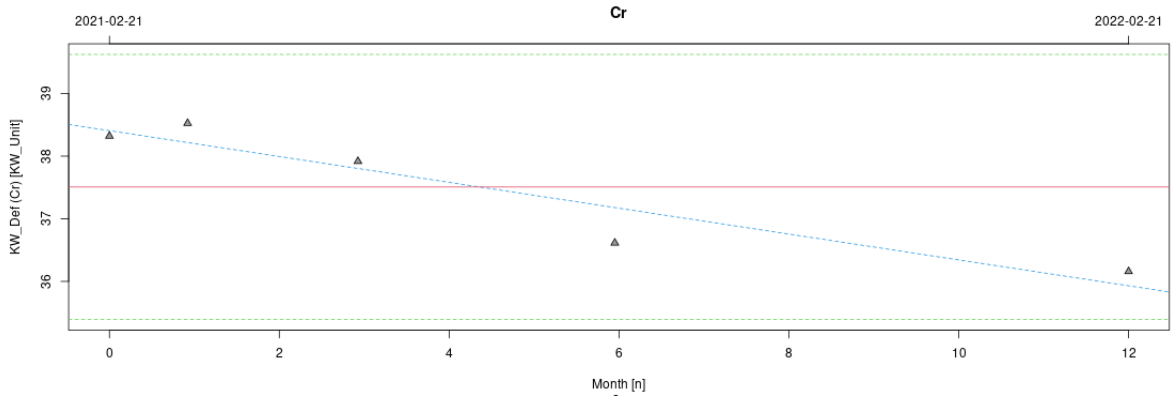

Cd
2021-02-21
2022-02-21
KW_Def (Cd) [KW_Unit]
2.2
2.4
2.6
2.8
3.0
0
2
4
6
8
10
12
Month [n]

Stability study						**ICP-OES**	**Cr**
Mass fraction in mg/kg							
Sample No.	storage temperature	#**1**	#**2**	#**3**	Mean	SD	$RSD_{\%}$
170/171	-20°C	39.466	37.347	38.666	38.493	1.070	2.78
170/171	-20°C	39.132	34.598	34.672	36.134	2.597	7.19
172/173	-20°C	37.719	37.285	37.558	37.521	0.219	0.58
172/173	-20°C	36.597	40.428	34.859	37.294	2.849	7.64
176/177	4°C; 1 month	37.417	39.836	38.321	38.525	1.222	3.17
176/177	4°C; 3 months	37.614	39.215	36.923	37.917	1.176	3.10
178/179	4°C; 6 months	34.017	37.203	38.622	36.614	2.358	6.44
178/179	4°C; 12 months	33.980	36.911	37.585	36.159	1.917	5.30
182/183	23°C; 1 month	33.297	36.303	35.021	34.873	1.508	4.33
182/183	23°C; 3 months	40.128	37.357	32.962	36.816	3.614	9.82
184/185	23°C; 6 months	39.877	35.871	35.238	36.995	2.516	6.80
184/185	23°C; 12 months	38.360	39.069	38.249	38.559	0.445	1.15
188/191	40°C; 1 month	35.797	36.253	34.847	35.632	0.717	2.01
188/191	40°C; 3 months	41.538	41.316	36.191	39.681	3.025	7.62
192/193	40°C; 6 months	37.182	34.384	35.145	35.570	1.446	4.07
192/193	40°C; 12 months	37.884	34.586	33.867	35.446	2.142	6.04
194/195	60°C; 1 month	35.772	34.960	36.657	35.796	0.849	2.37
194/195	60°C; 3 months	40.146	36.740	35.595	37.493	2.367	6.31

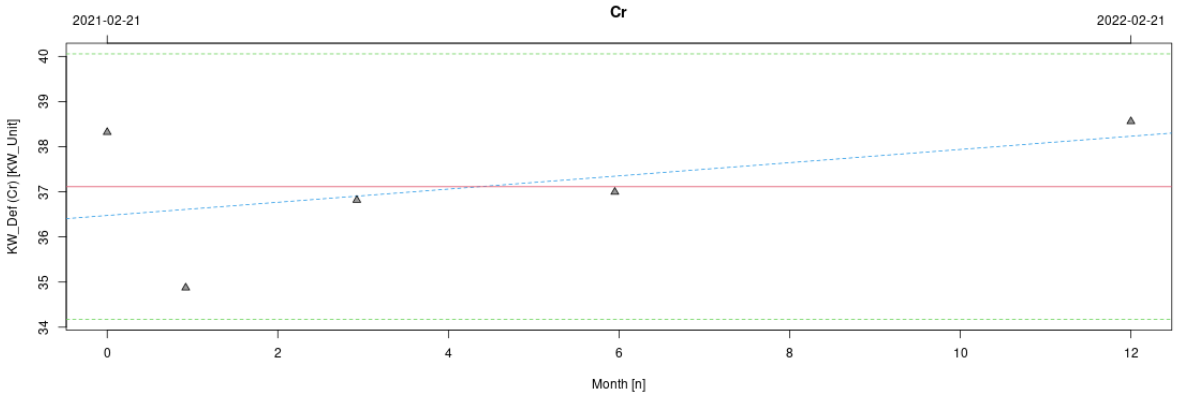
-20 °C:



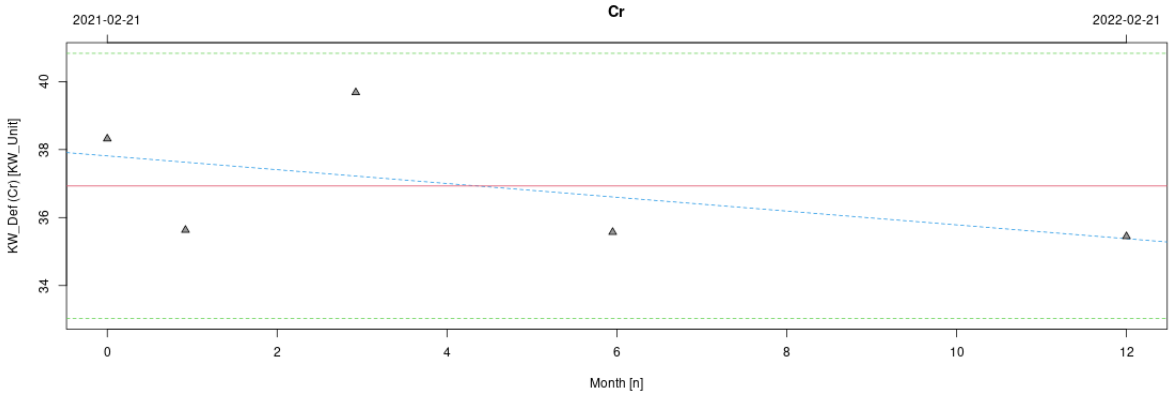
4 °C:


Cr
2021-02-21
2022-02-21
KW_Def (Cr) [KW_Unit]
36
37
38
39
0
2
4
6
8
10
12
Month [n]

23 °C:

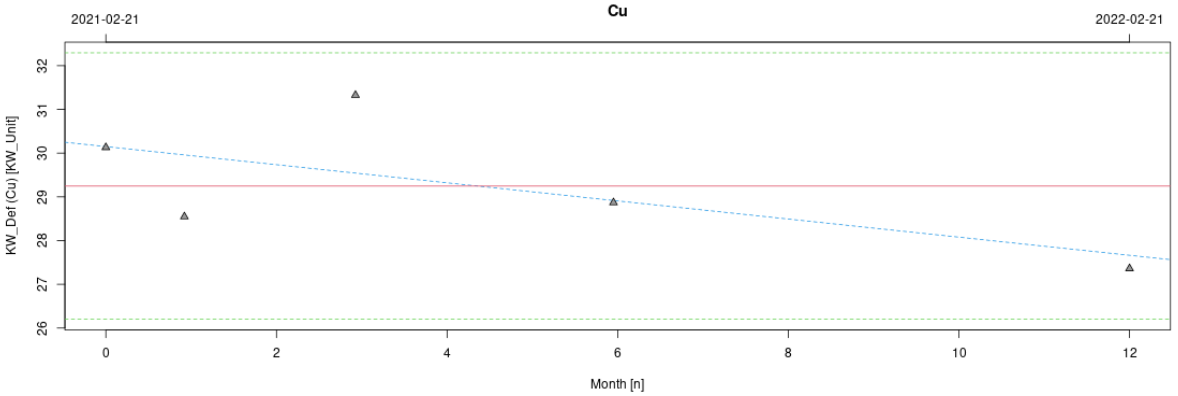

Cr
2021-02-21
2022-02-21
KW_Def (Cr) [KW_Unit]
34
35
36
37
38
39
40
0
2
4
6
8
10
12
Month [n]

40 °C:

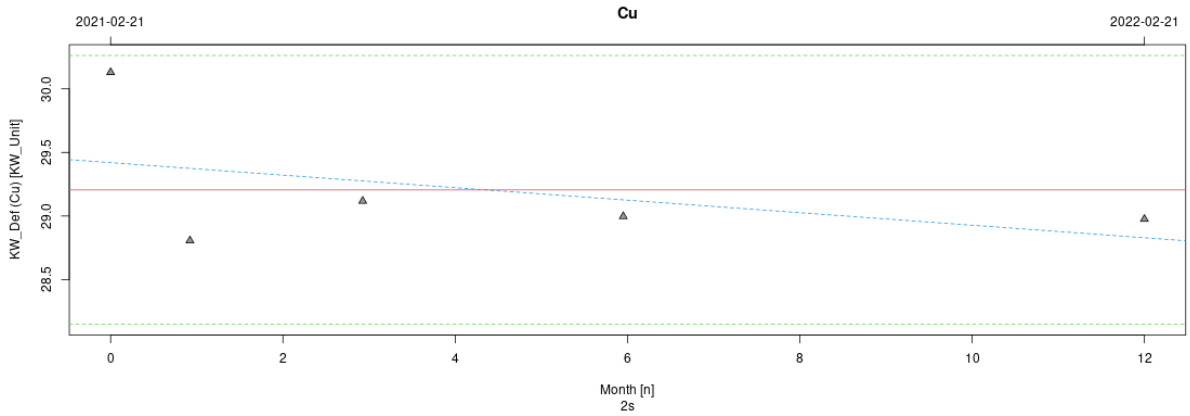

Cr
2021-02-21
2022-02-21
KW_Def (Cr) [KW_Unit]
34
36
38
40
0
2
4
6
8
10
12
Month [n]

Stability study						**ICP-OES**	**Cu**
Mass fraction in mg/kg							
Sample No.	storage temperature	#**1**	#**2**	#**3**	Mean	SD	$RSD_{\%}$
170/171	-20°C	28.818	28.722	28.104	28.548	0.387	1.36
170/171	-20°C	32.277	29.565	32.134	31.325	1.526	4.87
172/173	-20°C	30.479	26.661	29.469	28.870	1.979	6.85
172/173	-20°C	27.172	27.878	27.035	27.362	0.453	1.65
176/177	4°C; 1 month	27.251	28.599	30.568	28.806	1.668	5.79
176/177	4°C; 3 months	28.828	31.966	26.559	29.118	2.715	9.32
178/179	4°C; 6 months	33.305	26.906	26.780	28.997	3.732	12.87
178/179	4°C; 12 months	26.443	29.958	30.526	28.976	2.212	7.63
182/183	23°C; 1 month	28.339	29.268	28.326	28.644	0.540	1.89
182/183	23°C; 3 months	30.868	28.051	32.711	30.543	2.347	7.68
184/185	23°C; 6 months	27.516	28.120	29.945	28.527	1.265	4.43
184/185	23°C; 12 months	27.259	26.780	25.757	26.599	0.767	2.88
188/191	40°C; 1 month	29.483	26.307	27.289	27.693	1.626	5.87
188/191	40°C; 3 months	29.331	31.192	28.035	29.519	1.587	5.38
192/193	40°C; 6 months	29.417	31.061	30.508	30.329	0.836	2.76
192/193	40°C; 12 months	27.440	25.812	26.907	26.719	0.830	3.11
194/195	60°C; 1 month	27.638	28.607	28.358	28.201	0.503	1.79
194/195	60°C; 3 months	30.012	29.924	29.993	29.976	0.046	0.16

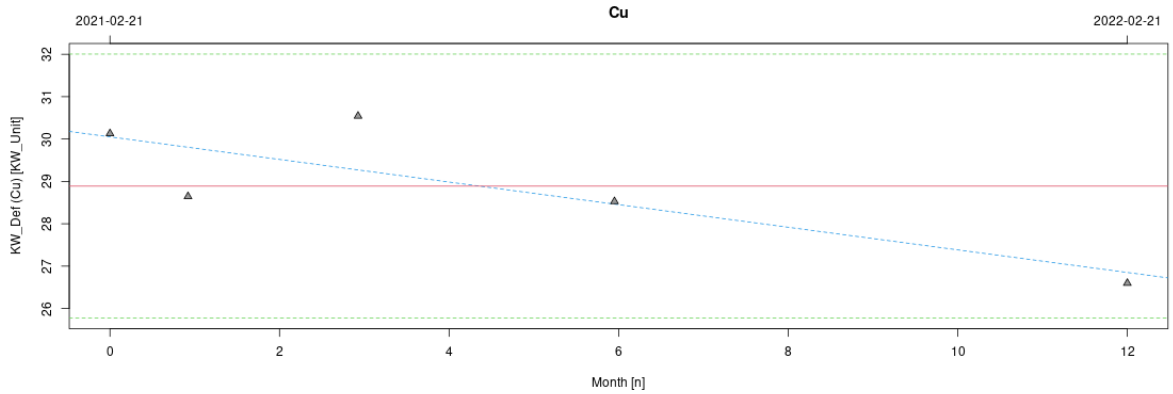
-20 °C:



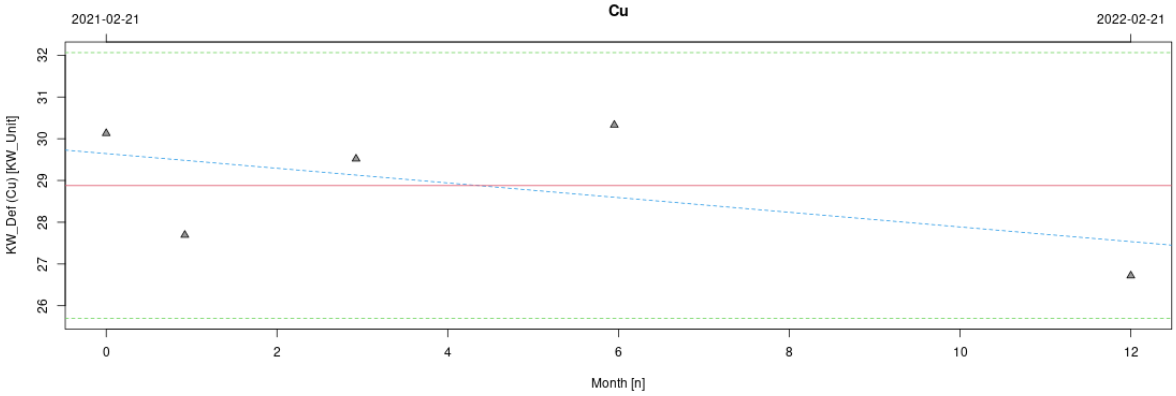
4 °C:


Cu
2021-02-21
2022-02-21
KW_Def (Cu) [KW_Unit]
30.0
29.5
29.0
28.5
0
2
4
6
8
10
12
Month [n]
2s

23 °C:

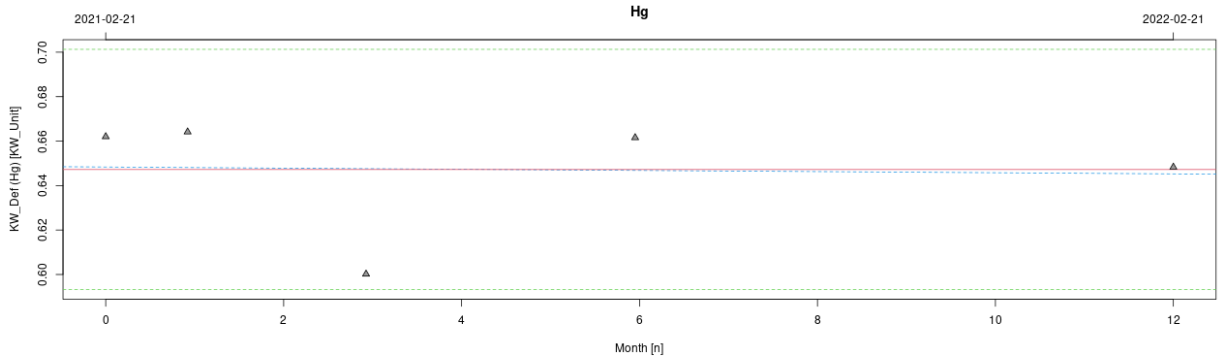

Cu
2021-02-21
2022-02-21
KW_Def (Cu) [KW_Unit]
32
31
30
29
28
27
26
0
2
4
6
8
10
12
Month [n]

40 °C:

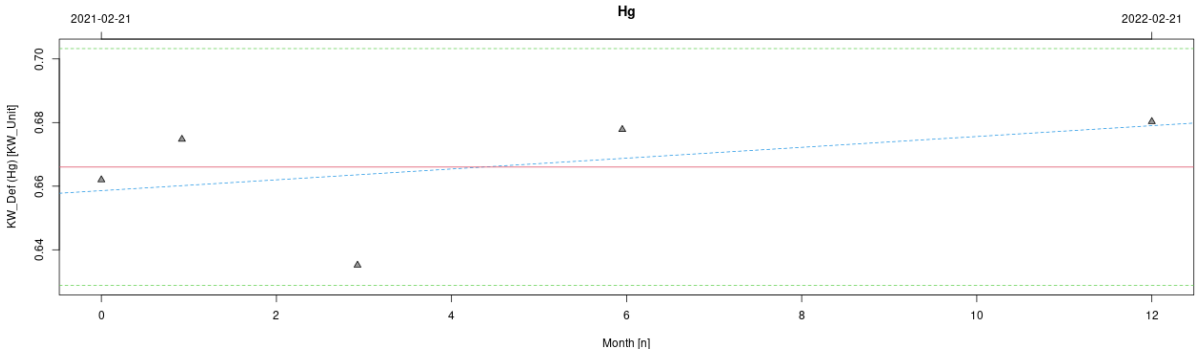

Cu
2021-02-21
2022-02-21
KW_Def (Cu) [KW_Unit]
32
31
30
29
28
27
26
0
2
4
6
8
10
12
Month [n]

Stability study						**ICP-MS**	**Hg**
Mass fraction in mg/kg							
Sample No.	storage temperature	#**1**	#**2**	#**3**	Mean	SD	$RSD_{\%}$
170/171	-20°C	0.649	0.677	0.666	0.664	0.014	2.13
170/171	-20°C	0.602	0.589	0.609	0.600	0.010	1.64
172/173	-20°C	0.672	0.632	0.681	0.662	0.026	3.96
172/173	-20°C	0.655	0.644	0.646	0.648	0.006	0.94
176/177	4°C; 1 month	0.667	0.671	0.687	0.675	0.011	1.56
176/177	4°C; 3 months	0.626	0.617	0.663	0.635	0.025	3.87
178/179	4°C; 6 months	0.694	0.665	0.674	0.678	0.015	2.15
178/179	4°C; 12 months	0.716	0.664	0.661	0.680	0.031	4.57
182/183	23°C; 1 month	0.667	0.660	0.645	0.657	0.011	1.71
182/183	23°C; 3 months	0.655	0.603	0.621	0.627	0.026	4.23
184/185	23°C; 6 months	0.690	0.697	0.703	0.697	0.006	0.89
184/185	23°C; 12 months	0.653	0.675	0.646	0.658	0.015	2.30
188/191	40°C; 1 month	0.668	0.621	0.627	0.639	0.026	4.00
188/191	40°C; 3 months	0.607	0.614	0.611	0.611	0.003	0.56
192/193	40°C; 6 months	0.650	0.599	0.605	0.618	0.028	4.50
192/193	40°C; 12 months	0.661	0.600	0.626	0.629	0.030	4.83
194/195	60°C; 1 month	0.645	0.668	0.642	0.651	0.015	2.24
194/195	60°C; 3 months	0.611	0.571	0.575	0.585	0.022	3.77

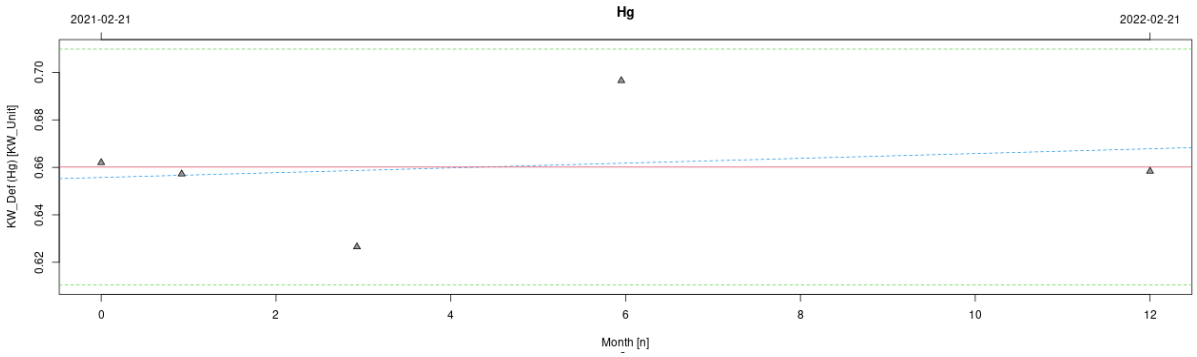
-20 °C:



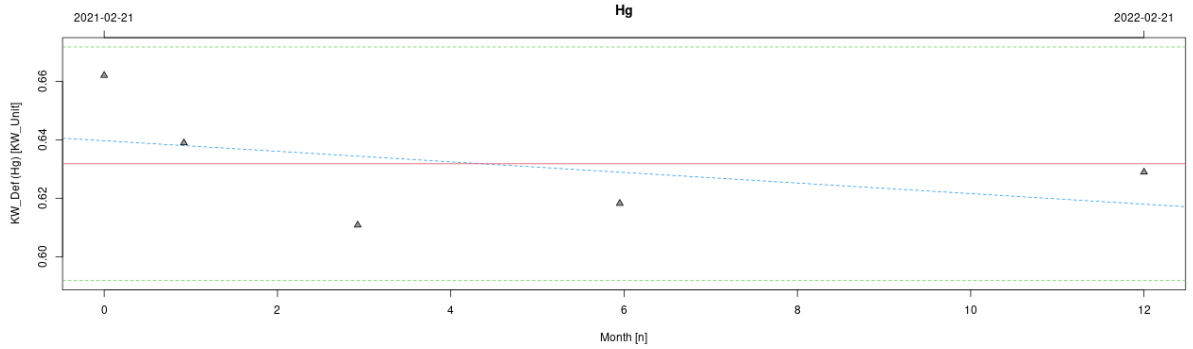
4 °C:


Hg
2021-02-21
2022-02-21
KW_Def (Hg) [KW_Unit]
0.64
0.66
0.68
0.70
0
2
4
6
8
10
12
Month [n]

23 °C:

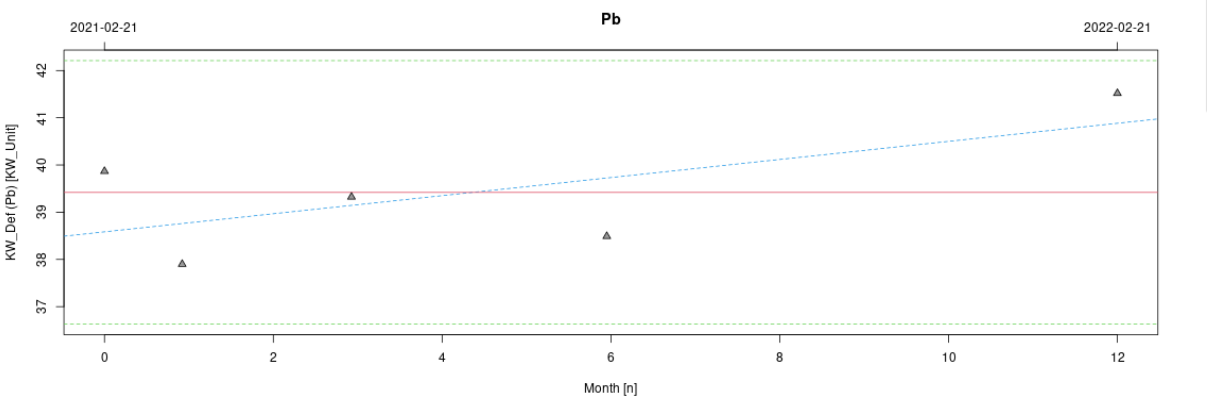

Hg
2021-02-21
2022-02-21
KW_Def (Hg) [KW_Unit]
0.62
0.64
0.66
0.68
0.70
0
2
4
6
8
10
12
Month [n]

40 °C:

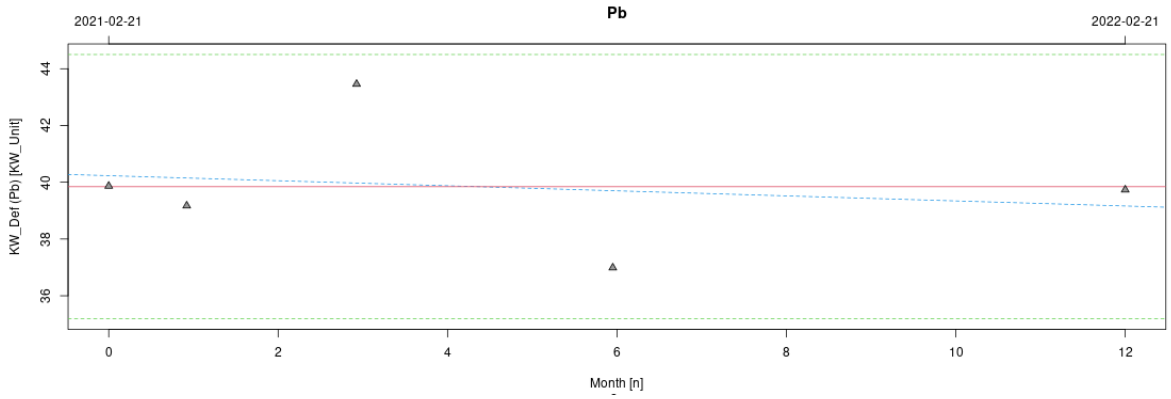

Hg
2021-02-21
2022-02-21
KW_Def (Hg) [KW_Unit]
0.60
0.62
0.64
0.66
0
2
4
6
8
10
12
Month [n]

Stability study						**ICP-OES**	**Pb**
Mass fraction in mg/kg							
Sample No.	storage temperature	#**1**	#**2**	#**3**	Mean	SD	$RSD_{\%}$
170/171	-20°C	37.551	39.435	36.711	37.899	1.395	3.68
170/171	-20°C	35.849	40.774	41.347	39.323	3.023	7.69
172/173	-20°C	38.894	38.296	38.280	38.490	0.350	0.91
172/173	-20°C	39.641	41.436	43.477	41.518	1.920	4.62
176/177	4°C; 1 month	41.127	37.645	38.744	39.172	1.780	4.54
176/177	4°C; 3 months	41.652	42.687	46.041	43.460	2.295	5.28
178/179	4°C; 6 months	38.728	36.289	35.948	36.988	1.516	4.10
178/179	4°C; 12 months	39.733	37.124	42.347	39.735	2.612	6.57
182/183	23°C; 1 month	37.371	41.205	39.106	39.227	1.920	4.89
182/183	23°C; 3 months	43.881	43.089	41.523	42.831	1.200	2.80
184/185	23°C; 6 months	39.604	43.006	44.777	42.462	2.629	6.19
184/185	23°C; 12 months	36.522	38.613	38.006	37.714	1.076	2.85
188/191	40°C; 1 month	38.977	38.734	34.724	37.478	2.389	6.37
188/191	40°C; 3 months	43.078	44.589	43.835	43.834	0.756	1.72
192/193	40°C; 6 months	39.856	39.120	43.133	40.703	2.136	5.25
192/193	40°C; 12 months	44.867	41.631	33.253	39.917	5.994	15.02
194/195	60°C; 1 month	37.382	35.584	36.183	36.383	0.916	2.52
194/195	60°C; 3 months	41.089	39.826	40.941	40.619	0.691	1.70

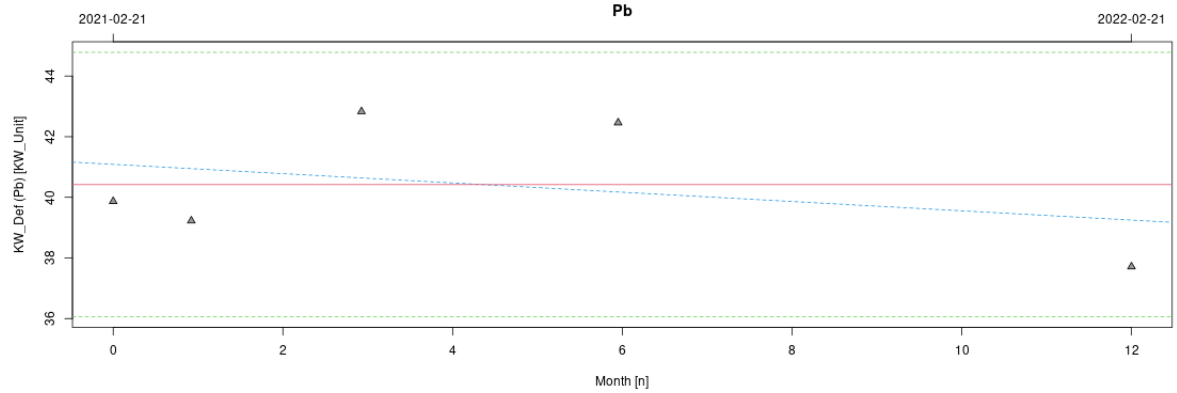
-20 °C:



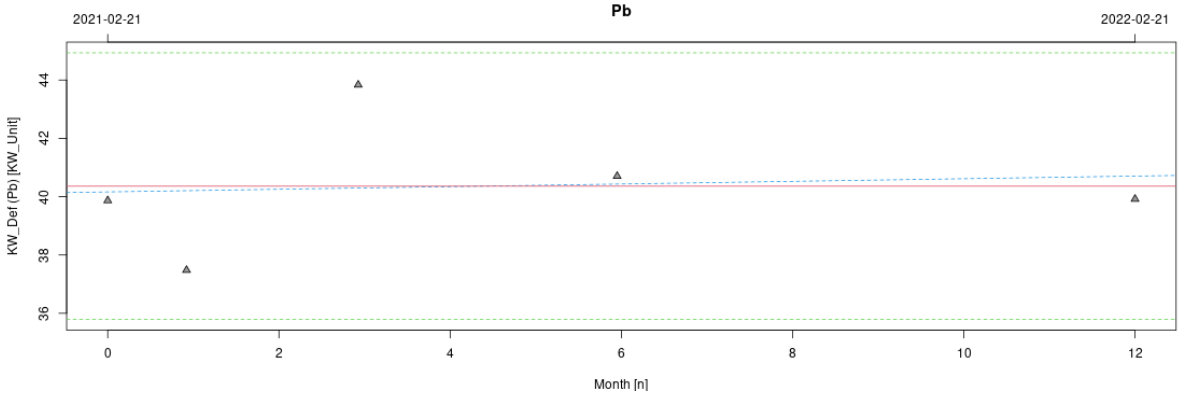
4 °C:


Pb
2021-02-21
2022-02-21
KW_Def (Pb) [KW_Unit]
36
38
40
42
44
0
2
4
6
8
10
12
Month [n]

23 °C:


Pb
2021-02-21
2022-02-21
KW_Def (Pb) [KW_Unit]
36
38
40
42
44
0
2
4
6
8
10
12
Month [n]

40 °C:


Pb
2021-02-21
2022-02-21
KW_Def (Pb) [KW_Unit]
36
38
40
42
44
0
2
4
6
8
10
12
Month [n]