Bundesanstalt für Materialforschung und -prüfung (BAM)

# The certification of total cyanide in soil

# BAM-U117

## Certification report

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S. Buttler, S. Penk, H. Witthuhn, S. Recknagel
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6 „Inorganic Reference Materials"
Richard-Willstätter-Str. 11
D-12489 Berlin

## Abstract

This report describes the preparation and certification of reference material BAM-U117, total cyanide in soil according to the analytical procedures prescribed by DIN ISO 11262:2012 and DIN EN ISO 17380:2013. The certified mass fraction is listed below.

| **Measurand** | **Mass fraction [1] in mg/kg** | **Uncertainty *U* [2] in mg/kg** |
|---|---|---|
| Total cyanide | 11.0 | 0.7 |

[1] The unweighted mean value of the means of accepted sets of data (consisting of 4 single results corrected to the dry mass content of the material at (105 ± 2) °C), 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).

CRM BAM-U117 is available as a powder with particle sizes below 125 µm and is supplied in 100 mL amber glass bottles containing (77 ± 1) g. The minimum amount of sample to be used for the determination of total cyanide is 5 g.

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

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## List of abbreviations

(if not explained elsewhere)

| | |
|---|---|
| $M$ | 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 |
| CGL | Central Geological Laboratory, Ulaanbaatar, Mongolia |

# 1 Introduction

Cyanide compounds in the environment originate mainly from a variety of industrial sources, such as the electroplating industry, blast furnaces, coke-producing plants and gasworks. Due to their toxicity, cyanides are among the most important inorganic pollutants to be tested and monitored not only in the aquatic environment, but also in soils and soil-like materials. They can be determined as easily liberatable cyanide, as complex cyanide or as total cyanide. However, in any case it should be kept in mind that the obtained measurement results are operationally-defined referring to the applied analytical methods. To make such analyses comparable, strict adherence to an agreed analytical protocol is an essential prerequisite.

The aim of the project described in this report was to certify a reference material (CRM) on the basis of the International Standards DIN ISO 11262:2012 [2] and DIN EN ISO 17380:2013 [3] which specify normative analytical methods for the determination of total cyanide in soil. According to the prescribed analytical protocol cyanides are released from the test sample using ortho-phosphoric acid. The released hydrogen cyanide is transported by an air flow and absorbed into a sodium hydroxide solution. The absorbed cyanide is then quantitatively determined either by a photometric method or a titrimetric method using an indicator.

The certification was carried out on the basis of ISO 17034 [4] and the relevant ISO-Guides [5,6].

# 2 Candidate material

The CRM BAM-U117 was produced from 31 kg of the original reference material BAM-U116/CGL306 by remixing and sample splitting the bottles still available at the time of the project start. The recertification was initiated because there were certain indications that the original certified cyanide content no longer corresponded to the actual content in the material.

The candidate CRM BAM-U117 (BAM-U116/CGL306) was prepared as a mixture of a sandy soil collected from a contaminated former gasworks area in the Berlin region (Germany) and an unpolluted sandy soil from Nalaikh region (Mongolia).

The two raw materials were processed separately at BAM and CGL, respectively. They were dried at ambient air to constant mass and then passed through a vibrating 2 mm sieve discarding the fraction > 2 mm. Afterwards the material passing the sieve was ground to particle sizes below 125 µm.

Blending and homogenization of the two soil fractions < 125 µm as well as bottling of the final candidate CRM were performed at CGL.

A total of 400 units of BAM-U117 with (77 ± 1) g of soil each were filled up into 100 mL amber glass bottles equipped with a screw cap. After bottling the whole batch was stored at (4 ± 1) °C.

# 3 Homogeneity study

A total of 10 bottled units of the candidate material were selected using a stratified random sample picking scheme following the sequence of bottling to give complete coverage of the production batch. From each unit three independent test portions of 5.0 g were analyzed using the continuous-flow analysis (CFA) method according to DIN EN ISO 17380 [3] after extraction of cyanides from the soil sample with 2.5 mol/L sodium hydroxide solution.

From all selected bottled units each three sub-samples were analyzed together under repeatability conditions in one run with one calibration.

All measurement results from the homogeneity study are given in Annex 2. The estimate of inhomogeneity contribution $u_{bb}$ was calculated based on the results of 1-way Analysis of Variance (ANOVA).

The following equations were used (Eq. 2 in case $MS_{among} < MS_{within}$):

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

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

where:

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

$s_{bb}$ signifies the between-bottle standard deviation, whereas $u_{bb}^{*}$ denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). In any case the larger of the two values was used as $u_{bb}$. Eq. (1) does not apply if $MS_{within}$ is larger than $MS_{among}$.

The calculated relative uncertainty component $u_{bb}$ (rel.) was 0.77 % calculated using Eq. 2, resulting in an absolute contribution to the uncertainty of the certified value of 0.084 mg/kg CN.

## 4 Stability study

Stability testing of former CRM BAM-U116/CGL306 started in December 2015 [7] Selected units of the bottled soil material were stored at temperatures 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, 6, 9 and 12 months, respectively, two bottles per temperature level were analyzed in duplicate for their contents of total cyanide using continuous-flow analysis (CFA) method according to DIN EN ISO 17380 (with a sample intake of 5.0 g each) under repeatability conditions in one run with one calibration. As a result of this stability investigation there was no change in the mass fraction of total cyanide after 12 months, when the samples were stored at 20° C. Between January 2019 and October 2020 post certification monitoring of BAM-U116/CGL306 was carried out by CGL (see Annex 3). All results laid within the uncertainty range of the CRM (12.0 ± 0.8 mg/kg). The certification interlaboratory comparison carried out in 2023 resulted in a certified value of 11.0 mg/kg which is below the lower limit of the uncertainty range of BAM-U116/CGL306. This indicates that the material is not perfectly stable at least at room temperature. Therefore, four measures have been taken:

1) The storage temperature of the CRM is set to 4 °C.
2) The CRM will be tested at least every six month. As reference some units are stored at - 60 °C.
3) The validity of the certificate is set to 12 months after dispatch of the material from BAM.

4) $CN^-$-determinations were carried out in BAM in September 2021, Mai 2023 and October 2023. The results are summerized in Table 1. There is no hint for instability.

As uncertainty contribution related to the stability the theoretical loss per year of 0.167 mg/kg (certified mass fraction (2017) - certified mass fraction (2023)) is taken into account.

Tab. 1: Additional stability measurements (BAM-U117), mass fraction of $CN^-$ in mg/kg

| Date of analysis/ storage temperatur | 09/2021 (stability) | 05/2023 (certification) | 10/2023 (stability) |
|---|---|---|---|
| + 4 °C | 10.9 | 11.1 | 11.0 |
| - 20 °C | 10.9 | | |
| - 70 °C | | | 10.9 |

# 5 Certification study

## 5.1 Design of the study

The certification study was organised as an interlaboratory comparison. 15 laboratories invited to participate were selected on the basis of their expertise demonstrated in the course of a preceding proficiency test where a similar soil material was requested to be analysed for total cyanide. Except of one all laboratories hold an accreditation according to ISO/ IEC 17025.
Each participant received one unit of bottled candidate material as well as one unit of a quality control material and was asked to analyse four independent sub-samples for their contents of total cyanide. The moisture content of the bottled soil material had to be determined in duplicate using separate sub-samples according to ISO 11465 [8]. All analytical results of the participants were reported on this dry mass basis.
Additionally, in order to identify potential "technical outliers" all participants had to analyze a control sample in the same manner as prescribed for the candidate CRM. The control sample (RV25/GCN1) was a homogeneous soil material whose content of total cyanide had been determined in the course of a former proficiency test (PT).
All participants were asked to give information on details of the applied analytical procedures. Table 2 shows the analytical parameters reported by the participating laboratories.

Tab. 2: Analytical parameters

| Lab code | Sample intake (g) | Calibrant | Analytical method | Dry matter % |
|---|---|---|---|---|
| 001* | 0.5 – 1 | Merck 1000 mg/L CN | DIN ISO 11262 | 99.4 |
| 002* | 10 | Commercial CN-standard | DIN EN ISO 17380 | 99.7 |
| 003* | 5 | Sigma Aldrich CN-standard 1000 mg/L | DIN EN ISO 17380 | 99.9 |
| 004* | 7.2 - 7.5 | Bernd Kraft CN-standard 100 mg/L | DIN EN ISO 17380 | 99.63 |
| 005* | 5 | Merck Certipur | DIN EN ISO 17380 | 99.17 |
| 006* | 5 | Sigma Aldrich CN-standard 1000 mg/L | DIN EN ISO 17380 | 99.7 |
| 007* | 5 | Sigma Aldrich CN-standard 1000 mg/L | DIN ISO 11262 | 99.3 |
| 008* | 2 | $K_4[Fe(CN)_6]$ | DIN ISO 11262 | 100 |
| 009* | 5 | $K_4[Fe(CN)_6]$ | DIN ISO 11262 | 99.7 |
| 010* | 10 | CN-standard solution 1000 mg/L | DIN EN ISO 17380 | 89.88 |
| 011* | 5<br>2.5 | KCN | DIN ISO 11262<br>DIN EN ISO 17380 | 99.5 |

| Lab code | Sample intake (g) | Calibrant | Analytical method | Dry matter % |
|---|---|---|---|---|
| 012* | 5 | Merck standard solution | DIN ISO 11262 | 100 |
| 013* | 5 | KCN | DIN ISO 11262 | 99.8 |
| 014* | 5 | Merck standard solution | DIN ISO 11262 | 99.6 |
| 015 | 5 | Thermo Fisher standard 1000 mg/L | DIN EN ISO 17380 | 99.5 |

*accredited acc. to ISO/IEC 17025

### 5.2 Participants

AWV- Dr. Busse GmbH, Plauen
AZBA Analytisches Zentrum Berlin-Adlershof GmbH, Berlin
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin
GEOTAIX Umwelttechnologie GmbH, Würselen
ICA - Institut für Chemische Analytik GmbH, Leipzig
IFU GmbH Gewerbliches Institut für Fragen des Umweltschutzes, Heitersheim
IHU Geologie und Analytik, Gesellschaft für Ingenieur- Hydro- und Umweltgeologie mbH, Stendal
Institut Dr. Lörcher und Partner mbB Handelschemiker, Ludwigsburg
Institut Dr. Nowak GmbH & Co. KG, Ottersberg
Laboratorien Dr. Döring GmbH, Bremen
Terrachem-Essen GmbH, Essen
Thüringer Umweltinstitut Henterich GmbH, Krauthausen
UCL Umwelt Control Labor GmbH, Lünen
Wartig Chemieberatung GmbH, Marburg
WESSLING GmbH, Weiterstadt

### 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.
In a first step, the results obtained for control sample RV25/GCN1 were evaluated. Participants' results for the content of total cyanide in this sample had to fall within the specified tolerance range of (21.35 – 33.68) mg/kg CN. The dataset of laboratory GCN014 did not fulfil this acceptance criterion and was considered as "technical outlier".
After elimination of the "technical outlier" the remaining data was tested for outlying results (Grubbs Test). No outlying value was detected.

The unweighted means of laboratories' means after removal of the "technical outlier" were taken as the best estimates $w_{char}$ for the value 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 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

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 15 laboratory means for the moisture content – see Annex 1 – was attributed with equal value to the mean dry matter content of 99.64 % 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. 3: Uncertainty components for the analytes in BAM-U117

| Analyte | $u_{char}$ (mg kg$^{-1}$) | $u_{bb}$ (mg kg$^{-1}$) | $u_{dm}$ (mg kg$^{-1}$) | $u_{lts}$ (mg kg$^{-1}$) | $u_{com}$ (mg kg$^{-1}$) |
|---|---|---|---|---|---|
| CN | 0.2714 | 0.084 | 0.0077 | 0.167 | 0.33 |

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 fraction and its expanded uncertainty is given on Page 2. Rounding was done according to DIN 1333 [9].

# 6 Information on the proper use of BAM-U117

## 6.1 Shelf life

As mentioned in Chapter 4 the validity of the certificate expires after 12 months starting with the dispatch of the material from BAM. 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 material allows the dispatch of the material at ambient temperature.
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.
Based on the sample intake from the homogeneity test the minimum sample size for total cyanide determination is 5 g.
All analytical results are corrected for dry mass content of the material which should be determined according to ISO 11465 [8] using a separate sub-sample. The mean value of the single results given in Table 1 (99.64 %) should be regarded as being indicative only.

### 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 cyanides. However, 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.
It should be kept in mind that hydrogen cyanide and its salts are toxic. Therefore, caution should be exercised when manipulating cyanide-contaminated samples. Volatile hydrogen cyanide (with an odor of bitter almonds) is released from acidified solutions containing cyanide salts. As a minimum, all work shall be carried out in a fume hood.

## 7 Metrological Traceability

It is important to note that the certified mass fraction of total cyanide in reference material BAM-U117 is operationally defined referring to the analytical protocol prescribed by DIN ISO 11262:2012 and DIN EN ISO 17380:2013. The photometric determination of the liberated cyanide is traceable to the International System of Units (SI) via calibration using substances with certified analyte content.

## 8 Additional material data

The main matrix constituents of the bottled material were determined by X-ray fluorescence analysis (WD-XRF) on the original material BAM-U116/CGL306 giving the following informative results:

| Element | Si | Al | K | Na | Ca | Fe |
|---|---|---|---|---|---|---|
| Mass fraction(in %) | 35.6 | 6.9 | 2.9 | 2.5 | 0.8 | 0.8 |

Further informative analytical results obtained in the course of sample characterization data from original Material BAM-U116/CGL306:

| Parameter | Mass fraction (in %) | Analytical method |
|---|---|---|
| Loss on ignition at 550 °C | 0.9 | DIN EN 15935 [10] |
| Total carbon (TC) | 0.2 | DIN ISO 10694 [11] |

## 9 References


[1] ISO/IEC Guide 98-3:2008: Messunsicherheit - Teil 3: Leitfaden zur Angabe der Unsicherheit beim Messen

[2] DIN ISO 11262:2012: Soil quality - Determination of total cyanide (Boden-beschaffenheit - Bestimmung von Gesamtcyanid)

[3] DIN EN ISO 17380:2013: Soil quality - Determination of total cyanide and easily liberatable cyanide - Continuous-flow analysis method (Bodenbeschaffenheit - Bestimmung des Gehalts an Gesamtcyanid und leicht freisetzbarem Cyanid - Verfahren mittels kontinuierlicher Durchflussanalyse)

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

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

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

[7] Certification report Certified Reference Material BAM-U116/CGL306, total cyanide in soil, January 2017 (Zertifizierungsbericht, certification report "BAM-U116")

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

[9] DIN 1333:1992-02 Zahlenangaben

[10] DIN EN 15935:2012: Schlamm, behandelter Bioabfall, Boden und Abfall - Bestimmung des Glühverlusts

[11] DIN ISO 10694:1996: Bodenbeschaffenheit - Bestimmung von organischem Kohlenstoff und Gesamtkohlenstoff nach trockener Verbrennung (Elementaranalyse)

## 10 Information on and purchase of the CRM

Certified reference material BAM-U117 is supplied by

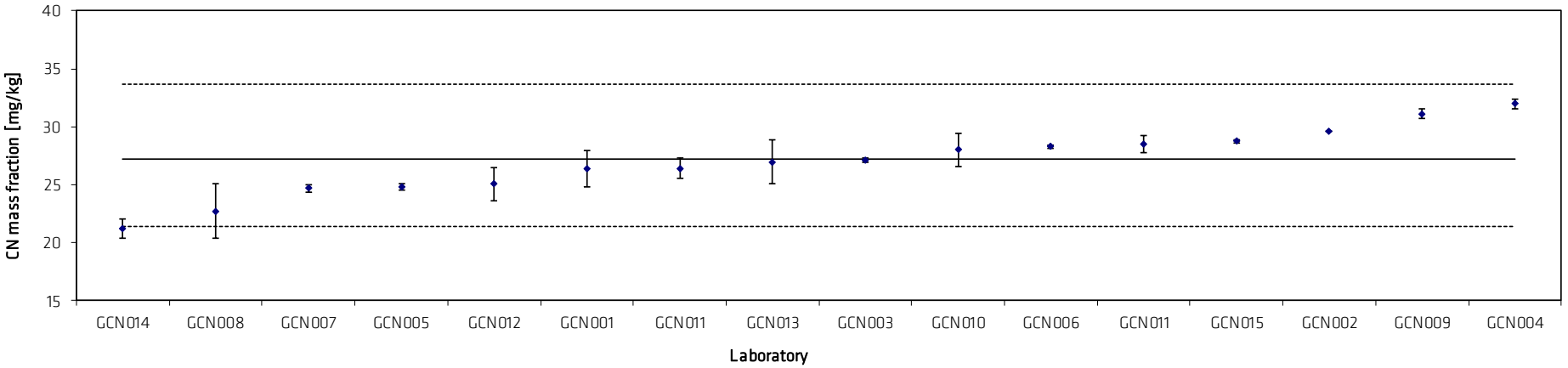
**Bundesanstalt für Materialforschung und -prüfung (BAM)**
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 72061
Email: sales.crm@bam.de
https://www.webshop.bam.de

Each unit will be distributed together with a detailed certificate containing the certified value and its uncertainty, the mean values and standard deviations of all accepted data sets, 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.

## Annex 1: Certification study

Table A1: Measurement results for control sample RV25-GCN1

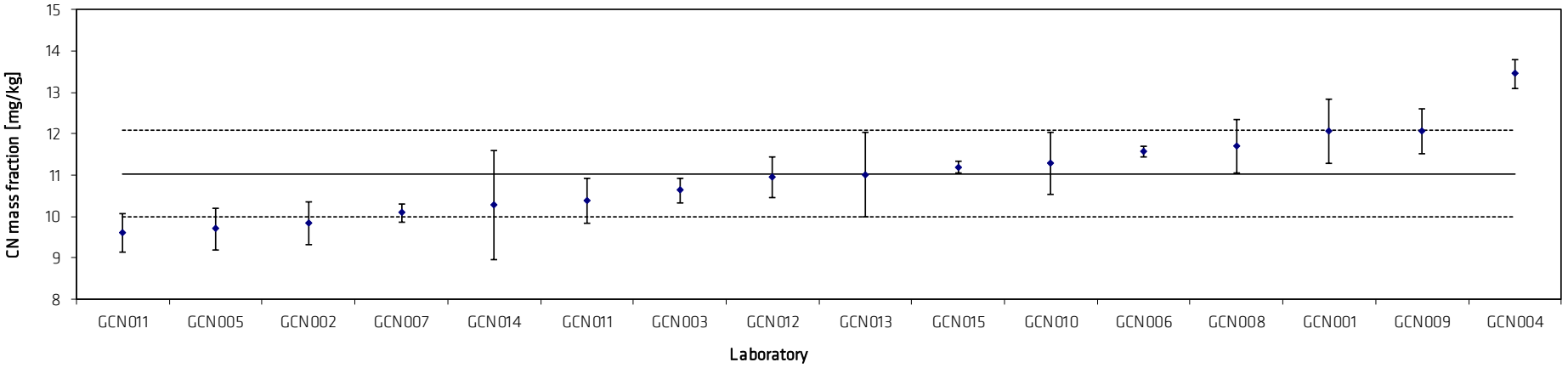
| Lab./Meth. | GCN014 | GCN008 | GCN007 | GCN005 | GCN012 | GCN001 | GCN011 | GCN013 | GCN003 | GCN010 | GCN006 | GCN011 | GCN015 | GCN002 | GCN009 | GCN004 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 20.6 | 24.4 | 24.9 | 25.0 | 26.2 | 25.3 | 27.0 | 24.7 | 27.0 | 27.4 | 28.2 | 28.0 | 28.6 | 29.6 | 31.4 | 31.7 | | *n* |
| | 21.8 | 21.1 | 24.4 | 24.6 | 25.5 | 27.5 | 25.8 | 29.2 | 27.3 | 28.8 | 28.4 | 29.0 | 28.9 | 29.6 | 30.8 | 32.3 | | 16 |
| | | | | | 23.5 | | | 26.3 | | 29.5 | | | | | | | | |
| | | | | | | | | 27.7 | | 26.3 | | | | | | | | |
| ***M* [mg/kg]** | **21.2** | **22.7** | **24.7** | **24.8** | **25.1** | **26.4** | **26.4** | **27.0** | **27.1** | **28.0** | **28.3** | **28.5** | **28.7** | **29.6** | **31.1** | **32.0** | | **27.0** |
| *s* [mg/kg] | 0.8 | 2.3 | 0.4 | 0.3 | 1.4 | 1.6 | 0.9 | 1.9 | 0.2 | 1.4 | 0.1 | 0.7 | 0.2 | 0.0 | 0.4 | 0.4 | $s_M$ [mg/kg] | 2.9 |
| | | | | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 1.1 |
| $s_{rel}$ | 0.04002 | 0.10275 | 0.01433 | 0.01140 | 0.05707 | 0.05893 | 0.03319 | 0.07133 | 0.00808 | 0.05109 | 0.00500 | 0.02481 | 0.00618 | 0.00000 | 0.01364 | 0.01282 | | 0.10619 |




Continuous line: reference value of QC-sample
Interupted lines: upper and lower tolerance limit
Yellow highlighted: DIN ISO 11262
White highlighted: DIN EN ISO 17380

Table A2: Measurement results for CRM BAM-U117

| Lab./Meth. | GCN011 | GCN005 | GCN002 | GCN007 | GCN014 | GCN011 | GCN003 | GCN012 | GCN013 | GCN015 | GCN010 | GCN006 | GCN008 | GCN001 | GCN009 | GCN004 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M_i$ [mg/kg] | 10.0 | 10.2 | 9.1 | 10.0 | 10.7 | 10.6 | 10.8 | 11.0 | 10.6 | 11.2 | 10.4 | 11.4 | 12.0 | 12.9 | 11.3 | 13.3 | | *n* |
| | 10.0 | 9.8 | 9.8 | 10.0 | 10.9 | 9.6 | 10.8 | 10.6 | 12.4 | 11.3 | 10.9 | 11.6 | 12.5 | 11.1 | 12.1 | 13.3 | | 16 |
| | 9.2 | 9.8 | 10.3 | 9.9 | 8.3 | 10.4 | 10.7 | 10.6 | 11.0 | 11.0 | 11.8 | 11.6 | 11.2 | 11.8 | 12.2 | 13.3 | | |
| | 9.2 | 9.0 | 10.1 | 10.4 | 11.2 | 10.9 | 10.2 | 11.6 | 10.0 | 11.2 | 12.0 | 11.7 | 11.2 | 12.4 | 12.6 | 14.0 | | |
| ***M* [mg/kg]** | **9.6** | **9.7** | **9.8** | **10.1** | ***10.3*** | **10.4** | **10.6** | **11.0** | **11.0** | **11.2** | **11.3** | **11.6** | **11.7** | **12.1** | **12.1** | **13.4** | | **11.0** |
| *s* [mg/kg] | 0.5 | 0.5 | 0.5 | 0.2 | 1.3 | 0.6 | 0.3 | 0.5 | 1.0 | 0.1 | 0.8 | 0.1 | 0.6 | 0.8 | 0.5 | 0.3 | $s_M$ [mg/kg] | 1.1 |
| | | | | | | | | | | | | | | | | | $\bar{s}_i$ [mg/kg] | 3.3 |
| $s_{rel}$ | 0.04811 | 0.05189 | 0.05292 | 0.02147 | 0.12867 | 0.05313 | 0.02792 | 0.04500 | 0.09271 | 0.01237 | 0.06691 | 0.01087 | 0.05530 | 0.06446 | 0.04520 | 0.02569 | | 0.09525 |




Continuous line: mean value of the laboratories' means
Interupted lines: ± standard deviation of the laboratories' means
Yellow highlighted: DIN ISO 11262
White highlighted: DIN EN ISO 17380
Note 1: The results of GCN014 were not used to calculate the mean value, because this laboratory failed when analysing the QC-sample

Table A3: Measurement results for CRM BAM-U117, differentiated by method (mass fraction in mg/kg)

| | DIN ISO 11262 | DIN EN ISO 17380 |
|---|---|---|
| | mean | mean |
| | 10.08 | 9.60 |
| | 10.38 | 9.70 |
| | 10.95 | 9.83 |
| | 11.00 | 10.64 |
| | 11.69 | 11.19 |
| | 12.05 | 11.28 |
| | 12.05 | 11.58 |
| | | 13.44 |
| M | **11.17** | **10.91** |
| SD | 0.786 | 1.281 |
| RSD (%) | 7.03 | 11.74 |
| n | 7 | 8 |

| Two-sample t-test assuming equal variances (a = 0.05) | | |
|---|---|---|
| | | |
| | *DIN ISO 11262* | *DIN EN ISO 17380* |
| Mean | 25.82795833 | 28.10225 |
| Variance | 9.946635252 | 4.608633357 |
| Observations | 8 | 8 |
| Pooled variance | 7.277634305 | |
| Hypothetical difference of means | 0 | |
| Degrees of freedom (df) | 14 | |
| t-statistics | -1.686091121 | |
| P(T<=t) one-sided | 0.056962972 | |
| Critical t-value for one-sided t-test | 1.761310136 | |
| P(T<=t) two-sided | 0.113925945 | |
| Critical t-value for two-sided t-test | 2.144786688 | |

Table A4: Measurement results for control sample RV25-GCN1 differentiated by method (mass fraction in mg/kg)

| | DIN ISO 11262 | DIN EN ISO 17380 |
|---|---|---|
| | mean | mean |
| | 21.20 | 24.80 |
| | 22.71 | 27.15 |
| | 24.68 | 27.13 |
| | 25.06 | 28.00 |
| | 26.40 | 28.30 |
| | 26.98 | 28.74 |
| | 28.50 | 29.60 |
| | 31.10 | 32.00 |
| M | **25.83** | **28.21** |
| SD | 3.154 | 2.089 |
| RSD (%) | 12.21 | 7.41 |
| n | 8 | 8 |

| Two-sample t-test assuming different variances (a = 0.05) | | |
|---|---|---|
| | | |
| | *DIN ISO 11262* | *DIN EN ISO 17380* |
| Mean | 25.82795833 | 28.10225 |
| Variance | 9.946635252 | 4.608633357 |
| Observations | 8 | 8 |
| Hypothetical difference of means | 0 | |
| Degrees of freedom (df) | 12 | |
| t-statistics | -1.686091121 | |
| P(T<=t) one-sided | 0.058790481 | |
| Critical t-value for one-sided t-test | 1.782287556 | |
| P(T<=t) two-sided | 0.117580963 | |
| Critical t-value for two-sided t-test | 2.17881283 | |

The t-Test (α = 0.05) showed no statistically significant difference between the results obtained with DIN ISO 11262 and DIN EN ISO 17380.

**Annex 2: Homogeneity study** (mass fraction in mg/kg)

| | | | |
|---|---|---|---|
| U117/038/1 | 12.32 | 12.12 | 12.42 |
| U117/074/1 | 13.22 | 12.17 | 12.14 |
| U117/110/1 | 12.32 | 12.00 | 12.49 |
| U117/146/1 | 12.21 | 12.04 | 12.33 |
| U117/182/1 | 12.33 | 11.94 | 12.49 |
| U117/218/1 | 12.50 | 12.07 | 12.40 |
| U117/254/1 | 12.47 | 12.05 | 12.31 |
| U117/290/1 | 12.59 | 11.98 | 12.30 |
| U117/362/1 | 12.47 | 12.11 | 12.48 |
| U117/398/1 | 12.61 | 12.15 | 12.36 |

| *Source of variation* | *sums of squares (SS)* | *degrees of freedom (df)* | *Mean squares (MS)* | *F-value* | *P-value* | *critical F-value* |
|---|---|---|---|---|---|---|
| Between groups | 0.19737968 | 9 | 0.021931075 | 0.257865 | 0.979187 | 2.392814 |
| Within groups | 1.70097262 | 20 | 0.085048631 | | | |
| | | | | | | |
| Total | 1.8983523 | 29 | | | | |
| | | | | | | |
| within-sd | 0.29163098 | | | status: | homogeneous | |
| | | | | | | |
| effective n | 3.00 | | | | | |
| $s_{bb}$ | 0 | | | | | |
| $u^*_{bb}$ | 0.09468322 | | | | | |
| $u_{bb}$ | 0.09468322 | | | | | |
| | | | | | | |
| $u_{bb}$(rel.) | 0.76892628 | | | | | |