CENTRAL
GEOLOGICAL
LABORATORY
www.cengeolab.com
When it comes to analyzing minerals in Mongolia

BAM
Bundesanstalt für Materialforschung und -prüfung

Certification Report

Certified Reference Material

BAM-U116/CGL306

Total Cyanide in Soil

Bundesanstalt für Materialforschung und -prüfung (BAM)
Department 1: Analytical Chemistry; Reference Materials
Berlin, Germany

in cooperation with

Central Geological Laboratory (CGL)
Department of Chemical and Physical Methods
Ulaanbaatar, Mongolia

January 2017

Summary

This report describes the certification of a reference material (CRM) for the determination of total cyanide in soil according to the analytical procedure prescribed by International Standard ISO 11262:2011.
The intended purpose of CRM BAM-U116/CGL306 is the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardized procedure ISO 11262:2011. As any reference material, it can also be used for routine performance checks (quality control charts) or validation studies.

The certified value and its uncertainty are:

Measurand	Mass fraction[1)] in mg/kg	Uncertainty U [2)] in mg/kg
Total cyanide according to ISO 11262:2011	12.0	0.8

[1)] Unweighted mean value of 14 laboratory means which were corrected to the dry mass content of the material after drying to constant mass at (105 ± 2) °C.

[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).

CRM BAM-U116/CGL306 is available as a powder with particle sizes below 125 µm and is supplied in 100 mL plastic (HDPE) containers containing (100 ± 3) 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 two years beginning with the dispatch of the reference material from BAM or CGL.

Contents

		Page
1	Introduction	1
2	Candidate material	1
3	Homogeneity study	1
4	Stability study	2
5	Certification study	4
	5.1 Design of the study	4
	5.2 Participants	5
	5.3 Statistical evaluation of results	6
6	Certified value and uncertainty	8
7	Traceability	9
8	Additional material data	9
9	Information on the proper use of CRM BAM-U116/CGL306	9
	9.1 Shelf life	9
	9.2 Transport, storage and use	9
	9.3 Safety instructions	10
	9.4 Legal notice	10
10	References	11
11	Annexes	12
Annex I:	Homogeneity study (measurement results)	13
Annex II:	Stability study (measurement results)	14
Annex III:	Certification study (measurement results of participants)	15

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 method. 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 Standard ISO 11262 [1] which specifies a normative analytical method for the determination of total cyanide in soil. According to the prescribed analytical protocol cyanides are liberated 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.

2 Candidate material

The candidate CRM 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 1000 units with (100 ± 3) g of soil each were filled up into 100 mL plastic (HDPE) containers equipped with a screw cap with tamper evident ring. After bottling the whole batch was stored at (20 ± 3) °C.

3 Homogeneity study

A total of 15 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 continuous-flow analysis (CFA) method according to ISO 17380 [2] (after extraction of cyanides from the soil sample with 2.5 mol/L sodium hydroxide solution).
Compared to ISO 11262, this method may give slightly different results for the total cyanide content. However, as stated in ISO 17380 "*these differences are not considered to be very significant*", and therefore there was no reason to question the suitability of the CFA method for homogeneity testing. Its main

advantages are the high level of automation, the large sample throughput and adequate repeatability.

From all selected bottled units each one sub-sample was analyzed together under repeatability conditions in one run with one calibration. To minimize the risk of a possible calibration bias between the different 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 from the homogeneity study are given in Annex I. The estimate of inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [3] on the basis of the results of 1-way Analysis of Variance (ANOVA). The following equation was used:

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

where

MS_{among}	mean of squared deviations between bottles
MS_{within}	mean of squared deviations within bottles
n	number of replicate sub-samples per bottle

The calculated relative uncertainty component u_{bb} was 1.60 %, resulting in an absolute contribution to the certified value of 0.192 mg/kg CN.

4 Stability study

In December 2015 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 ISO 17380 (with a sample intake of 5.0 g each) under repeatability conditions in one run with one calibration.
The measurement results (see Annex II) were evaluated by calculating the ratios R_t (2) and their corresponding uncertainties u_t (3):

$$R_t = X_t \,/\, X_{-20\,°C} \qquad (2)$$

$$u_t = (CV_t^2 + CV_{-20°C}^2)^{1/2} R_t \qquad (3)$$

where X_t and $X_{-20\,°C}$ are the mean values of four analyses of samples stored at temperature t (+20 °C, +40 °C or +60 °C) and of samples stored at the reference temperature -20 °C, respectively.
CV_t and $CV_{-20\,°C}$ are the corresponding coefficients of variation.

The results of this evaluation are given in Table 1.

Table 1: Results of the stability test after storage periods between 2 and 12 months

Storage time	$R_t \pm u_t$		
	Samples stored at 20 °C	Samples stored at 40 °C	Samples stored at 60 °C
2 months	0.9963 ± 0.0188	0.9784 ± 0.0141	0.9042 ± 0.0144
4 months	1.0033 ± 0.0237	0.9989 ± 0.0252	0.8876 ± 0.0199
6 months	0.9910 ± 0.0125	0.9402 ± 0.0126	0.8494 ± 0.0276
9 months	0.9943 ± 0.0215	1.0042 ± 0.0239	0.8546 ± 0.0167
12 months	1.0011 ± 0.0286	0.9976 ± 0.0349	0.8440 ± 0.0234

If one postulates that the total cyanide mass fraction of samples stored at -20 °C does not change over time, in case of ideal sample stability at a higher storage temperature t the ratio R_t should be 1. In reality, however, unavoidable random variations of measurement results have to be taken into account. Thus, a material can be considered stable at storage temperature t if the value 1 is comprised between $R_t - u_t$ and $R_t + u_t$. This precondition is fulfilled for samples stored at a temperature of (20 ± 3) °C.

On the other hand, for samples stored at 60 °C there is clear evidence for a non-negligible degradation of complex cyanides leading to lower measurement results when determining total cyanide. Most likely this is due to the fact that volatile degradation products present in the headspace of the closed bottle can be lost when taking a sub-sample for analysis.

In order to obtain an estimate for the long-term behaviour of samples stored at different temperatures, an *Arrhenius* model was assumed for the dependence of the reaction (degradation) rate k_{eff} on storage temperature [4]. A plot of k_{eff} over the inverse temperature t (in K) is given in Figure 1.

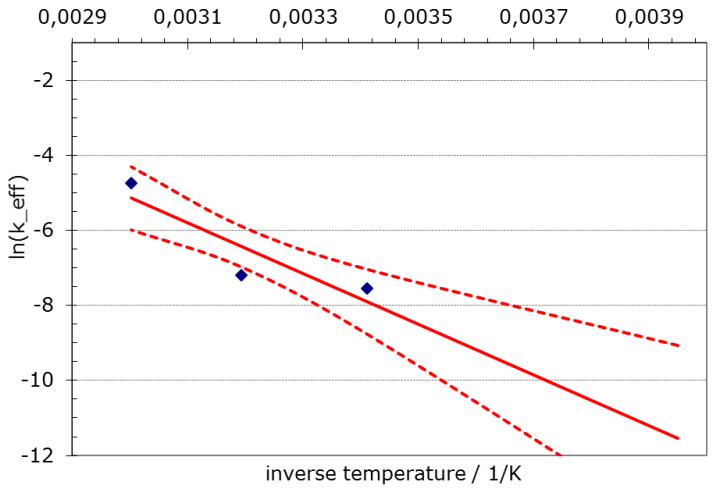


Figure 1: Regression of total cyanide degradation rate k_{eff} over the inverse temperature and 95 % one-sided confidence interval (Arrhenius plot)

Despite the apparent inadequacy of approximating the temperature dependence of k_{eff} by a straight line, this approach was used to get an estimate of the shelf life Δ_{max} of the reference material for any storage temperature. The term 'shelf life' herein refers to the period when degradation will presumably force the total cyanide content of the sample to fall below the certified lower expanded uncertainty limit. In the sense of a worst-case estimation, these calculations were carried out for the degradation rates at the upper confidence limit of the line shown in Fig. 1 according to Eq. (4):

$$\Delta_{max} = \ln[(w_{cert} - U_{cert})/w_{cert}]/k_{eff,upper} \quad (4)$$

with w_{cert} being the certified value of the total cyanide mass fraction and U_{cert} denoting its expanded uncertainty.

Calculated estimates of shelf life for different storage temperatures are given in Table 2.

Table 2: Shelf life of CRM BAM-U116/CGL306 at different storage temperatures

Storage temperature	-20 °C	+20 °C	+40 °C
Shelf life (months)	600	79	25

The data given in the table indicate a sufficient stability of samples stored at a typical room temperature of (20 ± 3) °C. However, any exposure to the laboratory environment or higher temperatures may reduce the time of validity of the certified mass fraction of total cyanide. Therefore, an expiry date of two years beginning with the dispatch of the reference material from BAM or CGL is established.

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 expiry date of two years after dispatch given in the certificate is maintained by post-certification measurements performed at BAM.

5 Certification study

5.1 Design of the study

The certification study was organized as an inter-laboratory comparison (ILC) and performed in March/April 2016.
Each participant received one unit of the bottled candidate CRM and was asked to analyze four independent sub-samples. The determinations should be spread over two days, each time using freshly prepared calibrants. The information was provided that the total cyanide content of the soil sample was to be expected between 10 and 20 mg/kg.

The analytical protocol prescribed by ISO 11262 had to be followed in full detail. For the determination of cyanide in the absorption solution, participating laboratories were requested to use the photometric method because of its better sensitivity and reproducibility compared to the titrimetric method. The photometric measurements should be carried out using calibration solutions prepared from a stock solution with a certified or at least verified cyanide concentration.

The dry mass content of the soil sample had to be determined on separate sub-samples by drying to constant mass at (105 ± 2) °C according to ISO 11465 [5]. 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 (QC/GCN-2016) was a homogeneous soil material whose content of total cyanide had been determined in the course of a former proficiency test (PT) by 50 participants.

5.2 Participants

Besides BAM and CGL, a total of 14 German laboratories participated in the certification study on candidate CRM BAM-U116/CGL306. All of them were operating an internal quality management system accredited to ISO/IEC 17025 [6] and covering the determination of cyanide in soil. The strict observance of the requirements of ISO 11262 and of additional instructions given by BAM had been assured by all laboratories in advance.

Participating laboratories in alphabetical order (not identical with the order of assigned laboratory code numbers):

AGROLAB Labor GmbH, Bruckberg (Germany)

ALS Analytik Labor Schirmacher GmbH, Hamburg (Germany)

BEGA.tec GmbH, Abteilung Labor, Berlin (Germany)

Bundesanstalt für Materialforschung und -prüfung (BAM), Division 1.6, Berlin (Germany)

Central Geological Laboratory (CGL), Department of Chemical and Physical Methods, Ulaanbaatar (Mongolia)

Chemlab – Gesellschaft für Analytik und Umweltberatung mbH, Bensheim (Germany)

Chemisches Labor Dr. Wirts + Partner, Sachverständigen GmbH, Hannover (Germany)

CLG Chemisches Labor Dr. Graser KG, Schonungen (Germany)

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

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

IHU – Geologie und Analytik, Gesellschaft für Ingenieur-, Hydro- und Umweltgeologie mbH, Stendal (Germany)

IUS Institut für Umweltanalytik und Schadstoffchemie GmbH, Stuttgart (Germany)

M&S Umweltprojekt GmbH, Labor Bad Muskau, Bad Muskau (Germany)

Umweltlabor ACB GmbH, Münster (Germany)

SGL Spezial- und Bergbau-Servicegesellschaft Lauchhammer mbH, Analytisches Labor, Lübbenau (Germany)

SGS Institut Fresenius GmbH, Herten (Germany)

5.3 Statistical evaluation of results

The measurement results obtained in the course of the inter-laboratory comparison are compiled in Annex III. The bars in the graphic presentations indicate the standard deviations of individual laboratory's results. The bar associated with the mean of laboratory means M in Fig. III.2 represents the standard deviation of laboratory means. Further explanations are given in the notes to the respective graphs in Annex III.

In a first step, the results obtained for control sample QC/GCN-2016 were evaluated. Participants' results for the content of total cyanide in this sample had to fall within the specified tolerance range of (15.4 ± 1.94) mg/kg CN. The dataset of laboratory 04 did not fulfil this acceptance criterion and was considered as "technical outlier". As a consequence, the dataset of this participant for candidate CRM BAM-U116/CGL306 was also supposed as being biased and therefore excluded from further data processing. The same decision applies to the respective dataset of laboratory 15, because the sample intake for analysis of both the control sample and the candidate CRM was only 0.2 g. This was considered as a too severe deviation from the analytical protocol prescribed by ISO 11262.

Statistical tests and evaluation of the accepted results for candidate material BAM-U116/CGL306 were performed using software SoftCRM, version 1.2.2 [7].

The following tests were carried out at different significance levels α:

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

Cochran test: Outlying variances?

Grubbs, Dixon and Nalimov tests: Outlying means?

Bartlett test: Variances homogeneous?

Snedecor F-test: Differences between datasets statistically significant?

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

Skewness & Kurtosis test: Normality of the distribution of the means?

The results of these tests are summarized in Table 3.

Table 3: Results of statistical tests carried out on accepted participants' results

Statistical test	Result of the test
Scheffé	Datasets differ significantly.
Cochran (α = 0.05)	No outlying variances.
Cochran (α = 0.01)	No outlying variances.
Grubbs (α = 0.05)	No outlying laboratory means.
Grubbs (α = 0.01)	No outlying laboratory means.
Dixon (α = 0.05)	No outlying laboratory means.
Dixon (α = 0.01)	No outlying laboratory means.
Nalimov (α = 0.05)	Laboratory 13 is an outlier.
Nalimov (α = 0.01)	No outlying laboratory means.
Bartlett (α = 0.05)	Variances are homogeneous.
Bartlett (α = 0.01)	Variances are homogeneous.
Snedecor (α = 0.05)	Differences between datasets are statistically significant.
Snedecor (α = 0.01)	Differences between datasets are statistically significant.
Kolmogorov-Smirnov-Lilliefors (α = 0.05)	Based on the available data, the hypothesis of normality cannot be rejected.
Kolmogorov-Smirnov-Lilliefors (α = 0.01)	Based on the available data, the hypothesis of normality cannot be rejected.
Skewness & Kurtosis (α = 0.05)	Based on the available data, the hypothesis of normality cannot be rejected.
Skewness & Kurtosis (α = 0.01)	Based on the available data, the hypothesis of normality cannot be rejected.
Pooling of individual data allowed?	No.

As no technical reasons could be identified for "suspicious" dataset 13, all datasets were retained for further data processing.

6 Certified value and uncertainty

The unweighted mean of accepted laboratory means was considered as the best estimate w_{CN} for the value to be certified. It is expressed on a dry mass basis corresponding to a drying temperature of (105 ± 2) °C.

When calculating the uncertainty of the certified mass fraction of total cyanide, the following contributions were taken into account:

u_{ILC} uncertainty resulting from the inter-laboratory comparison and representing the standard deviation of the mean of accepted dataset means ($u_{ILC} = SD_M/\sqrt{N}$),

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

u_{prec} uncertainty reflecting the average precision of laboratory means. u_{prec} was calculated according to the equation

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

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

The different contributions to the overall uncertainty of the certified mass fraction were combined according to GUM [8] using the following equation:

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

The calculated mass fraction w_{CN} and the values of the different uncertainty components are given in Table 4.

Table 4: Mass fraction and uncertainty components for total cyanide in CRM BAM-U116/CGL306

Mass fraction w_{CN} (in mg/kg)	Uncertainty components (in mg/kg)			
	u_{ILC}	u_{bb}	u_{prec}	u_{com}
12.02	0.233	0.192	0.182	0.352

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

After rounding the calculated numerical values, the certified mass fraction of total cyanide in CRM BAM-U116/CGL306 was assigned as

(12.0 ± 0.8) mg/kg.

7 Traceability

It is important to note that the certified mass fraction of total cyanide in reference material BAM-U116/CGL306 is operationally-defined referring to the analytical protocol prescribed by ISO 11262:2011. 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) giving the following non-certified 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:

Parameter	Mass fraction (in %)	Analytical method
Dry mass content at 105 °C	99.8	ISO 11465 [5]
Loss on ignition at 550 °C	0.9	EN 15935 [9]
Total carbon (TC)	0.2	ISO 10694 [10]

9 Information on the proper use of CRM BAM-U116/CGL306

9.1 Shelf life

The initial stability study after storage of selected units at different temperatures did not reveal any statistically significant deterioration of the certified property if the bottled material is stored at a temperature below 25 °C. However, starting with dispatch of the material from BAM or CGL the validity of the certificate expires after two years. Post-certification measurements will be conducted in appropriate periods to keep this information up to date.

9.2 Transport, storage and use

CRM BAM-U116/CGL306 can be shipped at ambient temperature. Upon receipt the material has to be stored at a temperature below 25 °C in its original tightly closed bottle. Although the stability of the reference material is not affected by short periods of handling at ambient temperature, the bottle shall be left unclosed as short as possible. Care should be taken to avoid moisture pick up once the bottle is opened.

The intended purpose of the reference material is the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardized procedure ISO 11262. As any reference

material, it can also be used for routine performance checks (quality control charts) or validation studies.

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.

When determining the content of total cyanide, the analytical protocol prescribed by ISO 11262 must be followed. All analytical results have to be corrected for dry mass content of the material which should be determined according to ISO 11465 using a separate sub-sample. The value given in the table above (99.8 %) should be regarded as being indicative only.

9.3 Safety instructions

No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with 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.

9.4 Legal notice

Neither BAM nor CGL, their 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 save for loss or damage arising solely and directly from the negligence of BAM or CGL.

10 References

[1] ISO 11262:2011: Soil quality – Determination of total cyanide

[2] ISO 17380:2013: Soil quality – Determination of total cyanide and easily liberatable cyanide. Continuous-flow analysis method

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

[4] W. Bremser, R. Becker, H. Kipphardt, P. Lehnik-Habrink, U. Panne and A. Töpfer: Stability testing in an integrated scheme, *Accred Qual Assur* (2006) 11:489-495

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

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

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

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

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

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

11 Annexes

Annex I: Homogeneity study (measurement results)

Annex II: Stability study (measurement results)

Annex III: Certification study (measurement results of participants)

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

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

Table I.1: Homogeneity study (measurement results)

Total cyanide

Sample intake: 5.0 g Analytical method: ISO 17380:2013

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD_i** (mg/kg)
003	11.02	11.09	11.29	11.13	0.140
088	11.24	11.47	11.69	11.47	0.225
146	11.24	11.09	11.18	11.17	0.075
214	11.64	11.63	11.35	11.54	0.165
267	11.30	11.41	11.49	11.40	0.095
319	11.35	10.87	11.40	11.21	0.293
358	11.05	11.17	11.48	11.23	0.222
447	11.64	11.48	11.84	11.65	0.180
522	11.64	11.78	11.82	11.75	0.095
609	11.65	11.48	10.93	11.35	0.376
699	11.58	11.36	11.22	11.39	0.181
786	11.46	11.52	11.86	11.61	0.216
864	11.93	11.77	11.77	11.82	0.092
911	11.12	11.46	11.44	11.34	0.191
955	11.65	11.48	11.75	11.63	0.137

M (mg/kg):	11.45
SD_M (mg/kg):	0.215
$\boldsymbol{u}_{\mathbf{bb}}$ (% rel.):	1.60

(acc. to ISO Guide 35)

Table II.1: Stability study (measurement results)

Total cyanide

Sample intake: 5.0 g Analytical method: ISO 17380:2013

Sample I.D.	**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	11.34	11.31	11.43	11.21	11.32	0.091
	+20 °C	11.09	11.15	11.50	11.38	11.28	0.193
	+40 °C	10.92	11.23	11.03	11.13	11.08	0.133
	+60 °C	10.30	10.03	10.34	10.28	10.24	0.141
4 months	-20 °C	10.94	11.28	11.38	11.50	11.28	0.241
	+20 °C	11.23	11.21	11.36	11.45	11.31	0.113
	+40 °C	11.14	11.25	11.48	11.18	11.26	0.152
	+60 °C	10.10	9.94	9.99	10.00	10.01	0.067
6 months	-20 °C	11.17	11.40	11.40	11.38	11.34	0.112
	+20 °C	11.15	11.17	11.32	11.30	11.24	0.087
	+40 °C	10.60	10.65	10.59	10.80	10.66	0.097
	+60 °C	9.76	9.72	9.85	9.19	9.63	0.298
9 months	-20 °C	11.17	11.36	11.28	11.52	11.33	0.147
	+20 °C	11.08	11.13	11.37	11.49	11.27	0.195
	+40 °C	11.61	11.51	11.10	11.30	11.38	0.227
	+60 °C	9.83	9.75	9.66	9.50	9.69	0.142
12 months	-20 °C	11.21	10.99	11.53	11.45	11.30	0.245
	+20 °C	11.19	11.08	11.42	11.54	11.31	0.210
	+40 °C	11.25	11.68	10.93	11.21	11.27	0.310
	+60 °C	9.37	9.66	9.69	9.41	9.53	0.166

Table III.1: Certification inter-laboratory comparison **Total cyanide**

Measurement results for control sample **QC/GCN-2016**

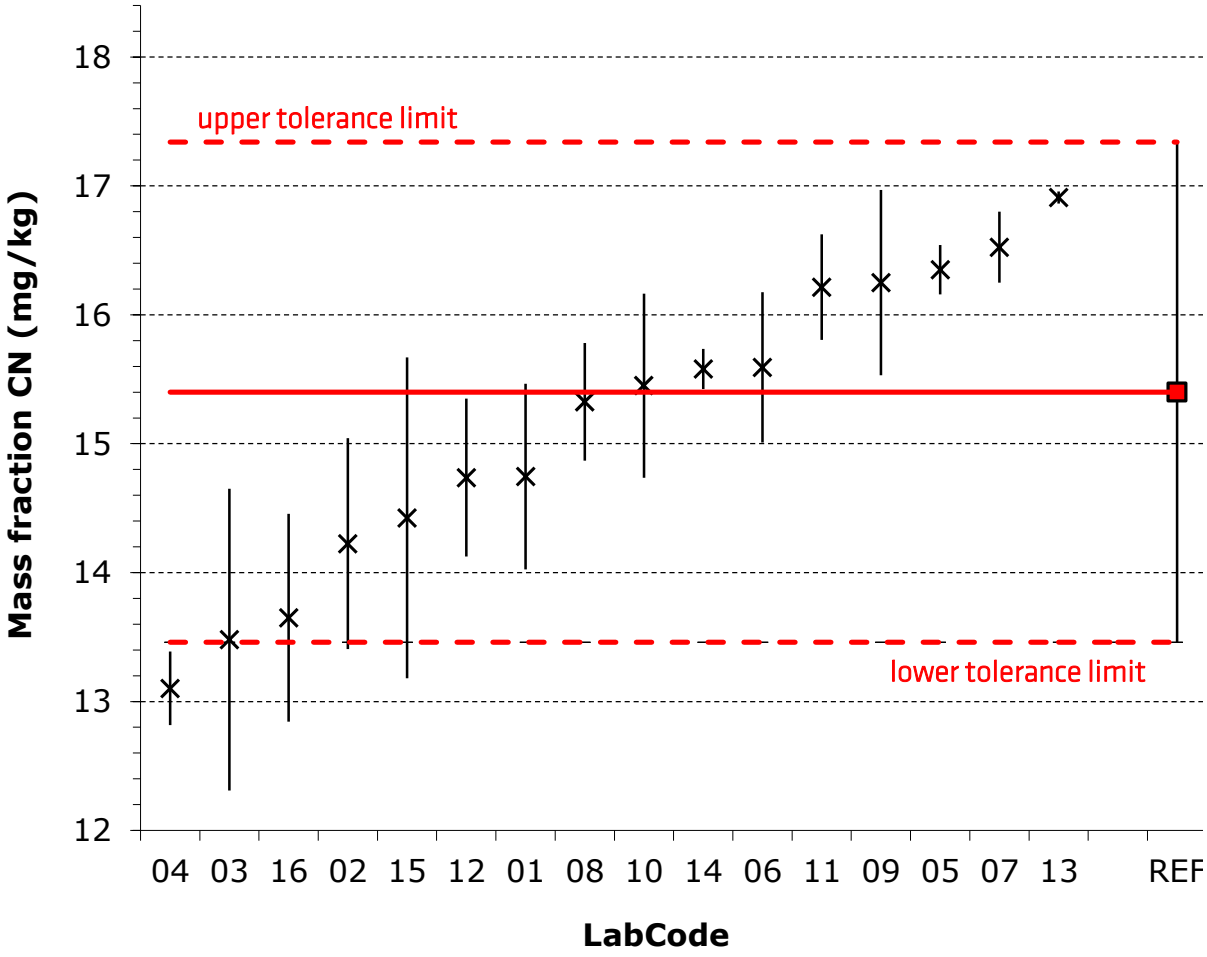
Analytical method: ISO 11262:2011

LabCode	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Mean** (mg/kg)	**SD_i** (mg/kg)
04	12.77	13.22	13.43	12.99	13.10	0.29
03	14.63	13.52	12.29		13.48	1.17
16	13.7	12.5	14.3	14.1	13.65	0.81
02	14.6	15.0	13.1	14.2	14.23	0.82
15	14.9	12.6	14.8	15.4	14.43	1.24
12	13.97	14.68	14.84	15.46	14.74	0.61
01	13.97	14.32	15.51	15.18	14.75	0.72
08	15.84	14.76	15.21	15.49	15.33	0.46
10	15.0	15.9	16.2	14.7	15.45	0.71
14	15.53	15.62	15.77	15.4	15.58	0.16
06	16.16	16.03	15.07	15.11	15.59	0.58
11	16.28	15.65	16.63	16.3	16.22	0.41
09	17.3	16.1	15.7	15.9	16.25	0.72
05	16.2	16.4	16.6	16.2	16.35	0.19
07	16.8	16.7	16.4	16.2	16.53	0.28
13	16.84	16.94	16.93	16.93	16.91	0.05

M (mg/kg):	15.16
SD_M (mg/kg):	1.161
RSD (%):	7.66

Figure III.1: Certification inter-laboratory comparison **Total cyanide**

Measurement results for control sample **QC/GCN-2016**



Control sample **QC/GCN-2016** was a homogeneous soil material whose content of total cyanide had been determined in the course of a former proficiency test (PT) by 50 participants.

The robust PT-mean (data analysis according to ISO 5725-5) was 15.4 mg/kg CN, being the assigned value REF for assessment of the technical performance of laboratories participating in the certification inter-laboratory comparison.

The tolerance limits for the results obtained for control sample **QC/GCN-2016** were set to **REF ± SR**, where SR is the reproducibility standard deviation of the PT-results (SR = 1.94 mg/kg CN).

Table III.2: Certification inter-laboratory comparison **Total cyanide**

Measurement results for candidate CRM **BAM-U116/CGL306** (all datasets)

Analytical method: ISO 11262:2011

LabCode	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Mean** (mg/kg)	**SD_i** (mg/kg)
04	9.95	8.65	9.43	9.49	9.38	0.54
01	11.03	10.60	10.40	11.08	10.78	0.33
15	12.2	10.5	10.5	10.2	10.85	0.91
03	11.20	10.74	10.54	11.04	10.88	0.30
02	10.3	10.8	11.8	11.5	11.10	0.68
12	11.16	11.02	11.21	11.49	11.22	0.20
08	11.91	11.37	11.98	11.66	11.73	0.28
14	12.00	12.05	12.02	11.41	11.87	0.31
09	12.4	11.8	11.9	11.5	11.90	0.37
06	11.99	11.94	11.99	11.91	11.96	0.04
05	12.4	12.7	11.9	12.1	12.28	0.35
10	11.9	12.8	12.3	12.4	12.35	0.37
11	12.47	12.41	12.66	12.96	12.63	0.25
07	13.0	12.9	12.6	12.2	12.68	0.36
16	13.6	12.2	12.9	13.1	12.95	0.58
13	14.05	14.05	13.98	13.57	13.91	0.23

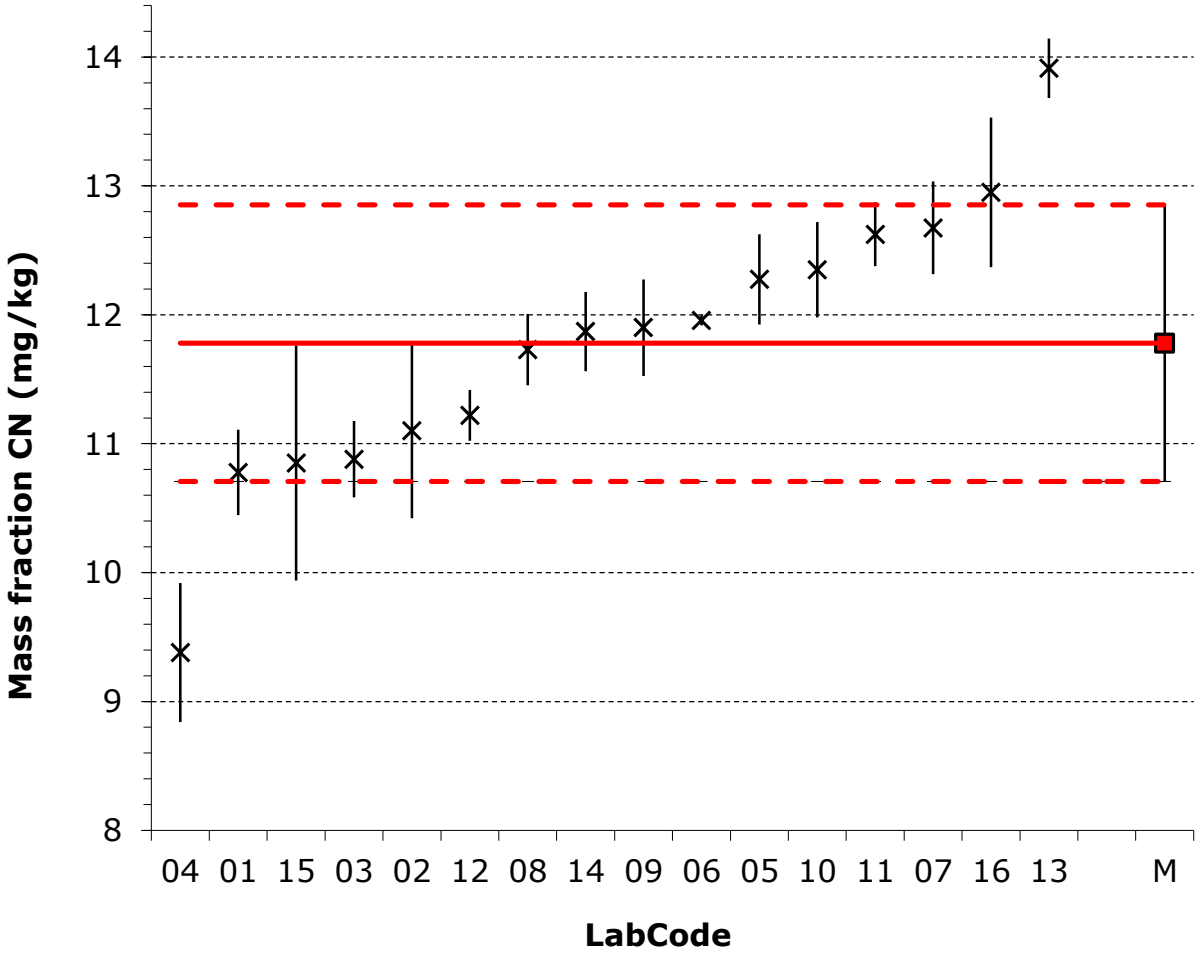
M (mg/kg): 11.78

SD_M (mg/kg): 1.073

RSD (%): 9.11

Figure III.2: Certification inter-laboratory comparison **Total cyanide**

Measurement results for candidate CRM **BAM-U116/CGL306**
(all datasets)



The dataset of laboratory **04** was considered as a technical outlier and excluded from further data processing because the mean result of this participant for control sample **QC/GCN-201**6 was outside the tolerance limits.

The dataset of laboratory **15** was excluded from further data processing because the sample intake for analysis was only 0.2 g (!!). This was considered as a too severe deviation from the analytical protocol prescribed by ISO 11262:2011.

Table III.3: Certification inter-laboratory comparison **Total cyanide**

Measurement results for candidate CRM **BAM-U116/CGL306** (accepted datasets)

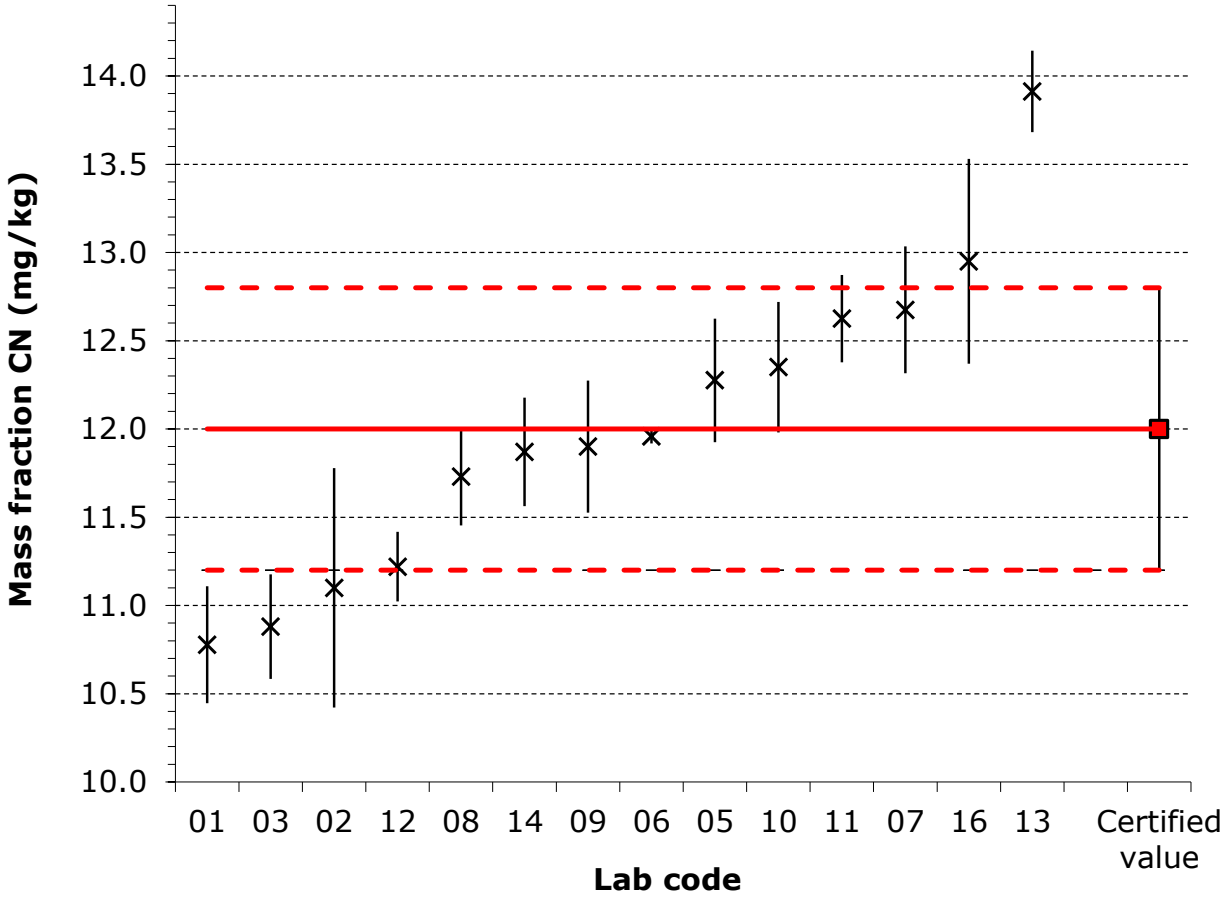
Analytical method: ISO 11262:2011

LabCode	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Mean** (mg/kg)	**SD_i** (mg/kg)
01	11.03	10.60	10.40	11.08	10.78	0.33
03	11.20	10.74	10.54	11.04	10.88	0.30
02	10.3	10.8	11.8	11.5	11.10	0.68
12	11.16	11.02	11.21	11.49	11.22	0.20
08	11.91	11.37	11.98	11.66	11.73	0.28
14	12.00	12.05	12.02	11.41	11.87	0.31
09	12.4	11.8	11.9	11.5	11.90	0.37
06	11.99	11.94	11.99	11.91	11.96	0.04
05	12.4	12.7	11.9	12.1	12.28	0.35
10	11.9	12.8	12.3	12.4	12.35	0.37
11	12.47	12.41	12.66	12.96	12.63	0.25
07	13.0	12.9	12.6	12.2	12.68	0.36
16	13.6	12.2	12.9	13.1	12.95	0.58
13	14.05	14.05	13.98	13.57	13.91	0.23

M (mg/kg):	12.02
SD_M (mg/kg):	0.871
RSD (%):	7.25

Figure III.3: Certification inter-laboratory comparison **Total cyanide**

Measurement results for candidate CRM **BAM-U116/CGL306**
(accepted datasets)



The bar associated with the plotted certified value represents its expanded uncertainty U.