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Certification Report

Certified Reference Material BAM-U114

Total Cyanide in Soil

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Summary

This report describes the certification of a reference material for the determination of total cyanide in soil according to the analytical procedure prescribed by ISO 11262:2011.
The intended purpose of reference material BAM-U114 is the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardised 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:

	Mass fraction[1)] in mg/kg	Uncertainty U [2)] in mg/kg
Total cyanide according to ISO 11262:2011	23.1	1.3

1) Unweighted mean value of 12 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-U114 is available as a powder with particle sizes below 125 µm and is supplied in screw-capped brown glass bottles containing (66 ± 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.

Contents

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, the determination of cyanides in soils has been a matter of international standardisation over several years. A result of these activities is the recently published international standard ISO 11262:2011 [1], which specifies a normative analytical method for the determination of total cyanide.

According to the prescribed analytical protocol cyanides are liberated from the test sample using orthophosphoric 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 aim of the project described in this report was to certify a reference material that can be used for the verification of analytical results obtained for the mass fraction of total cyanide in soils and soil-like materials applying the standardised procedure ISO 11262:2011. As any reference material, it can also be used for routine performance checks (quality control charts) or validation studies.

2 Candidate material

All process steps for producing the candidate CRM BAM-U114 (including homogeneity and stability testing) were performed by BAM Federal Institute for Materials Research and Testing. The starting material was a sandy soil collected from a stockpile excavated during a remediation campaign on the area of a former gasworks in the Berlin region (Germany). The raw material was dried at ambient air to constant weight and then passed through a vibrating 2 mm sieve discarding the fraction > 2 mm. The material passing the sieve was completely ground by means of a ball mill (with grinding bowls and balls made of zirconia) to particle sizes below 125 µm.

Homogenisation and bottling of the ground material were performed using a spinning riffler according to the so-called “cross-riffling scheme” [2]. In September 2010, a total of 256 units with (66 ± 1) g of soil each were filled up into 100 mL brown glass bottles equipped with screw caps and PP inserts. After bottling the whole batch was stored at (20 ± 3) °C.

3 Homogeneity study

8 bottles were selected equidistantly following the sequence of bottling. They were analysed in triplicate each according to 11262:2011 using sample intakes of 5 g.

Absorption solutions obtained after liberation of the cyanides from the soil sample were analysed under repeatability conditions after randomisation in one run with one calibration. All measurement results 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 results of 1-way Analysis of Variances (ANOVA). Since the mean of squared deviations within bottles (MS_{within}) was larger than the mean of squared deviations between bottles (MS_{among}), the following equation was used:

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

with:

n	number of replicate sub-samples per bottle
N	number of bottles selected for homogeneity study

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) and was estimated as 0.169 mg/kg.

4 Stability study

Immediately after bottling selected units were stored at temperatures of -20 °C, +20 °C, +40 °C and +60 °C, respectively. After a storage time of 0.5, 1, 3, 6 and 12 months, respectively, two bottles per temperature were analysed in duplicate for their contents of total cyanide according to ISO 11262:2011 (with a sample intake of 5 g each). After each time interval, the absorption solutions were analysed 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 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 0.5 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
0.5 months	1.0158 ± 0.0180	0.9880 ± 0.0085	0.8477 ± 0.0639
1 month	0.9887 ± 0.0277	0.9752 ± 0.0337	0.8298 ± 0.0479
3 months	1.0021 ± 0.0140	0.9895 ± 0.0243	0.8036 ± 0.0689
6 months	1.0034 ± 0.0141	0.9665 ± 0.0077	0.7796 ± 0.0619
12 months	0.9919 ± 0.0128	0.9550 ± 0.0069	

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 higher temperatures there are clear indications 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.
The dependence of the thermal degradation of complex cyanides on time is expected to be exponential. In order to obtain an estimate for the long-term behaviour of samples stored at different temperatures, an *Arrhenius* model is assumed for the dependence of the reaction (degradation) rate k_eff(T) on storage temperature [4]. A plot of k_eff(T) over the inverse temperature T (in K) is given in Figure 1.

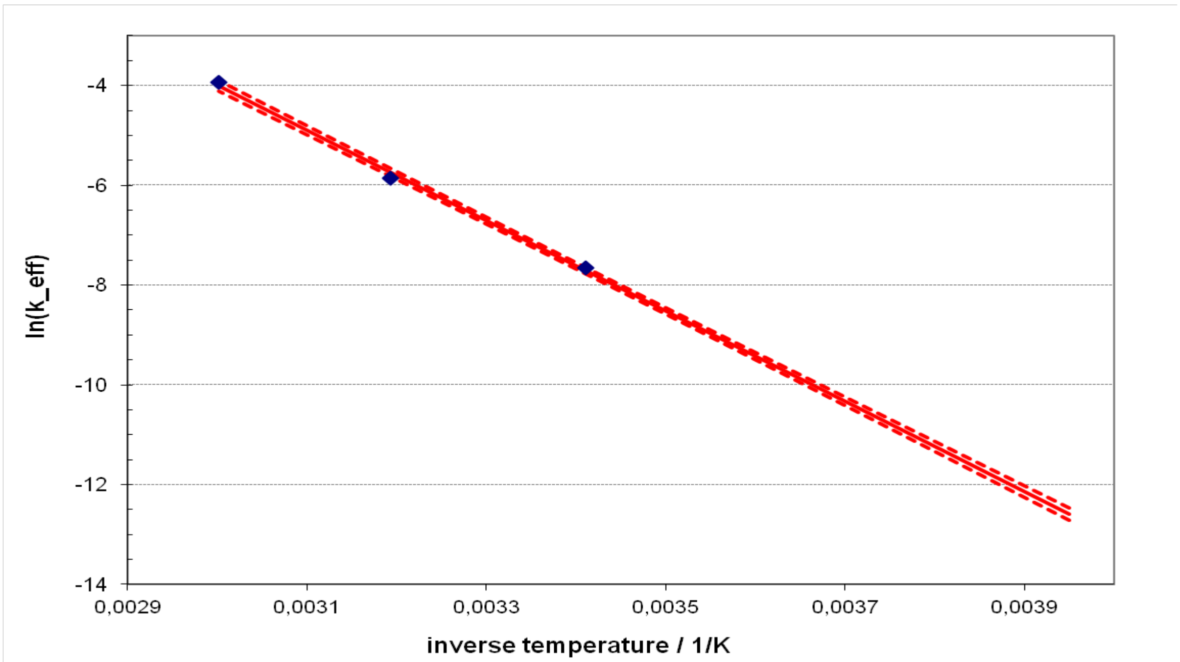

Figure 1: Dependence of the degradation rate of complex cyanides in CRM BAM-U114 on the inverse temperature (semi-logarithmic plot)

As can be seen from the plot, the temperature dependence can indeed be approximated by a straight line. The corresponding confidence interval for the line is also given in the figure.
By using the assumed model, an estimate of the shelf life of the reference material can be obtained 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.
Calculated estimates of shelf life for different storage temperatures are given in Table 2.

Table 2: Shelf life of CRM BAM-U114 at different storage temperatures

Storage temperature	-20 °C	+20 °C	+40 °C
Shelf life (months)	712	121	17

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 one year beginning with the dispatch of the reference material from BAM 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 one year 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 organised as an inter-laboratory comparison.
Each participant received one unit of the bottled candidate material and was asked to analyse four independent sub-samples. The determinations should be spread over two days, each time using freshly prepared calibrants. The information that the total cyanide content of the material was to be expected between 15 and 30 mg/kg was provided.
The standard procedure according to ISO 11262:2011 had to be followed strictly. 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.

5.2 Participants

A total of 12 German laboratories participated in the certification study on this candidate material. All but one 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 11262:2011 and of additional instructions given by BAM had been assured by all laboratories in advance.

Participating laboratories in alphabetical order:

Agrolab Labor GmbH, 84079 Bruckberg

ALS Analytiklabor Schirmacher GmbH, 21079 Hamburg

Analytik Institut Dr. Rietzler & Kunze GmbH & Co. KG, 09599 Freiberg

BAM Bundesanstalt für Materialforschung und -prüfung, Fachbereich 1.6, 12489 Berlin

BEGA.tec – Abteilung Labor, 10829 Berlin

Chemisches Labor Dr. Barbara Graser, 97453 Schonungen

DEKRA Industrial GmbH, Labor für Umwelt- und Produktanalytik, 06118 Halle (Saale)

EUROFINS Umwelt Ost GmbH, Niederlassung Freiberg, 09633 Halsbrücke/Tuttendorf

GEO-data GmbH, 30827 Garbsen

Landesamt für Natur, Umwelt u. Verbraucherschutz NRW, Fachgebiet 65.1, 45699 Herten

Lobbe Entsorgung West GmbH & Co. KG, 58642 Iserlohn

SGS Institut Fresenius GmbH, 45699 Herten

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 presentation indicate the standard deviation of individual laboratory’s results. The bar associated with the also plotted certified value represents the corresponding expanded uncertainty.

Statistical tests and data evaluation were performed using software SoftCRM version 1.2.2 [7]. The following tests were carried out:

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

Cochran test: Outlying variances?
(Significance levels 0.01 and 0.05, respectively.)

Grubbs, Dixon and Nalimov tests: Outlying means?

Bartlett test: Variances homogeneous?

Snedecor F-test: Differences between data sets statistically significant?

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

The results of these tests are summarised in Table 3.

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

Statistical test	Result of the test
Scheffé	Datasets differ significantly.
Cochran (0.01 and 0.05)	No outlying variances.
Grubbs (0.01 and 0.05)	No outlying laboratory means.
Dixon (0.01 and 0.05)	No outlying laboratory means.
Nalimov (0.01 and 0.05)	No outlying laboratory means.
Bartlett (0.01 and 0.05)	Variances are homogeneous.
Kolmogorov-Smirnov-Lilliefors (0.01 and 0.05)	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” datasets, all of them were retained for further data processing.

6 Certified value and uncertainty

The unweighted mean of laboratory means was taken as the best estimate w_{char} for the value to be certified. It is expressed on a dry mass basis corresponding to a drying temperature of (105 ± 2) °C. The standard deviation of the mean of laboratory means was taken as the uncertainty contribution u_{char} resulting from the inter-laboratory comparison.
Additionally, the following uncertainty components were taken into account:

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

u_{prec} uncertainty reflecting the average precision of laboratory means and being calculated according to the following equation:

$$u_{prec} = \sqrt{\sum_{i=1}^{N} (SD_i)^2 / n\,N} \qquad (4)$$

where SD_i is the standard deviation of the results of an individual participant, N is the number of individual datasets, and n is the number of analyses performed 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:

$$u_{com} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{prec}^2} \qquad (5)$$

The calculated mass fraction w_{char} 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-U114 (before rounding)

Mass fraction w_{char} (in mg/kg)	Uncertainty components (in mg/kg)			
	u_{char}	u_{bb}	u_{prec}	u_{com}
23.08	0.487	0.169	0.365	0.632

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.

Table 5: Certified mass fraction and expanded uncertainty of total cyanide in CRM BAM-U114 after rounding according to DIN 1333 [9]

	Mass fraction (in mg/kg)	Uncertainty *U* (in mg/kg)
Total cyanide according to ISO 11262:2011	23.1	1.3

7 Traceability

It is important to note that the certified mass fraction of total cyanide in reference material BAM-U114 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 semi-quantitative X-ray fluorescence analysis giving the following non-certified results:

Element	Si	Al	Ca	Fe	K
Mass fraction(in %)	36.4	1.8	1.4	0.8	0.8

Further informative analytical results obtained in the course of sample characterisation:

Parameter	Mass fraction (in %)	Analytical method
Dry mass content at 105 °C	99.4	ISO 11465 [5]
Loss on ignition at 550 °C	2.7	EN 12879 [10]
Total organic carbon (TOC)	1.4	ISO 10694 [11]
Total inorganic carbon (TIC)	0.2	ISO 10694 [11]

pH values in water and $CaCl_2$ solution (acc. to ISO 10390 [12]): 8.8 and 8.1, respectively.

9 Information on the proper use of CRM BAM-U114

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 the validity of the certificate expires after 12 months. Post-certification measurements will be conducted in appropriate periods to keep this information up to date.

9.2 Transport, storage and use

CRM BAM-U114 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 standardised procedure ISO 11262:2011. 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 11262:2011 must strictly 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.

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, care shall be exercised when manipulating cyanide-contaminated samples. Volatile hydrogen cyanide (with a smell 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 the BAM Federal Institute for Materials Research and Testing nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately owned intellectual property rights, or assume any liability with respect to the use, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

10 References

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

[2] A.M.H. van der Veen and D.A.G. Natter: Sample preparation from bulk samples: an overview, *Fuel Processing Technology*, 36 (1993) 1 - 7

[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] DIN 1333:1992: Zahlenangaben (*Presentation of numerical data*)

[10] EN 12879:2000: Characterization of sludges – Determination of the loss on ignition of dry mass

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

[12] ISO 10390:2005: Soil quality – Determination of pH

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 standard deviation of an individual dataset
SD_M standard deviation of the mean of dataset means

Homogeneity study (measurement results) **Total cyanide**

Sample intake: 5.0 g

Analytical method: ISO 11262:2011

Sample I.D.	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
021	22.93	23.09	23.19	23.07	0.133
051	23.09	22.72	23.25	23.02	0.272
081	23.19	23.51	23.67	23.46	0.243
111	23.46	22.77	23.67	23.30	0.471
141	23.62	22.40	23.30	23.10	0.632
171	23.40	22.56	23.56	23.18	0.541
201	23.25	22.50	23.93	23.23	0.716
231	23.30	22.50	23.72	23.18	0.619

M (mg/kg): 23.19

SD_M (mg/kg): 0.140

u_{bb} (% rel.): 0.733
(acc. to ISO Guide 35)

Stability study (measurement results) **Total cyanide**

Sample intake: 5.0 g Analytical method: ISO 11262:2011

Storage time	**Storage temperature**	**#1** (mg/kg)	**#2** (mg/kg)	**#3** (mg/kg)	**#4** (mg/kg)	**Mean** (mg/kg)	**SD** (mg/kg)
0.5 months	-20 °C	23.43	23.34	23.51	23.19	23.37	0.137
	+20 °C	23.62	24.29	23.70	23.35	23.74	0.396
	+40 °C	23.06	23.28	23.08	22.93	23.09	0.145
	+60 °C	21.07	21.07	18.89	18.19	19.81	1.488
1 month	-20 °C	22.92	23.16	22.57	23.45	23.03	0.373
	+20 °C	23.16	22.33	22.31	23.27	22.77	0.519
	+40 °C	21.76	22.02	23.21	22.86	22.46	0.685
	+60 °C	20.33	19.66	18.23	18.22	19.11	1.058
3 months	-20 °C	23.62	23.77	23.67	23.86	23.73	0.107
	+20 °C	24.20	23.45	23.68	23.78	23.78	0.314
	+40 °C	23.33	23.31	22.99	24.30	23.48	0.567
	+60 °C	20.62	20.34	17.68	17.64	19.07	1.632
6 months	-20 °C	23.43	23.28	23.12	23.28	23.28	0.127
	+20 °C	23.63	23.52	22.94	23.36	23.36	0.303
	+40 °C	22.42	22.36	22.56	22.65	22.50	0.132
	+60 °C	19.73	19.00	17.10	16.78	18.15	1.437
12 months	-20 °C	23.50	23.62	23.57	23.54	23.56	0.051
	+20 °C	23.06	23.28	23.37	23.77	23.37	0.297
	+40 °C	22.46	22.66	22.30	22.57	22.50	0.155

Certification study
(measurement results of participants)

Total cyanide

Lab code	#1 (mg/kg)	#2 (mg/kg)	#3 (mg/kg)	#4 (mg/kg)	Mean (mg/kg)	SD (mg/kg)
01	19.97	21.85	19.65	21.78	20.81	1.165
06	21.2	20.98	21.16	21.77	21.28	0.342
11	22.3	22.3	20.5	20.7	21.45	0.985
08	22.4	22.3	20.1	21.3	21.53	1.072
03	22	21.3	22.1	21.5	21.73	0.386
02	22.1	22.8	24.4	23.9	23.30	1.042
10	23.14	23.04	23.84	23.67	23.42	0.392
14	24.5	23.7	24	23.8	24.00	0.356
05	24.2	23.9	24	24.4	24.13	0.222
04	24.5	24.1	24.5	24	24.28	0.263
09	24.77	24.87	25.17	24.97	24.95	0.171
12	26.43	27.38	25.58	24.92	26.08	1.066

M (mg/kg):	23.08
SD_M (mg/kg):	1.687
$SD_M/\sqrt{N}$ (mg/kg):	0.487