Certification Report

Certified Reference Material

ERM®-EB108

Pure Lead

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Summary

This report describes preparation, analysis and certification of pure lead reference material ERM®-EB108.
The certified reference material is available in the form of discs (40 mm diameter and 40 mm height). It is intended for establishing and checking the calibration of spark optical emission spectrometers for the analysis of samples of similar materials. It is also suitable for wet chemical analysis.

The following mass fractions and uncertainties have been certified:

Element	**Mass fraction** in mg/kg	**Uncertainty** in mg/kg
Cd	26.0	1.3
Hg	8.3	0.9

The certified values are based on the results of 11 laboratories which participated in the certification interlaboratory comparison.

Content

List of abbreviations
(if not explained elsewhere)

AAS-FIMS	atomic absorption spectrometry flow injection mercury system
CRM	certified reference material
CVAAS	cold vapour atomic absorption spectrometry
ERM	European reference material
GFAAS	graphite furnace atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
SOES	spark optical emission spectrometry
M	mean value
n	number of accepted data sets
s	standard deviation of an individual data set
s_M	standard deviation of laboratory means
s_{rel}	relative standard deviation
$\bar{s}_i$	square root of mean of variances of data sets under repeatability conditions
M_i	single result
I	ICP-OES (Tables 5 - 6)
CV-I	ICP-OES after cold vapour generation (Table 6)
A	CVAAS (Table 6)
EA	GFAAS (Table 5)
DMA	direct mercury analyser (Table 6)

1. Introduction

In the metal-producing and metal-working industry mainly spark optical emission spectrometry (SOES) and X-ray fluorescence spectrometry (XRF) are used for reception inspection of raw materials, e.g. scrap, for quality control of end products and production control. These time saving analytical techniques require suitable reference materials for calibration and recalibration.

The idea to produce a reference material that in particular contains mercury was the outcome of an inquiry of a customer and of the discussions within the German Gesellschaft der Metallurgen und Bergleute e.V. (GDMB), especially of the working group „Lead“ of the Committee of Chemists within GDMB. The needs are defined by this working group, since the members are potential users of the prepared CRMs. Participating laboratories were recruited from this group. Since all of these laboratories are highly experienced with lead analysis and had participated in earlier interlaboratory comparisons, erspecially in the certification of ERM®-EB107, there was no preceding round robin test for qualification.

Certification of reference material ERM®-EB108 was carried out on the basis of the relevant ISO-Guides [1-3], the „Guidelines for the production of BAM Reference Materials“ [4] and the “Technical Guidelines for the Production and Acceptance of a European Reference Material” [5].

2. Companies/laboratories involved

Preparation of the material

- SUS Nell, Oberhausen, Germany

Test for homogeneity

- Aurubis AG, Hamburg, Germany

Participants in the certification interlaboratory comparison

- Aurubis AG, Hamburg, Germany
- BAM Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany
- BERZELIUS Stolberg GmbH, Stolberg, Germany
- Exide Technologies GmbH, Büdingen, Germany
- Harz-Metall GmbH, Goslar, Germany
- Hoppecke Batterien GmbH & Co. KG, Brilon-Hoppecke, Germany
- Johnson Controls Recycling GmbH, Buchholz, Germany,
- Johnson Controls Sachsen-Batterien GmbH & Co. KG, Zwickau, Germany
- Johnson Controls, VB Autobatterie GmbH & Co. KGaA, Hannover, Germany
- Muldenhütten Recycling und Umwelttechnik GmbH, Freiberg, Germany
- Treibacher Industrie AG, Treibach-Althofen, Austria
- WESER METALL GmbH, Nordenham

Statistical evaluation of the data

- BAM Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

3. Candidate material

Pure lead was used as basic material for the preparation of the candidate material. This material was milled, melted and doped with a Cd/Hg- and a Pb/Hg master alloy by SUS Nell, Oberhausen.
About 300 discs with a diameter of ca. 40 mm and 40 - 45 mm height were casted individually from one of the sub-batches (melts). Each disc was marked individually (A – H represent sub-batches).

4. Homogeneity testing

A homogeneity test on 24 discs (see Table 1) was performed by Aurubis AG, Hamburg, to check for homogeneity within the whole batch of discs. SOES was used for this homogeneity test, each disc was analysed five times on top and bottom, respectively.

Tab. 1: Discs analysed for homogeneity testing of ERM®-EB108

A2	B2	C1	D1	E2	F11	G2	H11
A16	B15	C14	D12	E11	F23	G14	H14
A25	B28	C26	D36	E33	F36	G27	H26

Due to equal production of the discs containing comparable weight fractions of Hg and Cd with respect to ERM®-EB107 an additional testing for homogeneity over the area of the disc has not being carried out again.
The estimate of analyte-specific inhomogeneity contribution u_{bb} to be included into the total uncertainty budget was calculated according to ISO Guide 35 [4] using Eq. (1) and Eq. (2):

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

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

where:

MS_{among}	mean of squared deviations between discs (from 1-way ANOVA, see Annex 1)
MS_{within}	mean of squared deviations within one disc (from 1-way ANOVA)
n	number of replicate measurements per disc
N	number of discs selected for homogeneity study

s_{bb} signifies the between-discs 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 values of s_{bb}, u^*_{bb} , and u_{bb} between discs (1) and within one disc (2) are given in the following Table 2.

Table 2: Uncertainty contributions due to possible sample inhomogeneity

Element	$s_{bb}(1)$ (mg/kg)	$u^*_{bb}(1)$ (mg/kg)	$u_{bb}(1)$ (mg/kg)	$s_{bb}(2)$ (mg/kg)	$u^*_{bb}(2)$ (mg/kg)	$u_{bb}(2)$ (mg/kg)
Cd	0.4382	0.0609	**0.4382**	0.2369	0.0302	**0.2369**
Hg	0.2222	0.0948	**0.2222**	0.0624	0.0522	**0.0624**

*Note: $s_{bb}(2)$, $u^*_{bb}(2)$, and $u_{bb}(2)$ are taken from ERM-EB107

5. Characterisation study

5.1 Analytical methods

11 laboratories participated in the certification interlaboratory comparison. Each laboratory received one randomly chosen disc (see Table 3).

Tab. 3: Discs sent out for certification analysis

A2	B2	C1	D1	E18	F11	G14	H11
A14	B15	C14	D12	E33	F18	G20	H18
A18	B18	C17	D18				H26

The laboratories were asked to analyse six subsamples which had to be prepared from the delivered disc for wet chemical analysis. They were free to choose any suitable analytical method for analysis. Table 4 shows the analytical methods used by the participating laboratories.
For all analytical methods where a calibration was necessary this calibration was performed using liquid standard solutions. All participating laboratories were asked to use only standard solutions prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Table 4: Analytical procedures used by the participating laboratories

Lab-No.	**Element.**	**Sample mass**	**Sample pretreatment**	**Analytical method**
1	Hg	0.01 g	Solid sampling technique	DMA (AAS), calibration with commercial solution (VWR)
2	Cd	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Kraft)
3	Cd, Hg	2 g	Dissolution with HNO_3/H_2O_2	ICP-OES, calibration with commercial solutions (Kraft)
4	Cd	5 g	Dissolution with HNO_3	ICP-OES, calibration with commercial solutions (standard addition)
	Hg	1 g	Dissolution with HNO_3	AAS-FIMS, calibration with commercial solution (SPEX)
5	Cd, Hg	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800), separation of lead as sulfate	ICP-OES calibration with pure metal or salt ($HgCl_2$)
6	Cd, Hg	2 g	Dissolution with HNO_3	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck)

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
7	Cd	1.5 g	Dissolution with HNO_3	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck)
	Hg	1.5 g	Dissolution with HNO_3	CVAAS with matrix matched standards, calibration with commercial solutions (Merck)
8	Cd	ca. 1 g	Dissolution with HNO_3	GFAAS, calibration with commercial solutions (Merck)
	Hg	ca. 1 g	Dissolution with HNO_3	CVAAS, calibration with commercial solutions (Merck)
9	Cd	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions
	Hg	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with hydride generation, calibration with commercial solutions (Merck)
10	Hg	0.5 g	Dissolution with HNO_3	CVAAS, calibration with commercial solutions (Merck)
11	Cd	0.1 g - 0.5 g	Dissolution with HNO_3	GF-AAS, calibration with solutions of pure metal
	Hg	0.1 g - 0.5 g	Dissolution with HNO_3	CVAAS, calibration with solutions of pure metal
12	Cd	1 g	Dissolution with HNO_3	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck)
	Hg	1 g	Dissolution with HNO_3	CVAAS with matrix matched standards, calibration with commercial solutions (Merck)

5.2 Analytical results and statistical evaluation

The analytical results of the certification interlaboratory comparison are listed in Tables 5 and 6. These tables show the single results (M_i) of each laboratory, the respective laboratory mean (M) together with the absolute and relative intralaboratory standard deviation (s, s_{rel}) and in addition the square root of mean of variances of data sets under repeatability conditions ($\bar{s}_i$) over all laboratories. The continuous line in the graphical presentation marks the certified value (mean of the laboratories' means), the broken lines mark the standard deviation, calculated from the laboratories' means.
In the related figures for each laboratory its mean value and single standard deviation is given.

Lab./Meth.	11/l	4/l	6/l	3/l	5/l	7/l	9/l	8/EA	12/l		
M_i [mg/kg]	23.70	24.50	24.75	25.75	25.88	26.10	26.39	28.11	27.70		*n*
	23.10	24.70	25.04	25.72	25.66	26.20	26.36	27.74	27.80		8
	26.40	24.50	25.04	25.52	25.74	26.20	26.12	28.02	27.70		
	25.20	24.50	24.90	25.58	26.38	26.20	26.28	27.93	27.80		
	25.10	24.50	24.81	25.57	25.47	26.30	26.44	27.58	27.80		
	23.60	24.60	24.91	25.11	25.82	26.40	26.37	27.05	27.90		
								27.17			
***M* [mg/kg]**	**24.52**	**24.55**	**24.91**	**25.54**	**25.82**	**26.23**	**26.33**	**27.66**	**27.78**		**25.93**
s [mg/kg]	1.254	0.084	0.118	0.230	0.309	0.103	0.114	0.416	0.075	s_M [mg/kg]	1.213
										$\bar{s}_i$ [mg/kg]	0.492
s_{rel}	0.051	0.003	0.005	0.009	0.012	0.004	0.004	0.015	0.003	$s_{M,rel}$ [%]	0.047

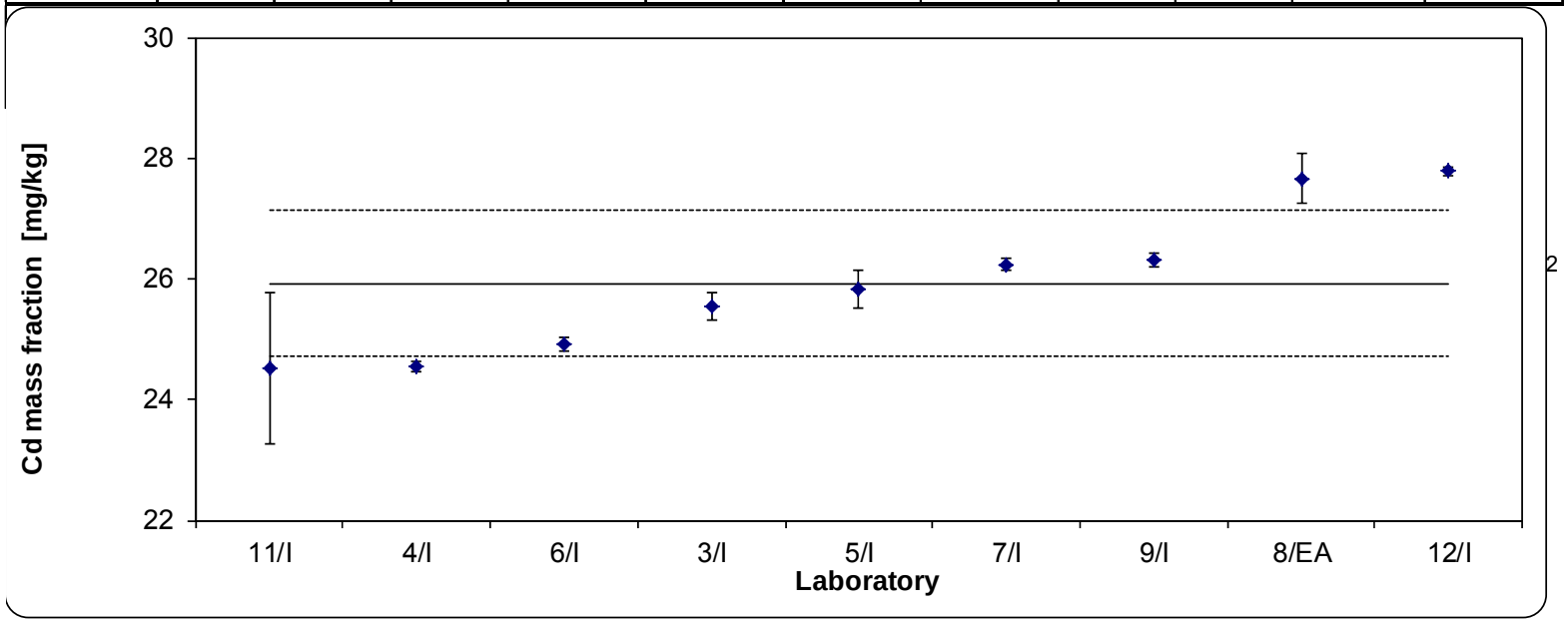

Table 5: Results for Cd

Lab./Meth.	12/A	9/CV-I	4/A	11/A	7/A	8/A	1/DMA	10/A	6/I	5/I	3/I		
M_i [mg/kg]	6.10	7.45	7.40	7.68	7.90	8.07	8.28	6.60	9.36	9.11	9.88		*n*
	6.20	7.30	7.20	7.21	7.80	8.20	8.05	9.94	9.20	9.98	10.36		11
	6.00	7.29	7.30	8.00	7.90	8.12	8.23	9.38	9.55	9.57	9.61		
	6.10	6.65	7.60	8.09	8.00	7.79	8.24	9.27	9.52	10.06	10.06		
	5.90	7.67	7.50	8.19	7.80	7.89	8.01	9.16	9.58	9.81	10.98		
	6.20	7.44	7.30	7.94	7.90	7.97	7.85	7.96	9.51	9.72	10.43		
***M* [mg/kg]**	**6.08**	**7.30**	**7.38**	**7.85**	**7.88**	**8.01**	**8.11**	**8.72**	**9.45**	**9.71**	**10.22**		**8.25**
s [mg/kg]	0.117	0.347	0.147	0.358	0.075	0.153	0.170	1.223	0.144	0.342	0.481	s_M [mg/kg]	1.200
												$\bar{s}_i$ [mg/kg]	0.479
s_{rel}	0.019	0.048	0.020	0.046	0.010	0.019	0.021	0.140	0.015	0.035	0.047	$s_{M,rel}$ [%]	0.145

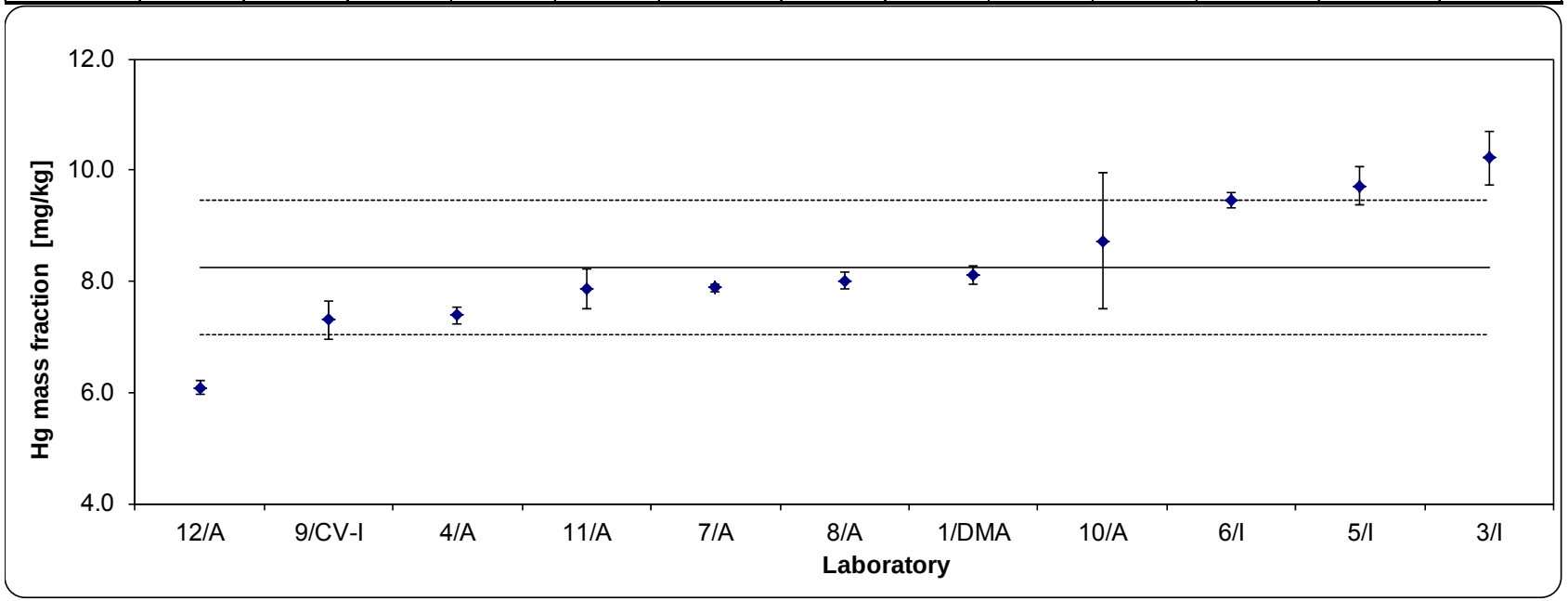

Table 6: Results for Hg

The statistical evaluation of the data was performed using the software program SoftCRM 1.2.2. [6]. The following results were received:

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

Number of data sets	10
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
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

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

Number of data sets	11
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
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

The resp. combined uncertainties were calculated from the spread resulting from the certification interlaboratory comparison (u_{ilc}) and the uncertainty contributions from possible inhomogeneity of the material using Equation 3.

$$u_{\text{combined}} = \sqrt{u_{ilc}^2 + u_{bb}^2(1) + u_{bb}^2(2)} \qquad (3)$$

with

$u_{ilc} = \sqrt{\frac{s_M^2}{n}}$: uncertainty contribution resulting from interlaboratory comparison

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

Table 9: Uncertainty calculation

	M	s_M	n	$u_{bb}(1)$	$u_{bb}(2)$	u_c	U
Cd	26.02	1.18	10	0.465	0.245	0.645	1.289
Hg	8.25	1.20	11	0.228	0.043	0.430	0.859

Note: The values for $u_{bb}(1)$ and $u_{bb}(2)$ differ from those given in Table 2 since they were recalculated using the mean values from the certification round robin instead of the mean values from homogeneity testing

The expanded uncertainties U are calculated by multiplication of $u_{combined}$ with a coverage factor of $k = 2$ using Equation 4.

$$U = 2 \cdot u_{combined} \quad (4)$$

The calculated mass fractions and their respective expanded uncertainties are given on Page 3 of this report. Rounding was done according to DIN 1333.

6. Instructions for users and stability statement

The certified reference material ERM®-EB108 is intended for the calibration and quality control of spark emission used for the analysis of similar materials. It can also be used for wet chemical analysis.
Before analysis the surface of the material should be cleaned by turning or milling. The preparation of the surface has to be done slowly to avoid heating of the disc.
If chips prepared from the compact material are used for wet chemical analysis, a minimum sample intake of 0.5 g should be used.
The material will remain stable provided that it is not subjected to excessive heat (e.g., during preparation of the working surface).

7. Literature

[1] ISO Guide 31, Contents of certificates of reference materials, 1981

[2] ISO Guide 34, General requirements for the competence of reference material producers, 2000

[3] ISO Guide 35, Reference materials - General and statistical principles for certification. Third edition, 2006

[4] Guidelines for the production of BAM Reference Materials, 2006

[5] Technical Guidelines for the Production and Acceptance of a European Reference Material (www.erm-crm.org)

[6] Bonas G, Zervou M, Papaeoannou T, Lees M: Accred Qual Assur (2003) 8:101-107

8. Information on and purchase of the CRM

Information and purchase is done by

BAM Bundesanstalt für Materialforschung und -prüfung
Fachgruppe 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, 12489 Berlin
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 1117
E-Mail: sales.crm@bam.de

Each disc of ERM®-EB108 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, Phone +49 (0)30 8104 1111.

Annex 1: Calculation of uncertainty contributions due to sample inhomogeneities

Sample	Spark	Cd ppm	Hg ppm
A2	1	24.6	8.3
A2	2	24.5	8.1
A2	3	24.7	8.3
A2	4	24.5	8.1
A2	5	24.8	8.2
A2	6	24.7	8.2
A2	7	24.7	8.0
A2	8	24.4	8.1
A2	9	24.6	8.0
A2	10	24.6	8.1
M(1-5)		24.6	8.2
M(6-10)		24.6	8.1
s(1-5)		0.1	0.10
s(6-10)		0.1	0.08
RSD(1-5)		0.5	1.2
RSD(6-10)		0.5	1.0

Sample	Spark	Cd ppm	Hg ppm
A16	1	25.1	7.9
A16	2	24.9	8.0
A16	3	24.7	8.0
A16	4	24.9	8.0
A16	5	24.8	8.1
A16	6	24.4	8.1
A16	7	23.9	8.0
A16	8	24.4	7.8
A16	9	24.0	7.9
A16	10	24	8.0
M(1-5)		24.9	8.0
M(6-10)		24.1	8.0
s(1-5)		0.15	0.07
s(6-10)		0.24	0.11
RSD(1-5)		0.6	0.9
RSD(6-10)		1.0	1.4

Sample	Spark	Cd ppm	Hg ppm
A25	1	24.7	8.2
A25	2	24.8	8.1
A25	3	24.7	7.9
A25	4	24.7	8.0
A25	5	24.8	8.0
A25	6	24.4	8.3
A25	7	24.6	7.9
A25	8	24.3	8.0
A25	9	24.4	8.0
A25	10	24.2	7.9
M(1-5)		24.7	8.0
M(6-10)		24.4	8.0
s(1-5)		0.05	0.11
s(6-10)		0.15	0.16
RSD(1-5)		0.2	1.4
RSD(6-10)		0.6	2.0

Sample	Spark	Cd ppm	Hg ppm
B2	1	24.7	8.1
B2	2	24.7	8.0
B2	3	24.9	7.9
B2	4	24.9	8.0
B2	5	24.7	8.2
B2	6	24.1	8.2
B2	7	24.2	8.0
B2	8	24.0	8.0
B2	9	23.9	7.9
B2	10	24.1	8.0
M(1-5)		24.8	8.0
M(6-10)		24.1	8.0
s(1-5)		0.11	0.11
s(6-10)		0.11	0.11
RSD(1-5)		0.4	1.4
RSD(6-10)		0.5	1.4

Sample	Spark	Cd ppm	Hg ppm
B15	1	24.3	8.2
B15	2	24.7	8.1
B15	3	24.5	8.0
B15	4	24.4	8.1
B15	5	24.5	8.1
B15	6	24.2	8.1
B15	7	23.8	7.9
B15	8	23.7	8.0
B15	9	24.0	8.0
B15	10	24.2	8.0
M(1-5)		24.5	8.1
M(6-10)		24.0	8.0
s(1-5)		0.15	0.07
s(6-10)		0.23	0.07
RSD(1-5)		0.6	0.9
RSD(6-10)		1.0	0.9

Sample	Spark	Cd ppm	Hg ppm
B28	1	24.3	8.2
B28	2	24.3	8.1
B28	3	24.5	8.2
B28	4	24.4	8.1
B28	5	24.0	8.1
B28	6	24.0	8.4
B28	7	24.3	8.1
B28	8	24.3	8.2
B28	9	24.5	8.3
B28	10	23.4	8.6
M(1-5)		24.3	8.1
M(6-10)		24.1	8.3
s(1-5)		0.19	0.05
s(6-10)		0.43	0.19
RSD(1-5)		0.8	0.7
RSD(6-10)		1.8	2.3

Sample	Spark	Cd ppm	Hg ppm
C1	1	24.2	8.3
C1	2	24.1	8.1
C1	3	24.2	8.3
C1	4	24.2	8.2
C1	5	24.1	8.1
C1	6	24.0	8.5
C1	7	23.9	8.4
C1	8	23.7	8.1
C1	9	24.2	8.2
C1	10	23.8	8.3
M(1-5)		24.2	8.2
M(6-10)		23.9	8.3
s(1-5)		0.05	0.10
s(6-10)		0.19	0.16
RSD(1-5)		0.2	1.2
RSD(6-10)		0.8	1.9

Sample	Spark	Cd ppm	Hg ppm
C14	1	24.5	8.2
C14	2	23.9	8.1
C14	3	24.0	8.2
C14	4	24.2	8.6
C14	5	23.7	8.3
C14	6	23.8	8.2
C14	7	23.8	8.0
C14	8	23.9	7.9
C14	9	23.5	8.1
C14	10	23.8	8.1
M(1-5)		24.1	8.3
M(6-10)		23.8	8.1
s(1-5)		0.30	0.19
s(6-10)		0.15	0.11
RSD(1-5)		1.3	2.3
RSD(6-10)		0.6	1.4

Sample	Spark	Cd ppm	Hg ppm
C26	1	24.1	8.6
C26	2	24.0	8.5
C26	3	24.1	8.6
C26	4	24.2	8.5
C26	5	23.7	8.5
C26	6	25.0	8.6
C26	7	24.9	8.4
C26	8	24.5	8.1
C26	9	24.8	8.0
C26	10	24.6	7.9
M(1-5)		24.0	8.5
M(6-10)		24.8	8.2
s(1-5)		0.19	0.05
s(6-10)		0.21	0.29
RSD(1-5)		0.8	0.6
RSD(6-10)		0.8	3.6

Sample	Spark	Cd ppm	Hg ppm
D1	1	24.5	8.6
D1	2	24.3	8.5
D1	3	24.0	8.6
D1	4	24.1	8.6
D1	5	23.7	8.4
D1	6	25.0	8.0
D1	7	25.1	7.7
D1	8	24.6	7.7
D1	9	24.7	7.8
D1	10	25.2	7.8
		24.1	8.5
		24.9	7.8
		0.30	0.09
		0.26	0.12
		1.3	1.0
		1.0	1.6

Sample	Spark	Cd ppm	Hg ppm
D12	1	24.0	8.9
D12	2	23.9	8.6
D12	3	24.5	8.7
D12	4	24.2	8.7
D12	5	23.8	8.8
D12	6	24.8	8.1
D12	7	24.9	7.7
D12	8	25.1	7.8
D12	9	25.1	7.8
D12	10	25	7.8
		24.1	8.7
		25.0	7.8
		0.28	0.11
		0.13	0.15
		1.2	1.3
		0.5	1.9

Sample	Spark	Cd ppm	Hg ppm
D36	1	23.9	8.6
D36	2	23.7	8.4
D36	3	23.4	8.5
D36	4	23.9	8.5
D36	5	23.5	8.5
D36	6	24.9	8.1
D36	7	24.7	7.7
D36	8	24.7	7.8
D36	9	24.8	7.7
D36	10	24.7	7.8
		23.7	8.5
		24.8	7.8
		0.23	0.07
		0.09	0.16
		1.0	0.8
		0.4	2.1

Sample	Spark	Cd ppm	Hg ppm
E2	1	25.3	8.1
E2	2	24.9	7.7
E2	3	24.7	7.7
E2	4	24.8	7.8
E2	5	25.4	7.8
E2	6	24.9	7.9
E2	7	25.0	7.6
E2	8	25.1	7.7
E2	9	25.0	7.8
E2	10	24.6	7.8
M(1-5)		25.0	7.8
M(6-10)		24.9	7.8
s(1-5)		0.31	0.16
s(6-10)		0.19	0.11
RSD(1-5)		1.2	2.1
RSD(6-10)		0.8	1.5

Sample	Spark	Cd ppm	Hg ppm
E11	1	25.2	8.0
E11	2	24.9	7.7
E11	3	25.0	7.8
E11	4	25.1	7.8
E11	5	24.7	7.9
E11	6	25.1	7.9
E11	7	24.9	7.8
E11	8	24.9	7.6
E11	9	24.7	7.8
E11	10	23.9	13.1
		25.0	7.8
		24.7	8.8
		0.19	0.11
		0.47	2.38
		0.8	1.5
		1.9	27.0

Sample	Spark	Cd ppm	Hg ppm
E33	1	25.0	7.9
E33	2	24.8	7.7
E33	3	25.0	7.7
E33	4	24.6	7.8
E33	5	24.5	7.8
E33	6	25.0	7.8
E33	7	24.8	7.6
E33	8	24.6	7.8
E33	9	24.9	7.7
E33	10	24.6	7.9
		24.8	7.8
		24.8	7.8
		0.23	0.08
		0.18	0.11
		0.9	1.1
		0.7	1.5

Sample	Spark	Cd ppm	Hg ppm
F11	1	25.0	7.9
F11	2	24.8	7.6
F11	3	25.2	7.6
F11	4	25.1	7.7
F11	5	24.4	7.9
F11	6	25.7	8.6
F11	7	24.9	8.1
F11	8	25.0	8.1
F11	9	24.9	8.3
F11	10	24.1	13.2
		24.9	7.7
		24.9	9.3
		0.32	0.15
		0.57	2.21
		1.3	2.0
		2.3	23.9

Probe	Funke	Cd ppm	Hg ppm
F23	1	24.7	7.8
F23	2	24.8	7.6
F23	3	24.5	7.4
F23	4	24.5	7.6
F23	5	24.5	7.8
F23	6	24.6	8.3
F23	7	25.1	8.2
F23	8	24.9	8.2
F23	9	24.9	8.1
F23	10	24.8	8.4
M(1-5)		24.6	7.6
M(6-10)		24.9	8.2
s(1-5)		0.1	0.2
s(6-10)		0.2	0.1
RSD(1-5)		0.6	2.2
RSD(6-10)		0.7	1.4

Probe	Funke	Cd ppm	Hg ppm
F36	1	25.0	7.8
F36	2	24.4	7.7
F36	3	24.9	7.6
F36	4	24.7	7.6
F36	5	24.4	7.8
F36	6	24.4	8.1
F36	7	24.6	7.9
F36	8	24.8	7.9
F36	9	24.9	7.8
F36	10	24.6	7.9
		24.7	7.7
		24.7	7.9
		0.3	0.1
		0.2	0.1
		1.1	1.3
		0.8	1.4

Probe	Funke	Cd ppm	Hg ppm
G2	1	25.0	8.6
G2	2	24.3	8.2
G2	3	24.5	7.9
G2	4	24.4	8.1
G2	5	24.8	8.0
G2	6	24.6	8.0
G2	7	24.5	7.8
G2	8	25.0	7.8
G2	9	24.9	8.0
G2	10	24.5	8.1
		24.6	8.2
		24.7	7.9
		0.3	0.3
		0.2	0.1
		1.2	3.3
		0.9	1.7

Probe	Funke	Cd ppm	Hg ppm
G14	1	24.6	8.1
G14	2	24.6	7.8
G14	3	24.9	7.8
G14	4	24.8	7.8
G14	5	24.5	8.0
G14	6	24.8	7.9
G14	7	24.6	7.7
G14	8	24.7	7.8
G14	9	24.5	7.8
G14	10	24.5	8.0
		24.7	7.9
		24.6	7.8
		0.2	0.1
		0.1	0.1
		0.7	1.8
		0.5	1.5

Probe	Funke	Cd	Hg
		ppm	ppm
G27	1	25.2	7.9
G27	2	24.8	7.7
G27	3	24.4	7.8
G27	4	24.6	8.3
G27	5	23.8	7.6
G27	6	24.8	8.0
G27	7	24.7	7.8
G27	8	24.5	7.9
G27	9	24.5	7.9
G27	10	24.4	8.0
M(1-5)		24.6	7.9
M(6-10)		24.6	7.9
s(1-5)		0.52	0.27
s(6-10)		0.16	0.08
RSD(1-5)		2.1	3.4
RSD(6-10)		0.7	1.1

Probe	Funke	Cd	Hg
		ppm	ppm
H11	1	24.6	8.1
H11	2	24.7	7.7
H11	3	24.4	7.8
H11	4	24.7	7.7
H11	5	24.3	8.0
H11	6	24.5	8.0
H11	7	24.3	7.8
H11	8	24.7	7.9
H11	9	24.6	7.8
H11	10	24.5	7.9
M(1-5)		24.5	7.9
M(6-10)		24.5	7.9
s(1-5)		0.18	0.18
s(6-10)		0.15	0.08
RSD(1-5)		0.7	2.3
RSD(6-10)		0.6	1.1

Probe	Funke	Cd	Hg
		ppm	ppm
H14	1	24.7	7.9
H14	2	24.4	7.6
H14	3	24.8	7.7
H14	4	23.9	7.9
H14	5	24.8	7.7
H14	6	24.4	8.1
H14	7	24.5	7.7
H14	8	24.4	7.7
H14	9	24.7	7.9
H14	10	24.2	8
M(1-5)		24.5	7.8
M(6-10)		24.4	7.9
s(1-5)		0.38	0.13
s(6-10)		0.18	0.18
RSD(1-5)		1.6	1.7
RSD(6-10)		0.7	2.3

Probe	Funke	Cd	Hg
		ppm	ppm
H26	1	24.8	7.9
H26	2	24.5	7.9
H26	3	24.2	7.7
H26	4	24.6	7.9
H26	5	24.4	7.9
H26	6	24.7	7.8
H26	7	24.3	7.6
H26	8	24.1	7.8
H26	9	23.9	7.8
H26	10	23.5	7.9
M(1-5)		24.5	7.9
M(6-10)		24.1	7.8
s(1-5)		0.22	0.09
s(6-10)		0.45	0.11
RSD(1-5)		0.9	1.1
RSD(6-10)		1.9	1.4

Results of ANOVA for Cd ($u_{bb}(1)$)

Summary

Groups	*Number*	*Sum*	*Mean value*	*Variance*
Sample A2	10	246.1	24.61	0.01433333
Sample A16	10	245.1	24.51	0.18766667
Sample A25	10	245.6	24.56	0.04711111
Sample B2	10	244.2	24.42	0.15511111
Sample B15	10	242.3	24.23	0.10233333
Sample B28	10	242	24.2	0.10888889
Sample C1	10	240.4	24.04	0.03377778
Sample C14	10	239.1	23.91	0.07655556
Sample C26	10	243.9	24.39	0.18766667
Sample D1	10	245.2	24.52	0.24844444
Sample D12	10	245.3	24.53	0.26677778
Sample D36	10	242.2	24.22	0.35066667
Sample E2	10	249.7	24.97	0.06233333
Sample E11	10	248.4	24.84	0.136
Sample E33	10	247.8	24.78	0.03733333
Sample F11	10	249.1	24.91	0.18766667
Sample F23	10	247.3	24.73	0.04233333
Sample F36	10	246.7	24.67	0.05122222
Sample G2	10	246.5	24.65	0.065
Sample G14	10	246.5	24.65	0.02055556
Sample G27	10	245.7	24.57	0.13122222
Sample H11	10	245.3	24.53	0.02455556
Sample H14	10	244.8	24.48	0.08177778
Sample H26	10	243	24.3	0.15555556
			24.5091667	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	15.9058333	23	0.69155797	5.9812814	1.4503E-13	1.57942371
Within groups	24.974	216	0.11562037			
Total	40.8798333	239				

(sbb)^2	0.1919792	(sbb)	0.43815431
		sbb, rel. %	1.78771607
ubb	0.06089766		
ubb^2	0.00370853		

Results of ANOVA for Hg ($u_{bb}(1)$)

Summary

Groups	*Number*	*Sum*	*Mean value*	*Variance*
Sample A2	10	81.4	8.14	0.01155556
Sample A16	10	79.8	7.98	0.00844444
Sample A25	10	80.3	8.03	0.01788889
Sample B2	10	80.3	8.03	0.01122222
Sample B15	10	80.5	8.05	0.00722222
Sample B28	10	82.3	8.23	0.02677778
Sample C1	10	82.5	8.25	0.01833333
Sample C14	10	81.7	8.17	0.03566667
Sample C26	10	83.7	8.37	0.07122222
Sample D1	10	81.7	8.17	0.16233333
Sample D12	10	82.9	8.29	0.241
Sample D36	10	81.6	8.16	0.14266667
Sample E2	10	77.9	7.79	0.01877778
Sample E11	10	83.4	8.34	2.80933333
Sample E33	10	77.7	7.77	0.009
Sample F11	10	85	8.5	2.82666667
Sample F23	10	79.4	7.94	0.11822222
Sample F36	10	78.1	7.81	0.02322222
Sample G2	10	80.5	8.05	0.05388889
Sample G14	10	78.7	7.87	0.01566667
Sample G27	10	78.9	7.89	0.03655556
Sample H11	10	78.7	7.87	0.01788889
Sample H14	10	78.2	7.82	0.02622222
Sample H26	10	78.2	7.82	0.01066667
			8.05583333	

ANOVA

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	9.84783333	23	0.42816667	1.52906554	0.06327266	1.57942371
Within groups	60.484	216	0.28001852			
Total	70.3318333	239				

(sbb)^2	0.04938272	(sbb)	0.22222222
		sbb, rel. %	2.75852557
ubb	0.09477129		
ubb^2	0.0089816		