Certification Report

Certified Reference Materials

ERM®-EB107

Pure Lead

October 2014

Coordinator: Dr. Sebastian Recknagel
BAM Federal Institute for Materials Research and Testing
Division 1.6 „Inorganic Reference Materials“
Richard-Willstätter-Str. 11
12489 Berlin
Phone: ++49/30/8104 1111
Fax.: ++49/30/8104 1117
Email: sebastian.recknagel@bam.de

Summary

This report describes preparation, analysis and certification of pure lead reference material ERM®-EB107.
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 optical emission and X-ray spectrometers (excluding micro-analysis) 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	26.1	1.1
Hg	11.3	0.9

This report contains detailed information on the preparation of the CRM as well as on homogeneity investigations and on the analytical methods used for certification analysis.
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
ERM	European reference material
FAAS	flame atomic absorption spectrometry
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)
A	FAAS (Tables 5 - 6)
EA	GFAAS (Tables 5 - 6)
DMA	Direct mercury analyser (Tables 5 - 6)

1. Introduction

In the metal-producing and metal-working industry mainly spark 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 especially with mercury is 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. Secondly participating the laboratories are recruited from this group. Since all of these laboratories are highly experienced with lead analysis and participated in earlier interlaboratory comparisons, there was no preceding round robin test for qualification. However, there was a feasibility study before starting the project. Three samples with different Hg-contents were analysed with SOES and wet chemical methods. Seven of 11 laboratories performed wet chemical analyses within this study. The results are shown in Annex 2.

Certification of reference materials is 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
- BAM Bundesanstalt für Materialforschung und -prüfung, Berlin, 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

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 grinded, melted and doped with a Cd/Hg- and a Pb/Hg master alloy by SUS Nell, Oberhausen.
335 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 17 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®-EB107

A4	B8	C5	D4	E13	F8	G6	H33
A16	B19	C21	D27	E37	F21		H43
		C31					
		C38					

In addition one disc was tested for homogeneity over the area of the disc. BAM performed this test using GFAAS for Cd and CVAAS for Hg after dissolution in nitric acid. Small pieces of sample were cut from slices which were taken from the top, the bottom and the middle of the disc.
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

$s_{bb}(1)$ signifies the between-discs standard deviation and $s_{bb}(2)$ the within-disc 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	0.3351	0.0489	**0.3351**	0.2369	0.0302	**0.2369**
Hg	0.3450	0.0477	**0.3450**	0.0624	0.0522	**0.0624**

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

A23	C20	D28	E14	F22	G6	H5
A25				F23	G7	H12
					G33	H23
						H36

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 show 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, Hg	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with commercial solutions (Kraft)
3	Cd, Hg	0.5 g	Dissolution with $HNO_3/H_2O_2/H_2O$	ICP-OES, calibration with commercial solutions (Kraft)
4	Cd	1 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	2 g	Dissolution with HNO_3, separation of lead as sulfate	ICP-OES calibration with pure metal
6	Cd, Hg	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck)
7	Cd, Hg	1.5 g	Dissolution with HNO_3	ICP-OES with matrix matched standards, calibration with commercial solutions (Merck)
	Cd, 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, Hg	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES
10	Cd	0.5 g	Dissolution with HNO_3	ICP-OES, calibration with commercial solutions (Merck)
	Hg	0.5 g	Dissolution with HNO_3	CVAAS, calibration with commercial solutions (Merck)
11	Cd	1 g	Dissolution with HNO_3, separation of lead as chloride	ICP-OES with matrix matched standards, calibration with commercial solutions

5.2 Analytical results and statistical evaluation

The analytical results of the certification interlaboratory comparison are listed in Tables 5 to 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 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.	8/EA	4/I	5/I	9/I	6/I	11/I	7/I	2/I	3/I		Ges.
M_i [mg/kg]	24.48	25.10	25.39	25.50	25.90	26.30	26.41	[21.3]	28.16		N
	25.14	25.20	25.46	25.90	25.80	26.40	26.81	26.77	28.34		9
	25.44	25.40	25.42	25.90	25.90	26.00	26.38	26.79	27.38		
	25.07	25.00	25.10		25.90	26.00	27.22	26.86	27.35		
	25.02	25.10	25.44		25.90	25.90	26.70	26.79	27.55		
	25.06	25.20	25.34		26.00	26.10	26.51	27.50	27.97		
***M* [mg/kg]**	**25.03**	**25.17**	**25.36**	**25.77**	**25.90**	**26.12**	**26.67**	**26.94**	**27.79**		**26.08**
s [mg/kg]	0.314	0.137	0.134	0.231	0.063	0.194	0.318	0.314	0.422	s_M [mg/kg]	0.908
										$\bar{s}_i$ [mg/kg]	0.260
s_{rel}	0.013	0.005	0.005	0.009	0.002	0.007	0.012	0.012	0.015	$s_{M,rel}$ [%]	0.035

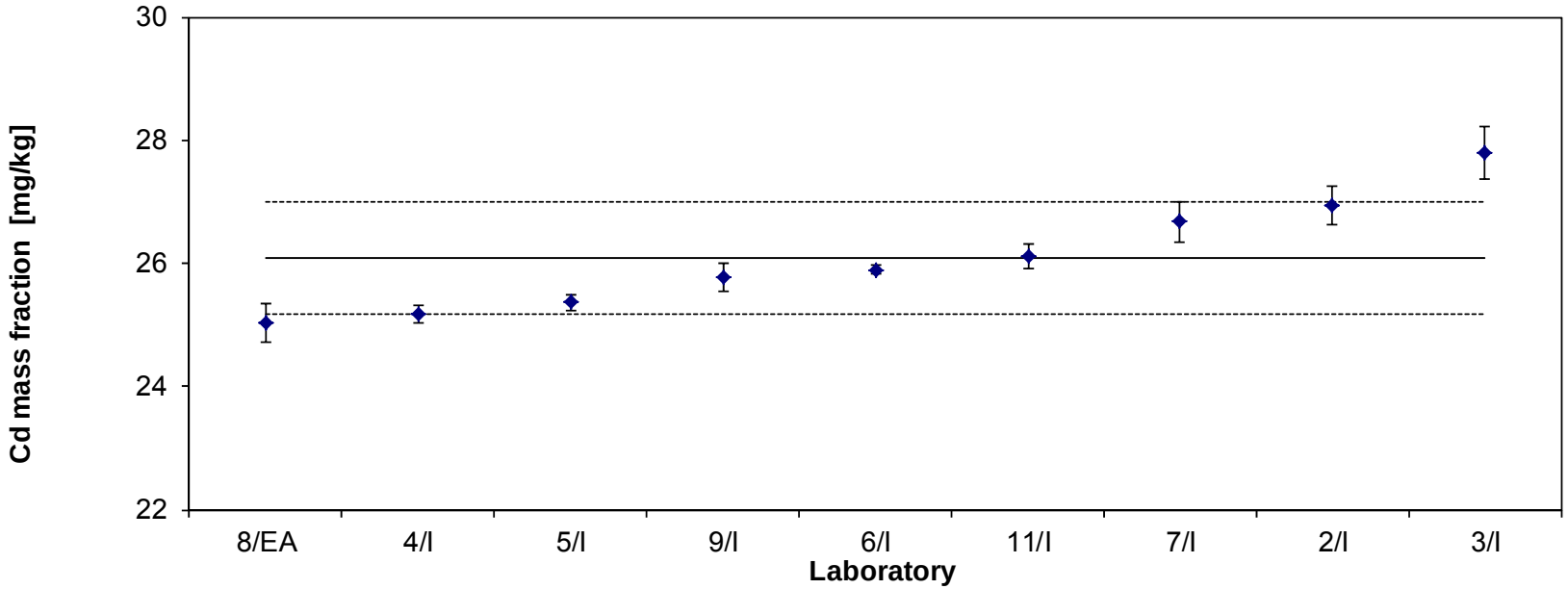


Table 5: Results for Cd

Lab./Meth.	10/I	3/I	7/I	7/A	1/DMA	9/I	8/A	4/A	11/A	2/I		Ges.
M_i [mg/kg]	10.99	10.06	10.69	10.80	11.48	11.60	11.86	11.60	12.50	[9.2]		N
	10.24	9.82	10.73	10.90	11.53	11.80	12.01	11.50	12.30	12.40		10
	8.97	9.97	10.48	11.30	11.70	11.60	11.85	12.00	12.20	12.30		
	9.88	10.07	10.83	11.20	11.24		11.67	12.40	12.50	12.48		
	9.67	9.81	10.88	11.10	11.20		11.68	12.00	12.35	12.90		
	9.10	10.16	10.91	11.20	10.98		11.84	12.50	12.20	12.68		
M [mg/kg]	**9.81**	**9.98**	**10.75**	**11.08**	**11.36**	**11.67**	**11.82**	**12.00**	**12.34**	**12.55**		**11.34**
s [mg/kg]	0.750	0.142	0.157	0.194	0.262	0.115	0.130	0.405	0.136	0.239	s_M [mg/kg]	0.934
											$\bar{s}_i$ [mg/kg]	0.321
s_{rel}	0.076	0.014	0.015	0.018	0.023	0.010	0.011	0.034	0.011	0.019	$s_{M,rel}$ [%]	0.082

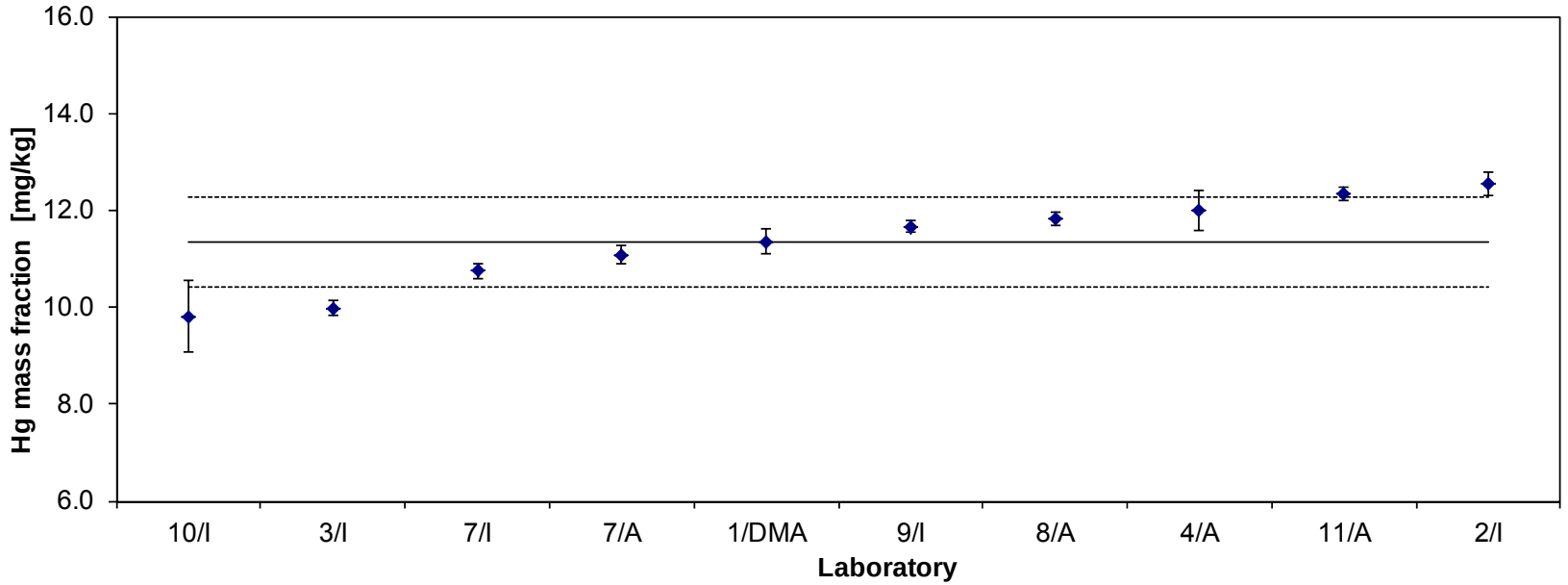


Table 6: Results for Hg

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	9
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)	Laboratory 3
Nalimov (α = 0.01)	Laboratory 3
Grubbs (α = 0.05)	Laboratory 3
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: not normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

The outlying value (Lab. 3) was not removed.

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

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

The certified mass fractions of all elements were calculated as mean of the accepted data sets. These values are given in Table 9.
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	26.08	0.908	9	0.355	0.245	0.527	1.054
Hg	11.34	0.934	10	0.292	0.060	0.420	0.839

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.

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

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

The certified reference material ERM®-EB107 is intended for the calibration and quality control of spark emission and X-ray fluorescence spectrometer 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 1.1: Anorganisch-chemische Analytik, 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®-EB107 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	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg
		mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg
A4	1	24.9	13.9		B8	1	25.2	14.1		C5	1	24.5	14.1		C31	1	24.9	14.2
A4	2	24.6	13.4		B8	2	24.9	13.9		C5	2	24.7	13.8		C31	2	24.6	13.6
A4	3	24.8	13.5		B8	3	24.9	13.6		C5	3	24.7	13.9		C31	3	24.8	13.8
A4	4	24.7	13.5		B8	4	24.7	13.9		C5	4	24.9	13.9		C31	4	24.8	13.9
A4	5	24.7	13.5		B8	5	24.5	13.6		C5	5	24.4	13.7		C31	5	24.5	14.0
A4	6	24.9	14.2		B8	6	24.8	14.0		C5	6	24.8	13.5		C31	6	24.7	13.6
A4	7	24.6	13.8		B8	7	24.7	13.3		C5	7	24.9	13.0		C31	7	24.6	13.5
A4	8	25.1	13.8		B8	8	24.9	13.4		C5	8	25.1	13.2		C31	8	25.0	13.2
A4	9	24.7	13.7		B8	9	24.5	13.4		C5	9	25.0	13.3		C31	9	24.9	13.1
A4	10	24.7	13.6		B8	10	24.7	13.4		C5	10	24.9	13.2		C31	10	24.8	13.1
M(1-5)		24.7	13.6				24.8	13.8				24.6	13.9				24.7	13.9
M(6-10)		24.8	13.8				24.7	13.5				24.9	13.2				24.8	13.3
s(1-5)		0.11	0.19				0.26	0.22				0.19	0.15				0.16	0.22
s(6-10)		0.20	0.23				0.15	0.28				0.11	0.18				0.16	0.23
RSD(1-5)		0.5	1.4				1.0	1.6				0.8	1.1				0.7	1.6
RSD(6-10)		0.8	1.7				0.6	2.1				0.5	1.4				0.6	1.8

Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg
		mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg
A16	1	24.5	13.7		B19	1	25.4	14.4		C21	1	25.2	13.6		C38	1	24.8	13.3
A16	2	25.0	13.5		B19	2	24.8	13.9		C21	2	24.8	13.9		C38	2	24.7	13.2
A16	3	24.8	13.5		B19	3	24.9	13.7		C21	3	24.7	13.8		C38	3	24.9	12.9
A16	4	25.0	13.6		B19	4	24.5	14.0		C21	4	24.7	13.9		C38	4	24.4	13.0
A16	5	24.7	13.7		B19	5	24.9	13.7		C21	5	25.0	13.9		C38	5	24.5	13.1
A16	6	24.7	13.9		B19	6	24.9	13.7		C21	6	24.8	13.3		C38	6	25.0	13.2
A16	7	24.8	13.6		B19	7	24.8	13.2		C21	7	24.8	13.3		C38	7	24.9	13.2
A16	8	24.9	13.6		B19	8	25.4	13.5		C21	8	25.1	13.1		C38	8	24.7	12.9
A16	9	24.7	13.6		B19	9	24.6	13.2		C21	9	25.0	13.2		C38	9	24.6	13.1
A16	10	24.9	13.6		B19	10	24.8	13.4		C21	10	24.9	13.3		C38	10	24.8	13.1
M(1-5)		24.8	13.6				24.9	13.9				24.9	13.8				24.7	13.1
M(6-10)		24.8	13.7				24.9	13.4				24.9	13.2				24.8	13.1
s(1-5)		0.21	0.10				0.32	0.29				0.22	0.13				0.21	0.16
s(6-10)		0.10	0.13				0.30	0.21				0.13	0.09				0.16	0.12
RSD(1-5)		0.9	0.7				1.3	2.1				0.9	0.9				0.8	1.2
RSD(6-10)		0.4	1.0				1.2	1.6				0.5	0.7				0.6	0.9

Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg
		mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg
D4	1	24.7	13.4		D27	1	24.6	13.5		E13	1	24.7	13.2		E37	1	24.5	13.0
D4	2	24.8	13.2		D27	2	25.1	13.2		E13	2	25.1	13.3		E37	2	24.6	13.2
D4	3	24.0	12.7		D27	3	24.6	13.2		E13	3	24.8	13.0		E37	3	24.7	13.3
D4	4	24.9	12.9		D27	4	24.4	13.0		E13	4	24.6	13.1		E37	4	24.4	13.2
D4	5	24.6	12.9		D27	5	24.4	13.2		E13	5	24.6	12.8		E37	5	24.7	13.2
D4	6	24.7	13.6		D27	6	24.9	13.5		E13	6	24.6	13.5		E37	6	24.5	13.5
D4	7	24.9	13.4		D27	7	24.7	13.4		E13	7	24.4	13.1		E37	7	24.6	13.2
D4	8	24.9	13.1		D27	8	24.5	13.2		E13	8	24.6	13.2		E37	8	24.6	13.2
D4	9	24.7	13.1		D27	9	24.4	13.1		E13	9	24.7	13.2		E37	9	24.5	13.3
D4	10	24.6	13.1		D27	10	24.7	13.1		E13	10	24.4	13.3		E37	10	24.3	13.3
M(1-5)		24.6	13.0				24.6	13.2				24.8	13.1				24.6	13.2
M(6-10)		24.8	13.3				24.6	13.3				24.5	13.3				24.5	13.3
s(1-5)		0.35	0.28				0.29	0.18				0.21	0.19				0.13	0.11
s(6-10)		0.13	0.23				0.19	0.18				0.13	0.15				0.12	0.12
RSD(1-5)		1.4	2.1				1.2	1.4				0.8	1.5				0.5	0.8
RSD(6-10)		0.5	1.7				0.8	1.4				0.5	1.1				0.5	0.9
Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg		Sample	Spark	Cd	Hg
		mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg				mg/kg	mg/kg
F8	1	24.8	13.4		F21	1	24.4	13.4		H33	1	24.1	13.7		H43	1	24.2	13.4
F8	2	24.8	13.2		F21	2	24.5	13.3		H33	2	24.4	13.2		H43	2	24.6	13.6
F8	3	24.5	13.2		F21	3	26.0	13.1		H33	3	24.3	13.0		H43	3	23.7	13.2
F8	4	24.5	13.2		F21	4	24.8	13.3		H33	4	24.3	13.1		H43	4	23.8	13.3
F8	5	24.6	13.3		F21	5	23.8	13.0		H33	5	24.3	13.2		H43	5	24.2	13.1
F8	6	24.8	13.5		F21	6	24.9	13.7		H33	6	24.3	13.5		H43	6	24.3	13.6
F8	7	24.6	13.2		F21	7	24.2	13.3		H33	7	24.2	13.2		H43	7	24.3	13.5
F8	8	24.6	13.5		F21	8	24.5	13.3		H33	8	24.5	13.3		H43	8	24.5	13.3
F8	9	24.7	13.1		F21	9	24.2	13.4		H33	9	24.4	13.3		H43	9	24.8	13.3
F8	10	24.7	13.3		F21	10	23.9	13.1		H33	10	24.1	13.6		H43	10	24.1	13.2
M(1-5)		24.6	13.3				24.7	13.2				24.3	13.2				24.1	13.3
M(6-10)		24.7	13.3				24.3	13.4				24.3	13.4				24.4	13.4
s(1-5)		0.15	0.09				0.81	0.16				0.11	0.27				0.36	0.19
s(6-10)		0.08	0.18				0.38	0.22				0.16	0.16				0.26	0.16
RSD(1-5)		0.6	0.7				3.3	1.2				0.5	2.0				1.5	1.4
RSD(6-10)		0.3	1.3				1.6	1.6				0.7	1.2				1.1	1.2

Sample	Spark	Cd	Hg
		mg/kg	mg/kg
G6	1	24.3	13.4
G6	2	24.3	13.2
G6	3	24.4	13.3
G6	4	24.3	13.3
G6	5	24.0	13.5
G6	6	24.5	13.5
G6	7	24.5	13.2
G6	8	24.5	13.2
G6	9	24.4	13.1
G6	10	24.1	13.3
M(1-5)		24.3	13.3
M(6-10)		24.4	13.3
s(1-5)		0.15	0.11
s(6-10)		0.17	0.15
RSD(1-5)		0.6	0.9
RSD(6-10)		0.7	1.1

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

Summary						
Groups	*Number*	*Sum*	*Mean value*	*Variance*		
Sample A4	10	247.7	24.77	0.02455556		
Sample A16	10	248	24.8	0.02444444		
Sample B8	10	247.8	24.78	0.044		
Sample B19	10	249	24.9	0.08666667		
Sample C5	10	247.9	24.79	0.04766667		
Sample C21	10	249	24.9	0.02888889		
Sample C31	10	247.6	24.76	0.02488889		
Sample C38	10	247.3	24.73	0.03566667		
Sample D4	10	246.8	24.68	0.07066667		
Sample D27	10	246.3	24.63	0.05344444		
Sample E13	10	246.5	24.65	0.04055556		
Sample E37	10	245.4	24.54	0.016		
Sample F8	10	246.6	24.66	0.01377778		
Sample F21	10	245.2	24.52	0.39288889		
Sample H33	10	242.9	24.29	0.01655556		
Sample H43	10	242.5	24.25	0.11388889		
Sample G6	10	243.3	24.33	0.029		
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6.39011765	16	0.39938235	6.3837756	8.4334E-11	1.71000734
Within groups	9.572	153	0.06256209			
Total	15.9621176	169				
(sbb)^2	0.11227342		(sbb)	0.33507226		
ubb	0.0488292					
ubb^2	0.00238429					

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

Summary						
Groups	*Number*	*Sum*	*Mean value*	*Variance*		
Sample A4	10	136.9	13.69	0.05877778		
Sample A16	10	136.3	13.63	0.01344444		
Sample B8	10	136.6	13.66	0.08488889		
Sample B19	10	136.7	13.67	0.13788889		
Sample C5	10	135.6	13.56	0.13822222		
Sample C21	10	135.3	13.53	0.10455556		
Sample C31	10	136	13.6	0.14666667		
Sample C38	10	131	13.1	0.01777778		
Sample D4	10	131.4	13.14	0.07377778		
Sample D27	10	132.4	13.24	0.02933333		
Sample E13	10	131.7	13.17	0.03566667		
Sample E37	10	132.4	13.24	0.016		
Sample F8	10	132.9	13.29	0.01877778		
Sample F21	10	132.9	13.29	0.03877778		
Sample H33	10	133.1	13.31	0.04988889		
Sample H43	10	133.5	13.35	0.02944444		
Sample G6	10	133	13.3	0.01777778		
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6.66447059	16	0.41652941	6.99934102	6.7095E-12	1.71000734
Within groups	9.105	153	0.0595098			
Total	15.7694706	169				
(sbb)^2	0.11900654		(sbb)	0.34497324		
ubb	0.04762317					
ubb^2	0.00226797					

Results of ANOVA for Cd ($u_{bb}(2)$)

Summary						
Groups	*Number*	*Sum*	*Mean value*	*Variance*		
sample H36, inner	2	50.1	25.05	0.005		
sample H36, outer	2	51	25.5	0		
sample H36, centre	2	49.9	24.95	0.005		
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.34333333	2	0.17166667	51.5	0.00476127	9.5520945
Within groups	0.01	3	0.00333333			
Total	0.35333333	5				
(sbb)^2	0.05611111		(sbb)	0.23687784		
ubb	0.03012007					
ubb^2	0.00090722					

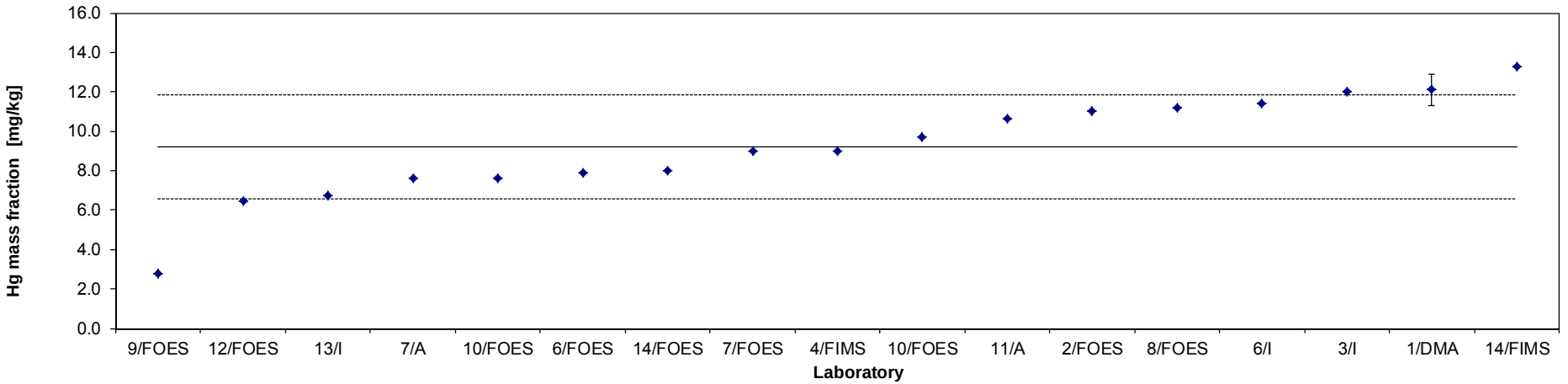
Results of ANOVA for Hg ($u_{bb}(2)$)

Summary						
Groups	*Number*	*Sum*	*Mean value*	*Variance*		
sample H36, inner	2	23.9	11.95	0.005		
sample H36, outer	2	23.6	11.8	0.02		
sample H36, centre	2	23.5	11.75	0.005		
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.04333333	2	0.02166667	2.16666667	0.26165542	9.5520945
Within groups	0.03	3	0.01			
Total	0.07333333	5				
(sbb)^2	0.00388889		(sbb)	0.06236096		
ubb	0.05216949					
ubb^2	0.00272166					

Annex 2: Results of feasibility study

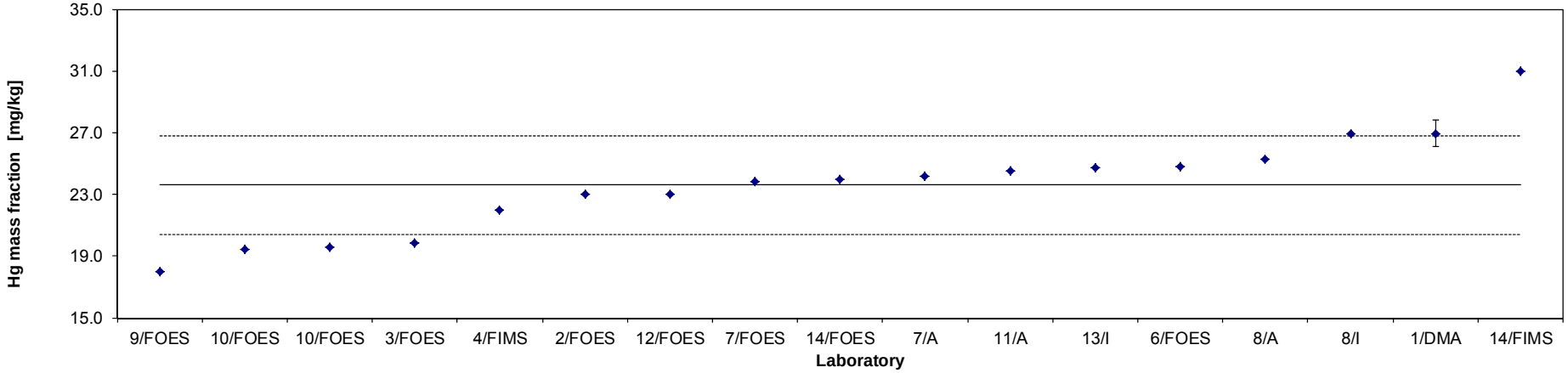
(FOES: spark emission spectrometry, KAAS: cold vapour atomic absorption spectrometry (AAS); FIMS: Flow injection AAS; DMA: direct mercury analyser)

Lab./Meth.	9/FOES	12/FOES	13/I	7/A	10/FOES	6/FOES	14/FOES	7/FOES	4/FIMS	10/FOES	11/A	2/FOES	8/FOES	6/I	3/I	1/DMA	14/FIMS		Ges.
M_i [mg/kg]		6.4	8.2		5.0					6.7	10.7				14.6	12.6			N
		6.7	4.4		8.0					11.2	10.7				11.6	11.5			17
		6.3	7.6		7.0					10.7	10.5				10.9	12.3			
		6.5			9.0					10.6					10.9	11.4			
		6.6			9.0					9.4						13.4			
		6.5														11.5			
		6.4																	
***M* [mg/kg]**	**2.8**	**6.5**	**6.7**	**7.6**	**7.6**	**7.9**	**8.0**	**9.0**	**9.0**	**9.7**	**10.6**	**11.0**	**11.2**	**11.4**	**12.0**	**12.1**	**13.3**		**9.2**
s [mg/kg]																0.799		s_M [mg/kg]	2.626
s_{rel}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.066		$s_{M,rel}$ [%]	0.285



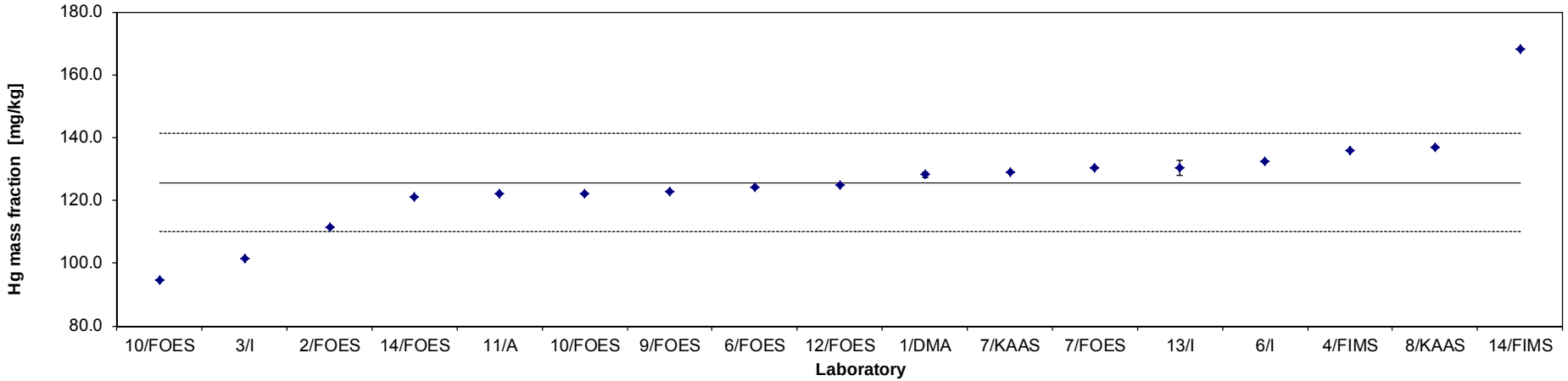
Sample Hg1

Lab./Meth.	9/FOES	10/FOES	10/FOES	3/FOES	4/FIMS	2/FOES	12/FOES	7/FOES	14/FOES	7/A	11/A	13/I	6/FOES	8/A	8/I	1/DMA	14/FIMS		Ges.
M_i [mg/kg]		21.2	18.0	19.8			23.00				24.8	29.90				27.2			N
		20.3	20.0	19.7			23.60				24.8	25.30				26.8			17
		19.4	21.0	20.2			22.80				24.0	19.00				25.6			
		19.7	19.0	19.8			22.70									28.3			
		16.5	20.0				23.30									27.0			
							22.60									26.8			
							23.10												
M [mg/kg]	**18.0**	**19.4**	**19.6**	**19.9**	**22.0**	**23.0**	**23.0**	**23.8**	**24.0**	**24.2**	**24.5**	**24.7**	**24.8**	**25.3**	**26.9**	**27.0**	**31.0**		**23.6**
s [mg/kg]																0.867		s_M [mg/kg]	3.220
s_{rel}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.032		$s_{M, rel}$ [%]	0.136



Sample Hg2

Lab./Meth.	10/FOES	3/I	2/FOES	14/FOES	11/A	10/FOES	9/FOES	6/FOES	12/FOES	1/DMA	7/KAAS	7/FOES	13/I	6/I	4/FIMS	8/KAAS	14/FIMS		Ges.
M_i [mg/kg]	93.60	103.2			120.0	121.0			125.70	129.1			132.10						N
	94.00	105.6			126.0	124.0			128.00	126.8			131.20						17
	93.60	97.2			120.0	120.0			123.40	127.7			127.50						
	95.20	99.8				124.0			127.20	128.6									
	96.70					121.0			125.00	128.4									
									123.90	128.7									
									121.90										
M [mg/kg]	**94.6**	**101.5**	**111.6**	**121.0**	**122.0**	**122.0**	**122.7**	**124.0**	**125.0**	**128.2**	**129.0**	**130.2**	**130.3**	**132.5**	**136.0**	**137.0**	**168.0**		**125.6**
s [mg/kg]										0.833			2.438					s_M [mg/kg]	15.697
s_{rel}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.019	0.000	0.000	0.000	0.000	$s_{M, rel}$ [%]	0.125



Sample Hg3