Certification Report

Certified Reference Materials

ERM®-EB104
ERM®-EB105
ERM®-EB106

Lead Alloy

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Summary

This report describes preparation, analysis and certification of three lead alloy reference materials ERM®-EB104, ERM®-EB105 and ERM®-EB106.
The certified reference materials are available in the form of discs (40 mm diameter and 40 mm height). They are 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.

The following mass fractions and uncertainties have been certified:

ERM®-EB104:

Element	Mass fraction in %	Uncertainty in %
Ca	0.0530	0.0018
Sn	1.27	0.07

ERM®-EB105:

Element	Mass fraction in %	Uncertainty in %
Ca	0.0595	0.0016
Sn	1.43	0.07
	in mg/kg	in mg/kg
Ag	32.1	0.9
Bi	133	5

ERM®-EB106:

Element	Mass fraction in %	Uncertainty in %
Ca	0.0782	0.0026
Sn	1.72	0.05

This report contains detailed information on the preparation of the CRMs as well as on homogeneity investigations and on the analytical methods used for certification analysis.
The certified values are based on the results of 13 laboratories which participated in the certification interlaboratory comparison.

Content

List of abbreviations
(if not explained elsewhere)

CRM	certified reference material
ERM	European reference material
FAAS	flame atomic absorption spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
SOES	spark optical emission spectrometry
M	arithmetic mean of means
n	number of accepted data sets
NAA	neutron activation analysis
s	standard deviation of an individual data set
s_M	standard deviation of the mean of means
s_{rel}	relative standard deviation
$\bar{s}$	mean standard deviation
EW	single result
I	ICP-OES (Tables 7 – 14)
I(R)	ICP-OES, revised value (Tables 7 – 14)
A	FAAS (Tables 7 – 14)
A(R)	FAAS, revised value (Tables 7 – 14)

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 series of the three certified reference materials ERM®-EB104, ERM®-EB105 and ERM®-EB106 are based on a PbCa alloy which is often used for the production of lead fences installed in accumulators.

The idea to produce a series of reference materials with graded mass fractions of calcium and tin is the outcome of an inquiry of a customer and of the discussions within the German Gesellschaft für Bergbau, Metallurgie, Rohstoff- und Umwelttechnik (GDMB), especially the working group „lead“ of the committee of chemists within GDMB. From this working group the needs are defined, since the members are potential users of the prepared CRMs. Secondly from this group the participating laboratories are recruited. Since all of these laboratories are highly experienced with lead alloy analysis and participated in earlier intralaboratory comparisons, there was no preceding round robin test for qualification.

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].

Starting material for the preparation of all three CRMs was a PbSnCa alloy (material number 975701) of Johnson Control Recycling GmbH, Buchholz, Germany.

2. Companies/laboratories involved

<u>Preparation of the material:</u>

– SUS Nell, Oberhausen, Germany

<u>Test for homogeneity:</u>

– SUS Nell, Oberhausen, Germany
– BAM Bundesanstalt für Materialforschung und -prüfung, Working Group “Inorganic Process Analytical Technology – X-ray Fluorescence Analysis“

<u>Participants in the certification interlaboratory comparison:</u>

– Aurubis AG, Hamburg, Germany
– BAM Bundesanstalt für Materialforschung und -prüfung, Working Group “Metal Analysis; Inorganic Reference Materials“, Berlin, Germany
– BERZELIUS Stolberg GmbH, Stolberg, Germany
– BSB Recycling GmbH, Braubach, Germany
– Exide Technologies GmbH, Büdingen, Germany
– GfE Fremat GmbH, Freiberg, Germany
– Johnson Controls Sachsen-Batterien GmbH & Co. KG, Zwickau, Germany
– Johnson Controls Power Solutions Mexico, García, Mexico
– Johnson Controls, VB Autobatterie GmbH & Co. KGaA, Hannover, Germany
– Muldenhütten Recycling und Umwelttechnik GmbH, Freiberg, Germany

– TU Bergakademie Freiberg, Freiberg, Germany
– ThyssenKrupp Steel Europe AG, Duisburg, Germany
– WESER-METALL GmbH, Nordenham, Germany

Statistical evaluation of the data
– BAM Bundesanstalt für Materialforschung und -prüfung, Berlin

3. Candidate material

A commercially available lead alloy was used as basic material for the preparation of the three candidate materials. 1180 kg of this lead alloy was delivered by Johnson Controls Recycling GmbH, Buchholz. This material was grinded, melted and doped with tin and calcium by SUS Nell, Oberhausen to obtain three different reference materials with graduated contents of these two elements. Aim mass fractions were:

1) 1.2 % Sn and 0.055 % Ca (ERM®-EB104)
2) 1.5 % Sn and 0.065 % Ca (ERM®-EB105)
3) 1.7 % Sn and 0.075 % Ca (ERM®-EB106)

From all of the three casts disc samples (about 450 per cast) with a diameter of ca. 40 mm and 40 - 45 mm height were casted. Each disc was marked individually (H: „hoch“, i.e. 106; M: „mittel“, 105; T: „tief“, 104; disc E25 is the 25th disc from the 5th sub-batch).

4. Homogeneity testing

A homogeneity test over all three reference materials (each comprising 10 sub-batches) was performed by SUS Nell, Oberhausen to check for homogeneity within the total of all 10 sub-batches, respectively. SOES was used for this homogeneity test, each disc was analysed five times. After measuring all five samples from one sub-batch (A, B, C, …) a drift control sample was analysed. Table 1 shows the discs used for homogeneity testing of ERM®-EB104, Table 2 shows those for ERM®-EB105 and Table 3 those for ERM®-EB106.
As a measure for the inhomogeneity of each CRM the standard deviation ($\boldsymbol{s}_{\text{radial}}$) of all mean values (47-50 samples, 5 sparks per sample) after drift compensation was used. The influence of the analytical method was neglected (see below).

Tab. 1: Discs analysed for homogeneity testing of ERM®-EB104

A1	B1	C1	D1	E1	F1	G1	H1	I1	J1
A9	B9	C9	D9	E9	F9	G9	H9	I9	J9
A27	B27	C27	D27	E27	F27	G27	H27	I27	J27
A36	B36	C36	D36	E36	F36	G36	H36	I36	J36
A48	B43	C45	D45	E45	F45	G43	H45	I45	J45

Tab. 2: Discs analysed for homogeneity testing of ERM®-EB105

A1	B1	C1	D1	E1	F1	G1	H1	I1	J1
A14	B14	C14	D9	E9	F9	G9	H9	I9	J9
A28	B28	C28	D27	E27	F27	G27	H27	I27	J27
A42	B42	C42	D36	E36	F36	G36	H36	I36	J36
			D41	E43	F43	G44	H44	I43	J43

Tab. 3: Discs analysed for homogeneity testing of ERM®-EB106

A1	B1	C1	D1	E1	F1	G1	H1	I1	J1
A9	B9	C9	D9	E9	F9	G9	H9	I9	J9
A27	B27	C278	D27	E27	F27	G27	H27	I27	J27
A36	B36	C36	D36	E36	F36	G36	H36	I36	J36
A45	B45	C43	D45	E46	F45	G45	H46	I45	J47

The samples listed in Table 4 were tested for homogeneity over the area (possible segregation from the outer part to the centre) and over the height of each cylinder (possible segregation from the top to the bottom). This investigation was carried out at BAM. To perform this test five cylinders from each type (104, 105, 106) were cut in the middle. SOES analysis was then carried out on top, on the bottom and on the middle area of each cylinder (outer circle: 15 sparks, inner circle: 10 sparks; centre: 3 sparks).

Tab. 4: Discs analysed for homogeneity testing: area and height

ERM®-EB104	**ERM®-EB105**	**ERM®-EB106**
A10	B34	D41
B41	D37	E9
D30	F34	G33
F13	H9	H3
I29	J33	J42

As a measure for the inhomogeneity of the samples (area and height) the standard deviation (s_{axial}) of all mean values (five samples, three rings, three areas: in total 45 values) was used. Both standard deviations (s_{axial} and s_{radial}) are the sum of spread deriving from inhomogeneities and spread deriving from the analytical method. In principle s_{eff} as defined in Equation (1) contributes to the total uncertainty. Therefore one has to determine the spread of the analytical method (s_{method}) by measuring an ideally homogenous sample.

$$s_{\text{eff, axial}} = \sqrt{s_{\text{axial}}^2 - s_{\text{method}}^2} \tag{1a}$$

$$s_{\text{eff, radial}} = \sqrt{s_{\text{radial}}^2 - s_{\text{method}}^2} \tag{1b}$$

Since such a sample was not available, the influence of the analytical method on the standard deviation was neglected ($\boldsymbol{s}_{\text{method}}$ = 0), i.e. the value which was used for the calculation of the total uncertainty was the „worst case“, i.e. all spread resulted from inhomogeneity of the sample.

5. Characterisation study

5.1 Analytical methods

13 laboratories participated in the certification interlaboratory comparison. Each laboratory received three randomly chosen discs (half a disc of each CRM).

Tab. 4: Discs sent out for certification analysis

ERM®-EB104	**ERM®-EB105**	**ERM®-EB106**
B11	A7	D43
C33	B16	E8
E29	C9	G45
E44	D19	I32
G6	E22	I35
H37	G10	I38
J4	I40	J36

The laboratories were told to analyse six subsamples. They were free to choose any suitable analytical method for analysis. Table 5 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 5: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment	Analytical method
1	Ca, Ag, Bi	1 g	Dissolution with HNO_3/HF	FAAS with matrix matched standards, calibration with commercial solutions (Merck)
	Sn	0.1 g	Dissolution with HNO_3	FAAS with matrix matched standards and $La(NO_3)_3$, calibration with commercial solutions (Merck)
2	Sn, Ca, Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with matrix matched standards, calibration with commercial solutions (Spex)
3	Sn, Ca, Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with pure metals
4	Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with commercial solutions (Merck, Kraft)
5	Sn, Ca, Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES with matrix matched standards, calibration with commercial solutions (Kraft (Sn, Ca) resp. pure metals (Bi, Ag))
7	Ca, Sn	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with pure chemicals
	Bi, Ag	2.5 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with pure chemicals
8	Sn, Bi	0.8 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with commercial solutions (Merck)
	Ag, Ca	0.8 g	Dissolution with tartaric acid/HNO_3	FAAS, calibration with commercial solutions (Merck)
9	Ca, Sn, Al, Bi, Ag, Cu	1 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with commercial solutions
10	Ag	2 g	Dissolution with tartaric acid/HNO_3	FAAS, calibration with pure metals
10-2	Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with pure metals
10-2	Sn, Ca, Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3 (acc. prEN 13800)	ICP-OES, calibration with pure metals
12	Ag, Bi	2 g	Dissolution with tartaric acid/HNO_3	FAAS, calibration with commercial solutions
	Sn, Ca	2 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with commercial solutions
13	Sn, Ca, Ag, Bi	0,5 g	Dissolution with HNO_3, fusion of residue with Na-tetraborate	ICP-OES with matrix matched standards, calibration with pure metals (Ag, Bi, Sn) resp. pure chemicals (Ca)
15				
16	Sn, Ca, Ag, Bi	0.5 g	Dissolution with tartaric acid/HNO_3	ICP-OES, calibration with commercial solutions

5.2 Analytical results and statistical evaluation

The analytical results of the certification interlaboratory comparison are listed in Tables 7 to 14. These tables show the single results (EW) of each laboratory, the resp. laboratories' mean values (MW) together with the intralaboratory standard deviation (s) and in addition the mean standard deviation ($\overline{s}$) of all laboratories. The continuous line 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.

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

Sn in ERM-EB104:

Number of data sets	10
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	Laboratory 2
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 2) was not removed.

Ca in ERM-EB104:

Number of data sets	11
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	Laboratory 8
Nalimov (a = 0.01)	Laboratory 8
Grubbs (a = 0.05)	Laboratory 8
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: not normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 8) was removed.

Ca in ERM-EB104 (after removal of Lab. 8):

Number of data sets	10
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	Laboratory 16
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 16) was not removed.

Sn in ERM-EB105:

Number of data sets	11
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	---
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

Ca in ERM-EB105:

Number of data sets	11
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	Laboratory 8
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 8) was not removed.

Bi in ERM-EB105:

Number of data sets	14
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	Laboratory 16
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 16) was not removed.

Ag in ERM-EB105:

Number of data sets	15
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	Laboratory 16
Dixon (a = 0.01)	Laboratory 16
Nalimov (a = 0.05)	Laboratory 16
Nalimov (a = 0.01)	Laboratory 16
Grubbs (a = 0.05)	Laboratory 16
Grubbs (a = 0.01)	Laboratory 16
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 16) was removed.

Ag in ERM-EB105 (after removal of Lab. 16):

Number of data sets	14
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	---
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

Sn in ERM-EB106:

Number of data sets	11
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	Laboratory 10-2
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 0.01)	Distribution: normal

The outlying value (Lab. 10-2) was not removed.

Ca in ERM-EB106:

Number of data sets	11
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (a = 0.05)	---
Dixon (a = 0.01)	---
Nalimov (a = 0.05)	---
Nalimov (a = 0.01)	---
Grubbs (a = 0.05)	---
Grubbs (a = 0.01)	---
Grubbs Pair (a = 0.05)	---
Grubbs Pair (a = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (a = 0.05)	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (a = 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 6.
The resp. combined uncertainties were calculated from the spread resulting from the certification interlaboratory comparison (***s***$_{ilc}$) and the uncertainty contributions from possible inhomogeneity of the material using Equation 2.

$$u_{\mathrm{combined}} = \sqrt{\frac{s_{\mathrm{ilc}}^2}{n} + s_{radial}^2 + s_{axial}^2} \quad (2)$$

with

$\frac{s_{\mathrm{ilc}}^2}{n}$: spread resulting from interlaboratory comparison

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

Table 6: Uncertainty calculation

	M	***n***	***s***$_{\mathrm{ilc}}$	***s***$_{\mathrm{radial}}$	***s***$_{\mathrm{axial}}$
ERM-EB104					
tin	1.28 %	12	0.022 %	0.032 %	0.0097 %
calcium	0.053 %	10	0.0014%	0.00053 %	0.00006 %
ERM-EB105					
tin	1.43 %	11	0.022 %	0.032 %	0.0097 %
calcium	0.0595 %	11	0.0014%	0.00053 %	0.00006 %
silver	32.1 mg/kg	14	1.18 mg/kg	0.23 mg/kg	0.21 mg/kg
bismuth	133.5 mg/kg	14	6.25 mg/kg	1.16 mg/kg	0.59 mg/kg
ERM-EB106					
tin	1.72 %	11	0.022 %	0.019 %	0.014 %
calcium	0.078 %	11	0.0014%	0.00052 %	0.0011 %

The expanded uncertainties ***U*** are calculated by multiplication of ***u***$_{\mathrm{combined}}$ with a coverage factor of ***k*** = 2 using Equation 3.

$$U = 2 \cdot u_{\mathrm{combined}} \quad (3)$$

The following mass fractions and their resp. expanded uncertainties were certified:

ERM®-EB104:

Element	**Mass fraction** in %	**Uncertainty** in %
Ca	0.0530	0.0018
Sn	1.27	0.07

ERM®-EB105:

Element	**Mass fraction** in %	**Uncertainty** in %
Ca	0.0595	0.0016
Sn	1.43	0.07
	in mg/kg	in mg/kg
Ag	32.1	0.9
Bi	133	5

ERM®-EB106:

Element	**Mass fraction** in %	**Uncertainty** in %
Ca	0.0782	0.0026
Sn	1.72	0.05

Lab./Meth.	2/I	8/I	16/I(R)	12/I	13/I(R)	7/I	5/I	10-2/I	3/I	1/A		Ges.
EW [%]	1.2470	1.257	1.2645	1.270	1.285	1.2812	1.280	1.290	1.280	1.287		N
	1.2800	1.262	1.2633	1.270	1.267	1.2912	1.290	1.291	1.280	1.281		10
	1.2340	1.260	1.2691	1.272	1.278	1.2675	1.280	1.278	1.280	1.288		
	1.2500	1.259	1.2694	1.274	1.276	1.2744	1.285	1.278	1.290	1.297		
	1.2610	1.257		1.274	1.279	1.2813	1.290	1.280	1.290	1.286		
	1.2460	1.255		1.286	1.268	1.2693	1.27		1.280	1.282		
M [%]	**1.2530**	**1.2583**	**1.2666**	**1.2743**	**1.2755**	**1.2775**	**1.2825**	**1.2833**	**1.2833**	**1.2868**		**1.2741**
s[%]	0.0158	0.0025	0.0031	0.0060	0.0069	0.0089	0.0076	0.0064	0.0052	0.0057		0.0114
$\bar{s}$ [%]												0.007
s_{rel}	0.01261	0.00199	0.00247	0.00470	0.00540	0.00695	0.00591	0.00501	0.00402	0.00443		0.00894
	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3		
	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3		
	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3		

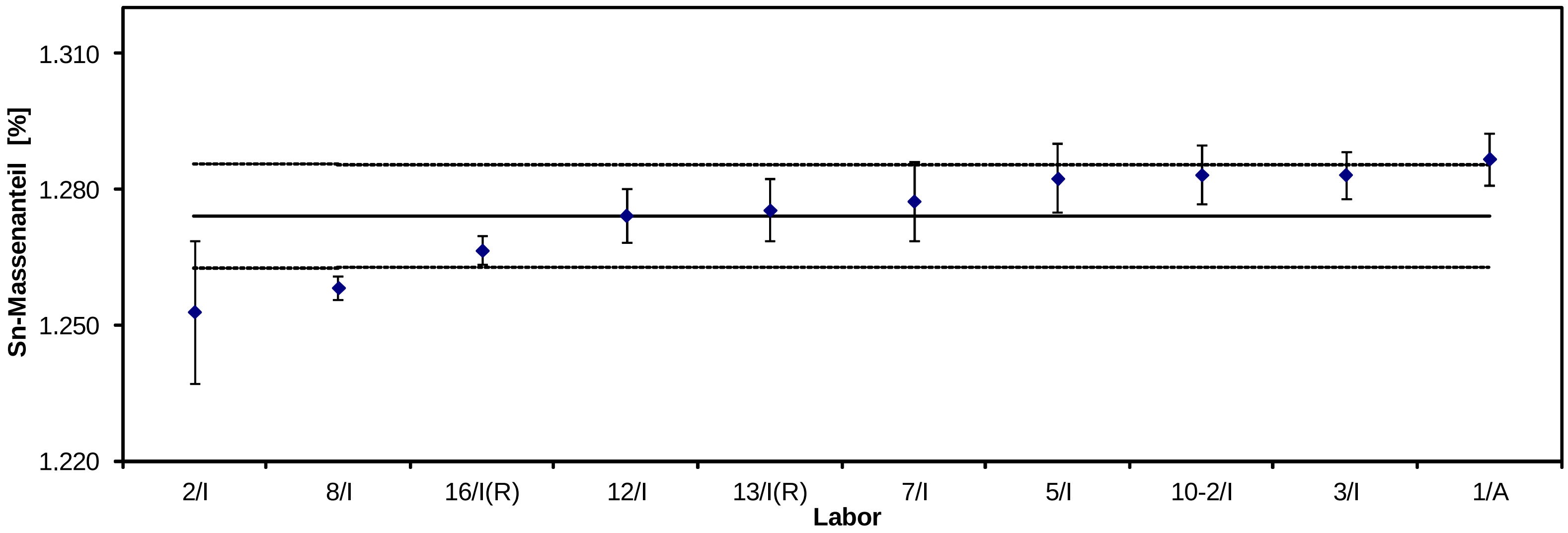

Table 7: Results for Sn in ERM-EB104

Lab./Meth.	1/A	9/I	3/I	7/I	5/I	13/I	2/I	12/I	10-2/I	16/I	8/A(R)		Ges.
EW [%]	0.0512	0.0507	0.0516	0.0521	0.0539	0.0531	0.0529	0.0521	0.0567	0.0563	0.0550		N
	0.0510	0.0509	0.0515	0.0532	0.0524	0.0531	0.0523	0.0531	0.0547	0.0536	0.0560		11
	0.0512	0.0522	0.0521	0.0530	0.0537	0.0532	0.0531	0.0534	0.0533	0.0572	0.0560		
	0.0511	0.0525	0.0524	0.0523	0.0520	0.0526	0.0531	0.0534	0.0540	0.0536	0.0590		
	0.0510	0.0528	0.0528	0.0529	0.0516	0.0534	0.0538	0.0535	0.0539		0.0630		
	0.0513	0.0527	0.0528	0.0530	0.0535	0.0525	0.0533	0.0536	0.0538		0.0590		
M [%]	**0.0511**	**0.0520**	**0.0522**	**0.0528**	**0.0529**	**0.0530**	**0.0531**	**0.0532**	**0.0544**	**0.0552**	**0.0580**		**0.0530**
s[%]	0.00012	0.00093	0.00057	0.00045	0.00097	0.00035	0.00049	0.00056	0.00121	0.00186	0.00297		0.00115
$\bar{s}$ [%]													0.00075
s_{rel}	0.00237	0.01787	0.01090	0.00844	0.01841	0.00669	0.00926	0.01046	0.02230	0.03363	0.05115		0.02180
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		

Grubbs 95 %

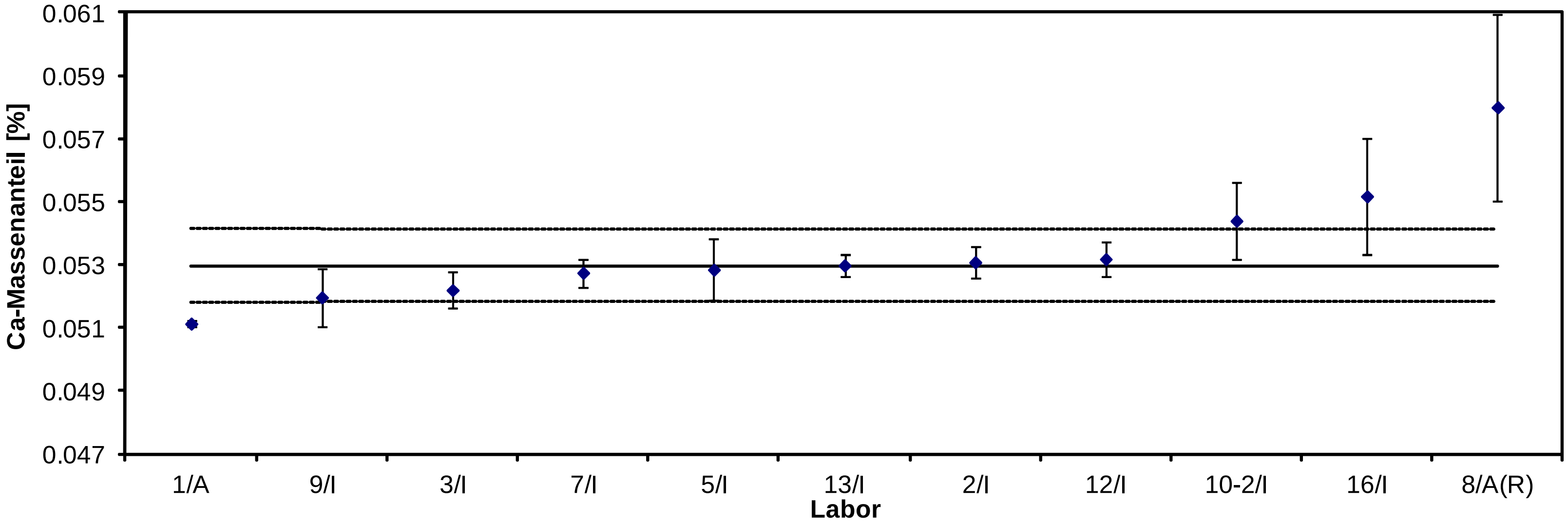

Table 8: Results for Ca in ERM-EB104

Lab./Meth.	2/I	8/I	7/I	13/I(R)	10-2/I	5/I	3/I	12/I	16/I(R)	1/A	10/I		Ges.
EW [%]	1.4010	1.385	1.4151	1.453	1.419	1.430	1.420	1.437	1.4600	1.461	1.466		N
	1.3910	1.402	1.4269	1.411	1.428	1.420	1.440	1.442	1.4498	1.458	1.473		11
	1.3770	1.397	1.4145	1.417	1.421	1.430	1.420	1.448	1.4472	1.465	1.489		
	1.3930	1.395	1.4110	1.418	1.455	1.435	1.450	1.453	1.4660	1.461	1.471		
	1.3760	1.414	1.4116	1.430	1.424	1.435	1.430	1.458		1.459	1.490		
	1.3871	1.410	1.4056	1.421	1.420	1.440	1.430	1.464		1.467	1.473		
M [%]	**1.3875**	**1.4005**	**1.4141**	**1.4250**	**1.4277**	**1.4317**	**1.4317**	**1.4503**	**1.4558**	**1.4618**	**1.4770**		**1.4330**
s[%]	0.0097	0.0106	0.0071	0.0151	0.0135	0.0068	0.0117	0.0101	0.0088	0.0035	0.0100		0.0268
$\bar{s}$ [%]													0.010
s_{rel}	0.00697	0.00754	0.00504	0.01057	0.00945	0.00477	0.00817	0.00693	0.00604	0.00239	0.00678		0.01868
	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4		
	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4		
	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5		

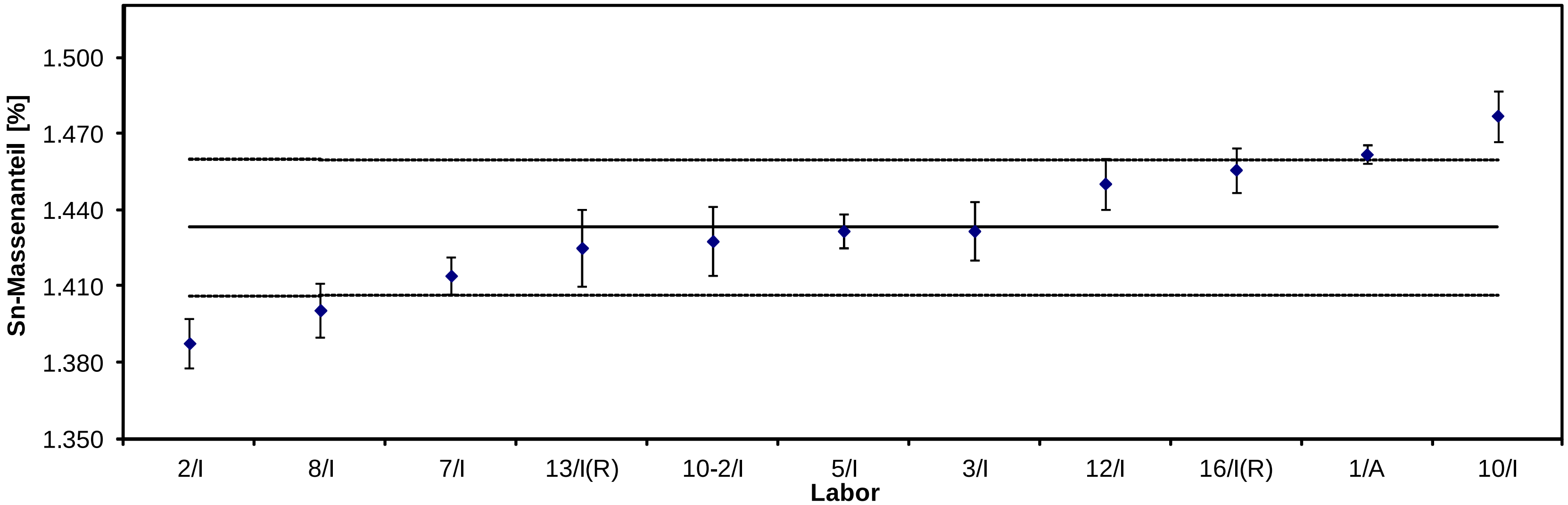

Table 9: Results for Sn in ERM-EB105

Lab./Meth.	9/I	8/A(R)	16/I(R)	1/A	5/I	13/I	7/I	12/I	2/I	10-2/I	3/I		Ges.
EW [%]	0.0591	0.06	0.0588	0.0592	0.0598	0.0603	0.0598	0.0599	0.0599	0.0602	0.0611		N
	0.0579	0.061	0.0581	0.0588	0.0585	0.0598	0.0592	0.0600	0.0593	0.0607	0.0624		11
	0.0566	0.059	0.0593	0.0593	0.0584	0.0600	0.0592	0.0600	0.0607	0.0608	0.0604		
	0.057	0.054	0.0586	0.0592	0.0603	0.0587	0.0594	0.0603	0.0605	0.0601	0.0613		
	0.0573	0.057		0.0593	0.0604	0.0587	0.0594	0.0607	0.0609	0.0606	0.0599		
	0.0583	0.056		0.0596	0.0588	0.0588	0.0598	0.0611	0.0612	0.0609	0.0616		
M [%]	**0.0577**	**0.0578**	**0.0587**	**0.0592**	**0.0594**	**0.0594**	**0.0595**	**0.0603**	**0.0604**	**0.0606**	**0.0611**		**0.0595**
s[%]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.0011
$\bar{s}$ [%]													0.001
s_{rel}	0.01592	0.04564	0.00846	0.00436	0.01532	0.01230	0.00468	0.00789	0.01158	0.00540	0.01447		0.01842
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		

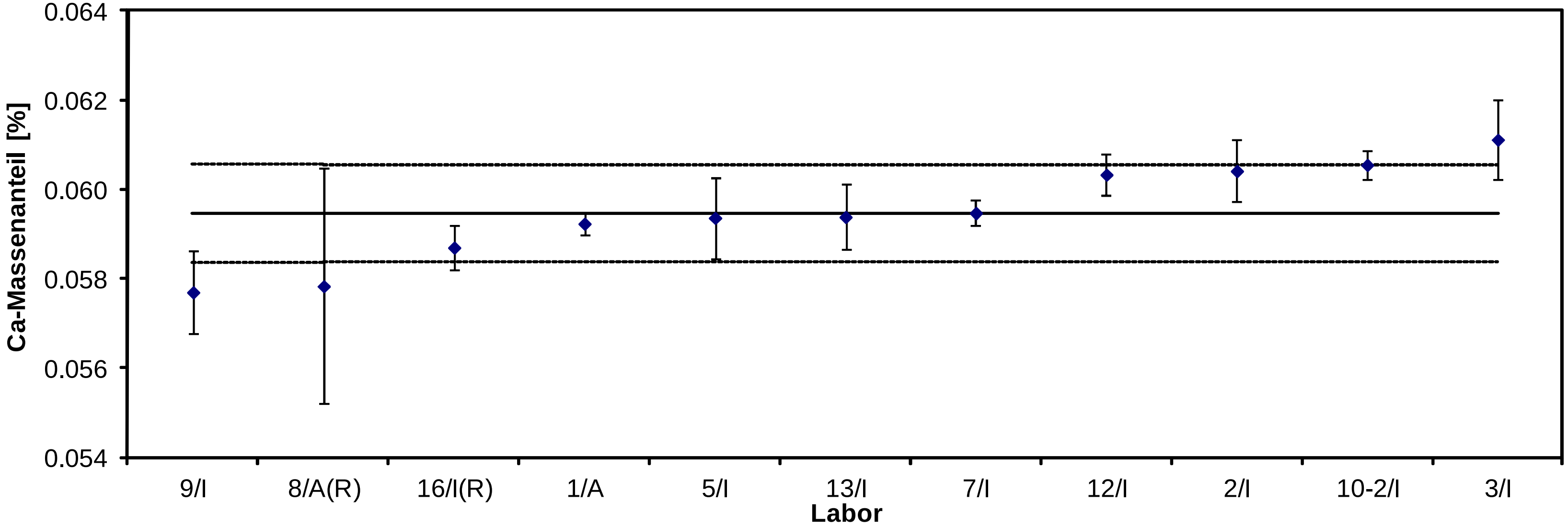

Table 10: Results for Ca in ERM-EB105

Lab./Meth.	12/A	4/I	1/A	15/I	5/I	8/A	10-2/I	3/I	10/I-1	2/I	9/I	13/I	10/A	7/I	16/I		Ges.
EW [µg/g]	29.7	30.0	31.2	31.3	32.2	32	32.1	32.4	32.47	32.90	33	33	32.64	34.5	39.50		N
	29.9	30.0	30.8	31.9	31.5	32	32.2	32.5	32.55	32.30	33	33	32.98	34.2	38.70		15
	30.0	30.0	31.3	30.7	31.3	32	32.3	32.4	32.65	33.10	33	33	33.42	34.8	38.90		
	30.2	30.0	31.1	31.4	32.3	32	32.3	32.8	32.58	32.60	33	33	32.96	34.4	38.40		
	29.7	30.0	31.3	31.0	32.1	32	32.3	31.8	32.40	32.80	33	33	33.51	33.0			
	30.3	30.0	30.8	31.7	32.0	32	32.1	32.9	32.70	32.90	33	33	34.18	32.7			
M [µg/g]	**29.96**	**30.00**	**31.08**	**31.33**	**31.90**	**32.00**	**32.19**	**32.47**	**32.56**	**32.77**	**33.00**	**33.00**	**33.28**	**33.93**	**38.88**		**32.10**
s[µg/g]	0.256	0.000	0.232	0.441	0.405	0.000	0.100	0.388	0.111	0.280	0.000	0.000	0.545	0.866	0.465		1.172
$\bar{s}$ [µg/g]																	0.259
s_{rel}	0.009	0.000	0.007	0.014	0.013	0.000	0.003	0.012	0.003	0.009	0.000	0.000	0.016	0.026	0.012		0.037
	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1		
	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9	30.9		
	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3		
															Grubbs 99%		

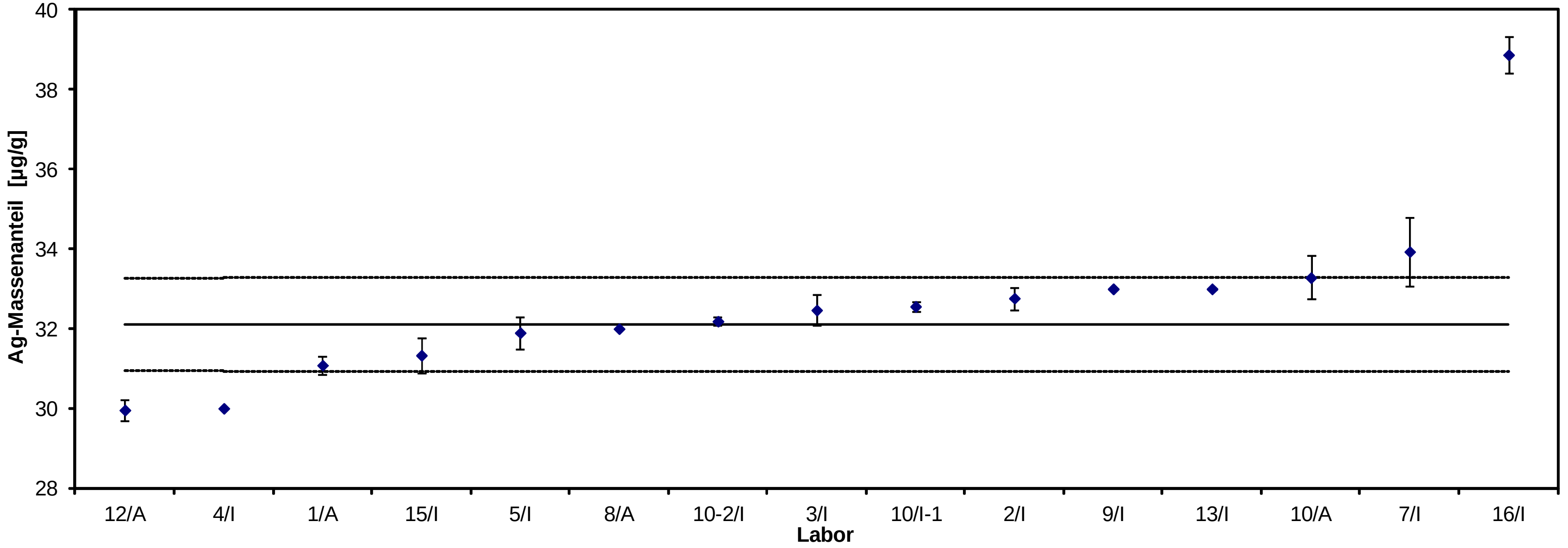

Table 11: Results for Ag in ERM-EB105

Lab./Meth.	8/I	2/I	12/A	4/I	10/I	15/I	1/A	3/I	9/I	13/I	10-2/I	5/I	7/I	16/I		Ges.
EW [µg/g]	122.0	123.0	126.5	130.0	132.1	132.0	133.3	133	136.0	137.0	137.3	139.6	139.40	147.2		N
	124.0	121.0	126.6	130.0	131.1	133.0	133.2	135	135.0	137.0	138.7	136.5	139.30	143.0		14
	122.0	124.0	128.0	130.0	131.3	133.0	133.8	133	136.0	136.0	137.9	135.3	141.70	147.0		
	122.0	[154]	129.0	130.0	129.5	134.0	133.6	132	135.0	137.0	139.4	140.0	141.30	147.0		
	122.0	122.0	129.0	130.0	131.1	134.0	133.5	135	134.0	136.0	137.6	139.0	135.90			
	126.0	126.0	130.0	130.0	130.4	133.0	133.2	135	135.0	136.0	137.9	139.0	136.30			
M [µg/g]	**123.00**	**123.20**	**128.18**	**130.00**	**130.88**	**133.17**	**133.43**	**133.83**	**135.17**	**136.50**	**138.13**	**138.23**	**138.98**	**146.05**		**133.48**
s[µg/g]	1.673	1.924	1.415	0.000	0.882	0.753	0.242	1.329	0.753	0.548	0.776	1.885	2.438	2.036		6.246
$\bar{s}$ [µg/g]																1.190
s_{rel}	0.014	0.016	0.011	0.000	0.007	0.006	0.002	0.010	0.006	0.004	0.006	0.014	0.018	0.014		0.047
	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5	133.5		
	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2	127.2		
	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7	139.7		

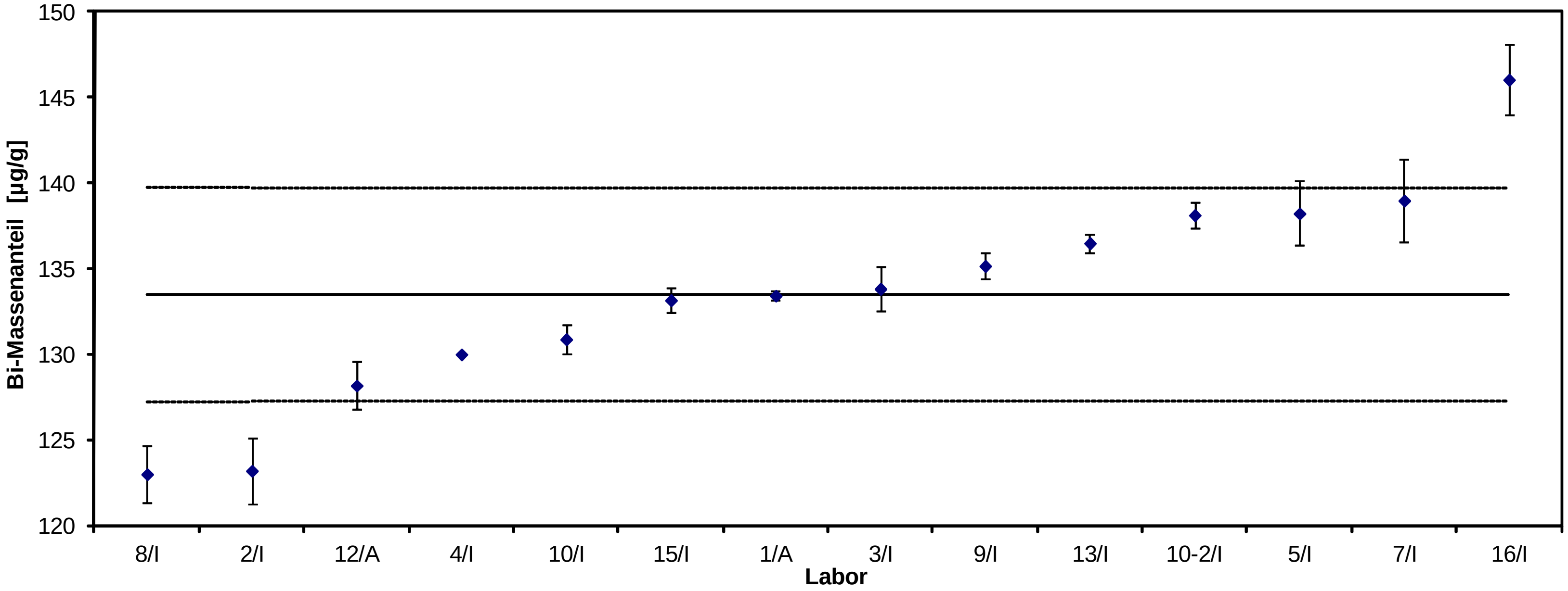

Table 12: Results for Bi in ERM-EB105

Lab./Meth.	7/I	10/I	2/I	13/I(R)	8/I	16/I(R)	5/I	3/I	12/I	1/A	10-2/I		Ges.
EW [%]	1.6903	1.693	1.7030	1.701	1.717	1.7237	1.735	1.730	1.730	1.745	1.813		N
	1.6829	1.698	1.7099	1.699	1.722	1.7232	1.720	1.740	1.746	1.751	1.794		11
	1.7001	1.673	1.7062	1.698	1.728	1.7357	1.740	1.720	1.748	1.752	1.779		
	1.6824	1.703	1.6987	1.722	1.700	1.7161	1.740	1.730	1.750	1.751	1.754		
	1.6932	1.707	1.6915	1.725	1.712		1.745	1.720	1.754	1.762	1.777		
	1.6659	1.703	1.6777	1.714	1.726		1.680	1.720	1.758	1.754	1.789		
M [%]	**1.6858**	**1.6960**	**1.6978**	**1.7098**	**1.7175**	**1.7247**	**1.7267**	**1.7267**	**1.7477**	**1.7525**	**1.7843**		**1.7245**
s[%]	0.0118	0.0123	0.0117	0.0121	0.0104	0.0081	0.0244	0.0082	0.0097	0.0055	0.0197		0.0286
$\bar{s}$ [%]													0.012
s_{rel}	0.00700	0.00725	0.00691	0.00707	0.00605	0.00471	0.01415	0.00473	0.00553	0.00316	0.01104		0.01660
	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7		
	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7		
	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8		

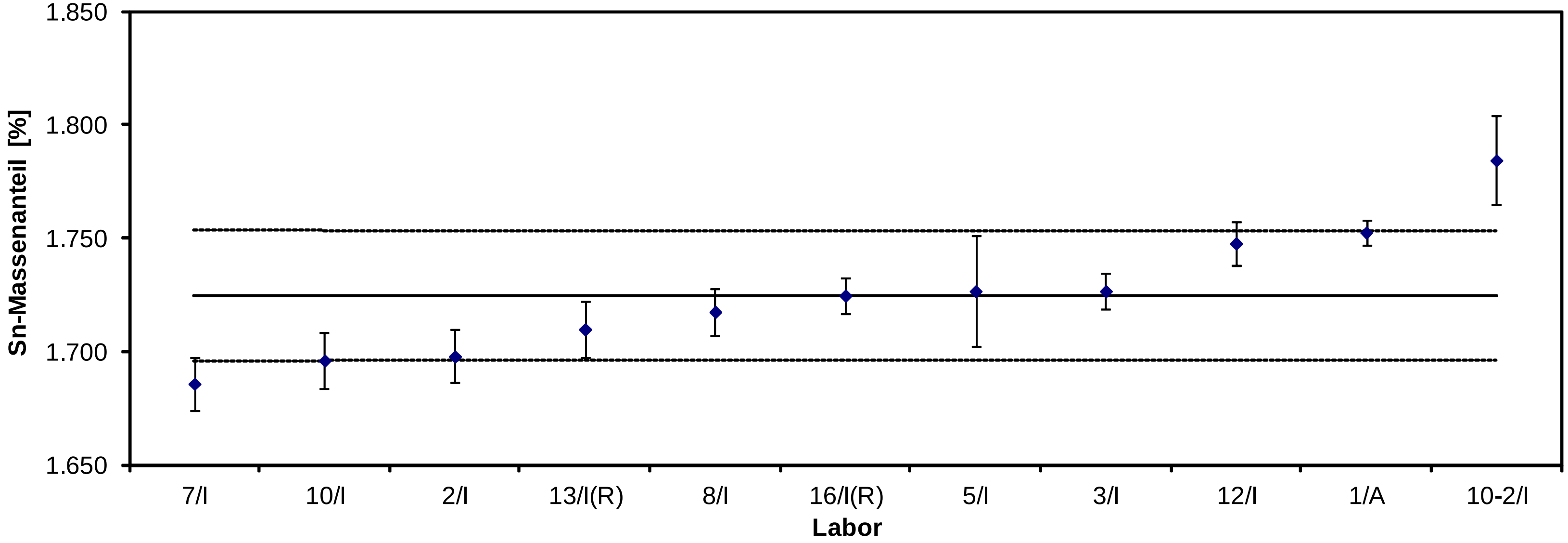

Table 13: Results for Sn in ERM-EB106

Lab./Meth.	16/I(R)	8/A	1/A	9/I	12/I	5/I	3/I	13/I	7/I	2/I	10-2/I		Ges.
EW [%]	0.0753	0.0720	0.0756	0.0797	0.0778	0.0763	0.0790	0.0791	0.0801	0.0795	0.0817		N
	0.0743	0.0710	0.0760	0.0775	0.0782	0.0784	0.0790	0.0786	0.0799	0.0804	0.0814		11
	0.075	0.0790	0.0755	0.0787	0.0785	0.0791	0.0800	0.0788	0.0799	0.0799	0.0807		
	0.0749	0.0750	0.0759	0.0745	0.0785	0.0798	0.0790	0.0803	0.0805	0.0803	0.0806		
		0.0800	0.0760	0.0740	0.0788	0.0789	0.0790	0.0803	0.0805	0.0800	0.0809		
		0.0740	0.0756	0.0760	0.0788	0.0793	0.0800	0.0800	0.0799	0.0824	0.0807		
M [%]	**0.0749**	**0.0752**	**0.0758**	**0.0767**	**0.0784**	**0.0786**	**0.0793**	**0.0795**	**0.0801**	**0.0804**	**0.0810**		**0.0782**
s[%]	0.00042	0.00366	0.00019	0.00229	0.00038	0.00123	0.00052	0.00077	0.00029	0.00102	0.00045		0.00219
$\bar{s}$ [%]													0.00102
s_{rel}	0.00560	0.04864	0.00253	0.02986	0.00488	0.01567	0.00651	0.00972	0.00363	0.01272	0.00552		0.02802
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		

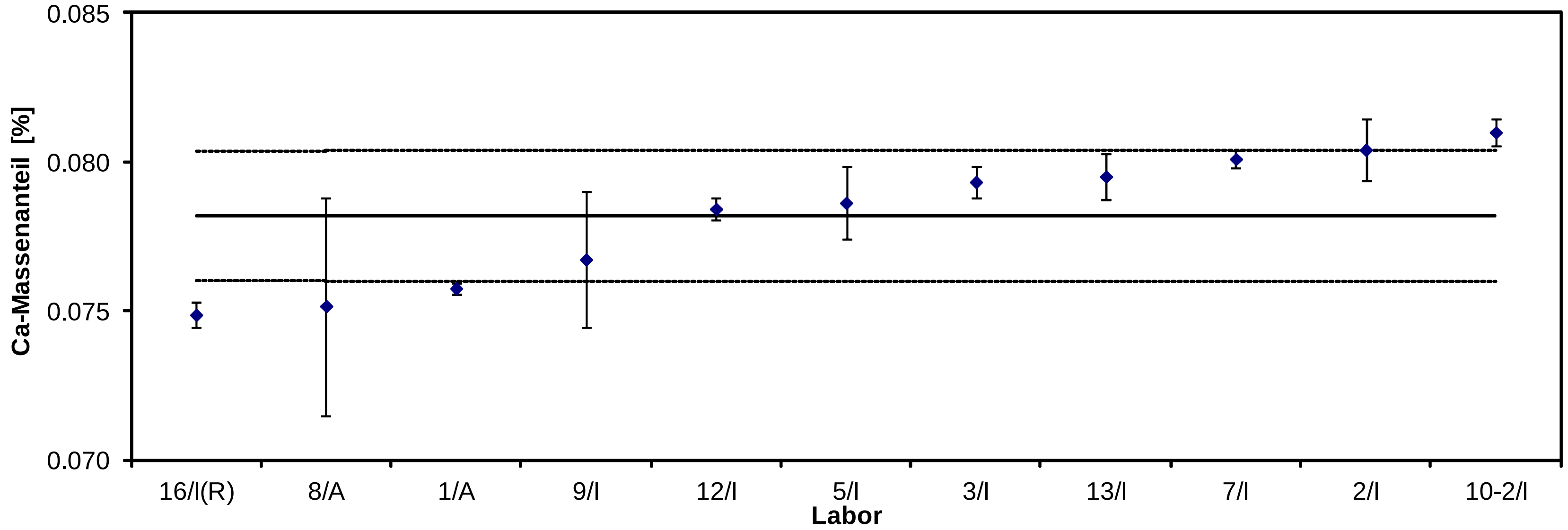

Table 14: Results for Ca in ERM-EB106

6. Instructions for users and stability

The certified reference materials ERM®-EB104, -105 and -106 are intended for the calibration and quality control of spark emission and X-ray fluorescence spectrometer used for the analysis of similar materials.
Before analysis the surface of the material should be cleaned by turning or milling.
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 (eg, 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-Straße 11, 12489 Berlin
Phone +49 (0)30 - 8104 2061 or 1119
Fax: +49 (0)30 - 8104 1117
E-Mail: sales.crm@bam.de

Each disc of ERM®-EB104, -105 and -106 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, Tel. +49 30 8104 1111.

Annex: Calculation of uncertainty

CRM "ERM-EB104" PbCaSn											
Result						Uncertainty					
			interlaboratory comparison (ILC)			axial		ILC + radial + axial			
Element	**M**	**Unit**	s_{ilc}	$100*(s_{ilc}/M)$	**n**	u_{axial}	u_{axial} rel. %	u_{total}	u_{total} rel. %	u_{radial}	$U_{expanded}$
Ca	0.0528	%	0.00139	**2.6**	10	0.00060	**1.1**	0.00092	**1.7**	0.00053	**0.0018**
Sn	1.2823	%	0.02157	**1.7**	12	0.00970	**0.8**	0.03345	**2.6**	0.03140	**0.0669**

CRM "ERM-EB105" PbCaSn											
Result						Uncertainty					
			interlaboratory comparison (ILC)			axial		RV + radial + axial			
Element	**M**	**Unit**	s_{ilc}	$100*(s_{ilc}/M)$	**n**	u_{axial}	u_{axial} rel. %	u_{total}	u_{total} rel. %	u_{radial}	$U_{expanded}$
Ca	0.0595	%	0.00110	**1.8**	11	0.00050	**0.8**	0.00080	**1.3**	0.00053	**0.0016**
Sn	1.4330	%	0.02680	**1.9**	11	0.01150	**0.8**	0.03440	**2.4**	0.03140	**0.0688**
Bi	133.5	mg/kg	6.24600	**4.7**	14	0.59000	**0.4**	2.11312	**1.6**	1.15350	**4.2262**
Ag	32.1	mg/kg	1.17200	**3.7**	14	0.21000	**0.7**	0.44120	**1.4**	0.22900	**0.8824**

CRM "ERM-EB106" PbCaSn											
Result						Uncertainty					
			interlaboratory comparison (ILC)			axial		RV + radial + axial			
Element	**M**	**Unit**	s_{ilc}	$100*(s_{ilc}/M)$	**n**	u_{axial}	u_{axial} rel. %	u_{total}	u_{total} rel. %	u_{radial}	$U_{expanded}$
Ca	0.0782	%	0.00139	**1.8**	11	0.00110	**1.4**	0.00129	**1.6**	0.00052	**0.0026**
Sn	1.7245	%	0.02157	**1.3**	11	0.01390	**0.8**	0.02404	**1.4**	0.01851	**0.0481**