BAM

Certification Report

Certified Reference Materials

ERM®-EB506
ERM®-EB507
ERM®-EB508

Gold Alloys

May 2014

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Summary

This report describes preparation, analysis and certification of the three gold alloy reference materials ERM®-EB506, ERM®-EB507 and ERM®-EB508.
The certified reference materials are available in the form of slices (15.8 mm diameter and 0.25 to 0.3 mm thickness). They are intended for establishing and checking the calibration of X-ray spectrometers (especially handheld instruments) for the analysis of samples of similar composition.

The following mass fractions and expanded uncertainties (k = 2.5) have been certified:

ERM®-EB506:

Element	Mass fraction in %	Uncertainty in %
Au	58.56	0.06
Ag	3.90	0.05
Cu	35.65	0.06
Zn	1.891	0.018

ERM®-EB507:

Element	Mass fraction in %	Uncertainty in %
Au	75.10	0.11
Ag	3.02	0.05
Cu	14.69	0.05
Ni	4.99	0.04
Zn	2.107	0.016

ERM®-EB508:

Element	Mass fraction in %	Uncertainty in %
Au	75.12	0.11
Ag	24.90	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 9 laboratories which participated in the certification interlaboratory comparison.

Content

List of abbreviations
(if not explained elsewhere)

CRM	certified reference material
ERM	European reference material
ICP-OES	inductively coupled plasma 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
$\bar{s}_i$	mean of standard deviations of data sets under repeatability conditions
M_i	single result
I	ICP-OES (Tables 11 – 22)
Dok	Fire assay (Tables 11 – 22)

1. Introduction

X-ray fluorescence spectrometry (XRF), especially with handheld instruments is often used for the characterisation of precious metal alloys used for the production of jewellery. The accuracy of these measurements depends on the existence of suitable reference materials. BAM was asked by one of the producers of handheld instruments to produce certified reference materials for common gold alloys. In a first step three gold based alloys were taken to produce slices of white gold, yellow gold and rose gold reference materials. Chemical characterisation of these materials was done in an interlaboratory comparison with laboratories organised in the “Precious Metals” working group within the committee of chemists of the German Gesellschaft der Metallurgen und Bergleute e.V. (GDMB).
Since all participating laboratories are highly experienced with precious metals analysis and participated in several interlaboratory comparisons organised within the working group, there was no preceding round robin test for qualification.

Certification of the reference materials 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:
- FEM Forschungsinstitut für Edelmetalle & Metallchemie, Schwäbisch Gmünd, Germany

Test for homogeneity:

- BAM Bundesanstalt für Materialforschung und -prüfung, Division 1.4 “Process Analysis“

Participants in the certification interlaboratory comparison:

- Allgemeine Gold- und Silberscheideanstalt AG, Pforzheim (Germany)
- AMI Doduco, Pforzheim (Germany)
- Forschungsinstitut Edelmetalle & Metallchemie, Schwäbisch Gmünd (Germany)
- Heimerle + Meule GmbH, Pforzheim (Germany)
- Heraeus Precious Metals, Hanau (Germany)
- Institut für Materialprüfung Glörfeld GmbH, Willich (Germany)
- SAXONIA Edelmetallrecycling GmbH, Halsbrücke (Germany)
- Wieland Edelmetalle GmbH, Pforzheim (Germany)
- Zentralamt für Edelmetallkontrolle, Bern (Switzerland)

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

3. Candidate material

FEM Forschungsinstitut für Edelmetalle & Metallchemie, Schwäbisch Gmünd, Germany produced ca. 270 slices with 15.75 mm diameter and 250 to 300 µm thickness from each of the three different gold alloys.

The following alloys were used:

1) 585 ‰ Rose Gold (ERM®-EB506),
   composition: Au 585.9 ‰, Ag 39.5 ‰, Cu 357.0 ‰, Zn 19.1 ‰
2) 750 ‰ White Gold (ERM®-EB507),
   composition: Au 751.8 ‰, Ag 30.7 ‰, Cu 147.5 ‰, Ni 49.5 ‰, Zn 20.9 ‰
3) 750 ‰ Yellow Gold (ERM®-EB508),
   composition: Au 751.6 ‰, Ag 249.7 ‰

The slices were embedded in acrylic glass discs with 40 mm diameter and 5 mm thickness.

4. Homogeneity testing

All three alloys were tested for homogeneity using wavelength dispersive X-ray fluorescence. 30 slices from each material were analysed. One additional puck was used as drift control sample and to determine the spread coming from the analytical method. This is easily possible because XRF is a non-destructive method. The drift control samples were measured ten times in the beginning and then after ten pucks have been measured. For none of the materials a drift correction was necessary.

As a measure for the inhomogeneity of the samples the standard deviation (s_{eff}) of all mean values (in total 30 values) was used.

Because the standard deviation s_{sample} is the sum of spread deriving from inhomogeneities and spread deriving from the analytical method, it has to be corrected for random deviations inherent to the analytical method applied. 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}).

$$s_{\text{eff, sample}} = \sqrt{s_{\text{sample}}^2 - s_{\text{method}}^2} \qquad (1)$$

The standard deviation of the mean values of 10 single measurements of the drift control sample was taken as s_{method}.

5. Characterisation study

5.1 Analytical methods

9 laboratories participated in the certification interlaboratory comparison. Seven laboratories received one slice of each material; two laboratories got two slices each.

The laboratories were requested to analyse as much subsamples as possible. Since the raw material was very expensive and therefore limited, most of the laboratories could only report between two and four single results. All laboratories were free to choose any suitable analytical method for analysis. Table 1 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 1: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pre-treatment	Analytical method
1	Au	0.145 g (506) 0.185 g (507) 0.185 g (508)	Pb-melt	Fire assay
2	Au	0.2 g	Pb-melt	Fire assay
3	Au	0.125 g		Fire assay
	Ag	0.05 g (506) 0.05 g (507) 0.025 g (508)	Aqua regia	ICP-OES, calibration with Ag 99.99+ %
	Cu	0.05 g	Aqua regia	ICP-OES, calibration with Cu 99.9999 %
	Zn	0.05 g	Aqua regia	ICP-OES, calibration with Zn 99.99+ %
	Ni	0.05 g	Aqua regia	ICP-OES, calibration with Ni 99.994 %
4	Au	0.25 g		Fire assay
	Ag, Cu, Zn, Ni	0.1 g (506) 0.067 g (507) 0.067 g (508)	Aqua regia	ICP-OES, calibration with commercial calibration solution
5	Au	0.25 g		Fire assay, Au 99.99 %
	Ag	0.05 g	Aqua regia	ICP-OES, calibration with Ag 99.99 %
	Cu	0.05 g	Aqua regia	ICP-OES, calibration with Cu 99.99 %
	Zn	0.05 g	Aqua regia	ICP-OES, calibration with Zn 99.99 %
	Ni	0.05 g	Aqua regia	ICP-OES, calibration with Ni 99.99 %
6	Au	0.18 g (506) 0.21 g (507) 0.22 g (508)		ICP-OES, calibration with Au metal
	Ag	0.05 g	Aqua regia	ICP-OES, calibration with Ag metal
	Cu, Zn, Ni	0.18 g (506) 0.21 g (507) 0.22 g (508)	Aqua regia	ICP-OES, calibration with commercial calibration solution
7	Au	0.15 g		Fire assay
8	Au	0.25 g		Fire assay
	Ag	0.1 g	Aqua regia	ICP-OES, calibration with Ag 99.99 %
	Cu	0.1 g	Aqua regia	ICP-OES, calibration with Cu 99.99 %
	Zn	0.1 g	Aqua regia	ICP-OES, calibration with Zn 99.99 %
	Ni	0.1 g	Aqua regia	ICP-OES, calibration with Ni 99.99 %
9	Ag	0.1 g	Aqua regia	ICP-OES, calibration with Ag 99.99 %
	Cu	0.1 g	Aqua regia	ICP-OES, calibration with Cu 99.99 %
	Zn	0.1 g	Aqua regia	ICP-OES, calibration with Zn 99.99 %
	Ni	0.1 g	Aqua regia	ICP-OES, calibration with Ni 99.99 %

5.2 Analytical results and statistical evaluation

The analytical results of the certification interlaboratory comparison are listed in Tables 11 to 22. These tables show the single results (M_i) of each laboratory, the respective laboratory mean (M) together with the absolute and relative interlaboratory standard deviation (s, s_{rel}) and in addition the mean repeatability standard deviation ($\bar{s}_i$) 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.

Since the number of datasets available for all elements is not so big (in most cases n = 6) and except for Au only one analytical method (ICP-OES) was used, a plausibility check was done summarising the contents of all elements present in the samples (Tables 2 to 4). In all cases the sum of all element mass fractions is very close to 100 %.

Table 2: Summation of mass fractions of elements contained in ERM®-EB506:

Laboratory / Element	3	4	5	6	8	Mean
Au	58.568	58.583	58.578	58.565	58.547	
Ag	3.900	3.860	3.922	3.948	3.890	
Cu	35.673	35.690	35.638	35.598	35.595	
Zn	1.883	1.878	1.917	1.873	1.903	
	100.02	100.01	100.05	99.98	99.93	100.00

Table 3: Summation of mass fractions of elements contained in ERM®-EB507:

Laboratory / Element	3	4	5	6	8	Mean
Au	75.103	75.102	75.152	75.115	75.110	
Ag	3.048	2.943	3.063	3.048	3.008	
Cu	14.665	14.713	14.710	14.735	14.683	
Zn	2.110	2.103	2.120	2.083	2.118	
Ni	5.005	4.945	4.985	5.010	5.003	
	99.93	99.80	100.03	99.99	99.92	99.93
Fe (Lab. 8)						0.014
Mn (Lab. 8)						0.03
						99.98

Table 4: Summation of mass fractions of elements contained in ERM®-EB508:

Laboratory / Element	3	4	5	6	8	Mean
Au	75.105	75.120	75.141	75.133	75.133	
Ag	24.903	24.880	24.971	24.858	24.905	
	100.01	100.00	100.11	99.99	100.04	100.03

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

Table 5: Outcome of statistical tests on the results obtained for Au:

	ERM-EB506	ERM-EB507	ERM-EB508
Number of data sets	8	8	8
Scheffe's test data compatible	yes	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---	---
Dixon (α = 0.01)	---	---	---
Nalimov (α = 0.05)	Lab. 1	---	Lab. 7
Nalimov (α = 0.01)	---	---	Lab. 7
Grubbs (α = 0.05)	Lab. 1	---	Lab. 7
Grubbs (α = 0.01)	---	---	Lab. 7
Grubbs Pair (α = 0.05)	---	---	---
Grubbs Pair (α = 0.01)	---	---	---
Cochran	---	---	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal	Distribution: normal
Skewness & Kurtosis test (α = 0.05)	Distribution: normal	Distribution: normal	Distribution: not normal
Skewness & Kurtosis test (α = 0.01)	Distribution: normal	Distribution: normal	Distribution: normal

The outlying values (Lab. 1, ERM-EB506 and Lab. 7, ERM-EB508) were not removed.

Table 6: Outcome of statistical tests on the results obtained for Ag:

	ERM-EB506	ERM-EB507	ERM-EB508
Number of data sets	6	6	6
Scheffe's test data compatible	yes	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---	---
Dixon (α = 0.01)	---	---	---
Nalimov (α = 0.05)	---	Lab. 4	Lab. 5
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	Distribution: normal	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal	Distribution: normal

The outlying values (Lab. 4, ERM-EB507 and Lab. 5, ERM-EB508) were not removed.

Table 7: Outcome of statistical tests on the results obtained for Cu:

	ERM-EB506	ERM-EB507
Number of data sets	6	6
Scheffe's test data compatible	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	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	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal

Table 8: Outcome of statistical tests on the results obtained for Zn:

	ERM-EB506	ERM-EB507
Number of data sets	6	6
Scheffe's test data compatible	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	Lab. 6
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	Distribution: normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal	Distribution: normal

The outlying value (Lab. 6, ERM-EB507) was not removed.

Table 9: Outcome of statistical tests on the results obtained for Ni:

	ERM-EB507
Number of data sets	6
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)	Lab. 4
Nalimov (α = 0.01)	Lab. 4
Grubbs (α = 0.05)	Lab. 4
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: not normal
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal

The outlying value (Lab. 4, ERM-EB507) was not removed.

The certified mass fractions of all elements were calculated as mean of the accepted data sets. These values are given in Table 10.
The resp. combined uncertainties were calculated from the spread resulting from the certification interlaboratory comparison (s_M) and the uncertainty contributions from possible inhomogeneity of the material using Equation 2.

$$u_{\mathrm{combined}} = \sqrt{u_{ilc}^2 + s_{eff,sample}^2} \qquad (2)$$

with

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

Table 10: Uncertainty calculation

	M	n	s_M	u_{ilc}	s_{eff}	$u_{combined}$
ERM-EB506						
Au	58.56 %	8	0.0266 %	0.0094 %	0.0206 %	0.0244 %
Ag	3.895 %	6	0.0362%	0.0148 %	0.0123 %	0.0183 %
Cu	35.65 %	6	0.0476 %	0.0194 %	0.0108 %	0.0265 %
Zn	1.891 %	6	0.0167 %	0.0068 %	0.0019 %	0.0079 %
ERM-EB507						
Au	75.10 %	8	0.0308 %	0.0109 %	0.0403 %	0.0417 %
Ag	3.018 %	6	0.0445%	0.0182 %	0.0061 %	0.0196 %
Cu	14.69%	6	0.0365 %	0.0149 %	0.0121 %	0.0192 %
Zn	2.107 %	6	0.0136%	0.0056 %	0.0028 %	0.0062 %
Ni	4.992 %	6	0.0246%	0.0101 %	0.0102 %	0.0143 %
ERM-EB508						
Au	75.12 %	8	0.0296 %	0.0105 %	0.0323 %	0.0405 %
Ag	24.90 %	6	0.0381 %	0.0156 %	0.0313 %	0.0196 %

The expanded uncertainties U are calculated by multiplication of $u_{combined}$ with a coverage factor of k = 2.5 using Equation 3.

$$U = 2.5 \cdot u_{\text{combined}} \tag{3}$$

The calculated mass fractions and their respective expanded uncertainties are given on Page 3 of this report.

Lab./Meth.	1/Pb-Dok.	8/Dok.	6/I	3/Dok.	2/Pb-Dok.	5/Dok.	4/Dok.	7/Dok.		Ges.
M_i [%]	58.490	58.550	58.710	58.580	58.564	58.578	58.582	58.640		N
	58.510	58.550	58.480	58.560	58.554	58.603	58.583	58.520		8
	58.529	58.540	58.630	58.580	58.578	58.597		58.660		
	58.509		58.440	58.550	58.577	58.570		58.570		
						58.562				
						58.557				
***M* [%]**	**58.5095**	**58.5467**	**58.5650**	**58.5675**	**58.5683**	**58.5778**	**58.5825**	**58.5975**		**58.5643**
s [%]	0.0156	0.0058	0.1266	0.0150	0.0114	0.0187	0.0007	0.0645	s_M [%]	0.0266
									$\bar{s}_i$ [%]	0.0514
s_{rel}	0.00027	0.00010	0.00216	0.00026	0.00020	0.00032	0.00001	0.00110		0.00045

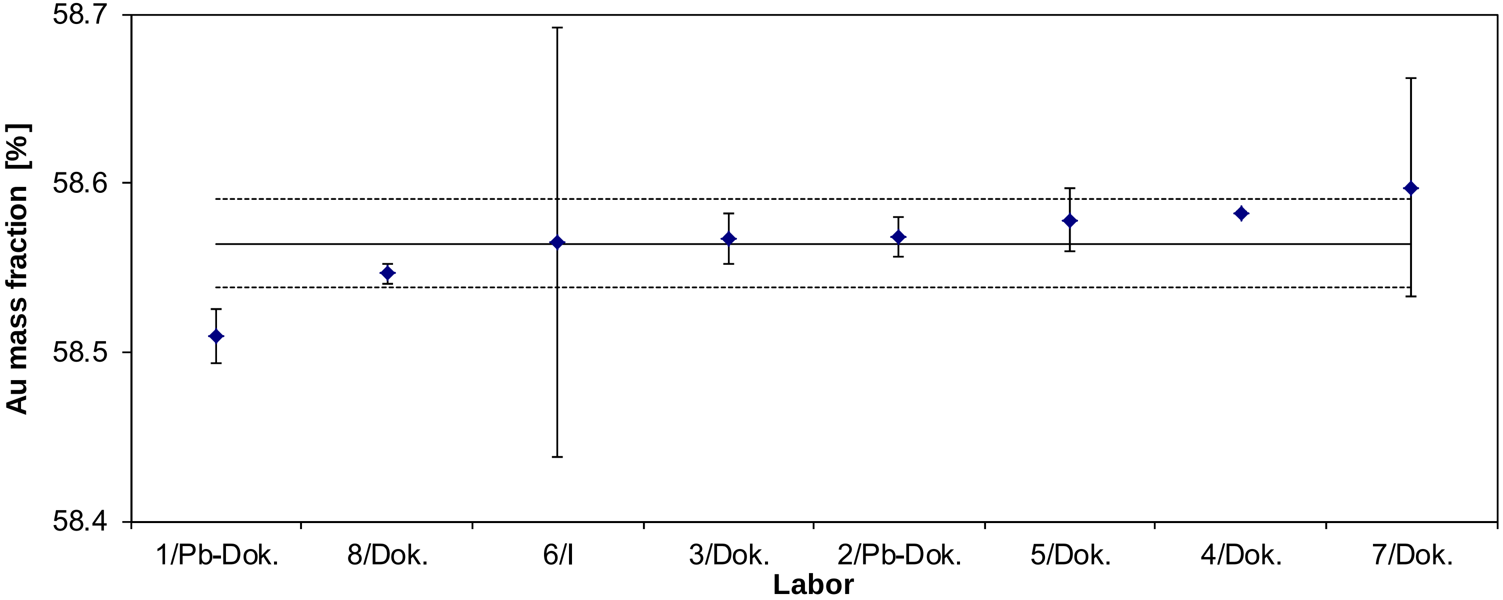

Table 11: Results for Au in ERM-EB506

Lab./Meth.	9/I	4/I	8/I	3/I	5/I	6/I		Ges.
M_i [%]	3.85	3.85	3.89	3.91	3.95	3.89		N
	3.85	3.87	3.89	3.91	3.94	4.00		6
	3.86	3.86	3.89	3.88	3.96	3.91		
	3.85	3.86	3.89	3.90	3.89	3.99		
					3.89			
					3.90			
M [%]	**3.8525**	**3.8600**	**3.8900**	**3.9000**	**3.9217**	**3.9475**		**3.8953**
s [%]	0.0050	0.0082	0.0000	0.0141	0.0319	0.0556	s_M [%]	0.0362
							$\bar{s}_i$ [%]	0.0271
s_{rel}	0.00130	0.00212	0.00000	0.00363	0.00813	0.01409		0.00929

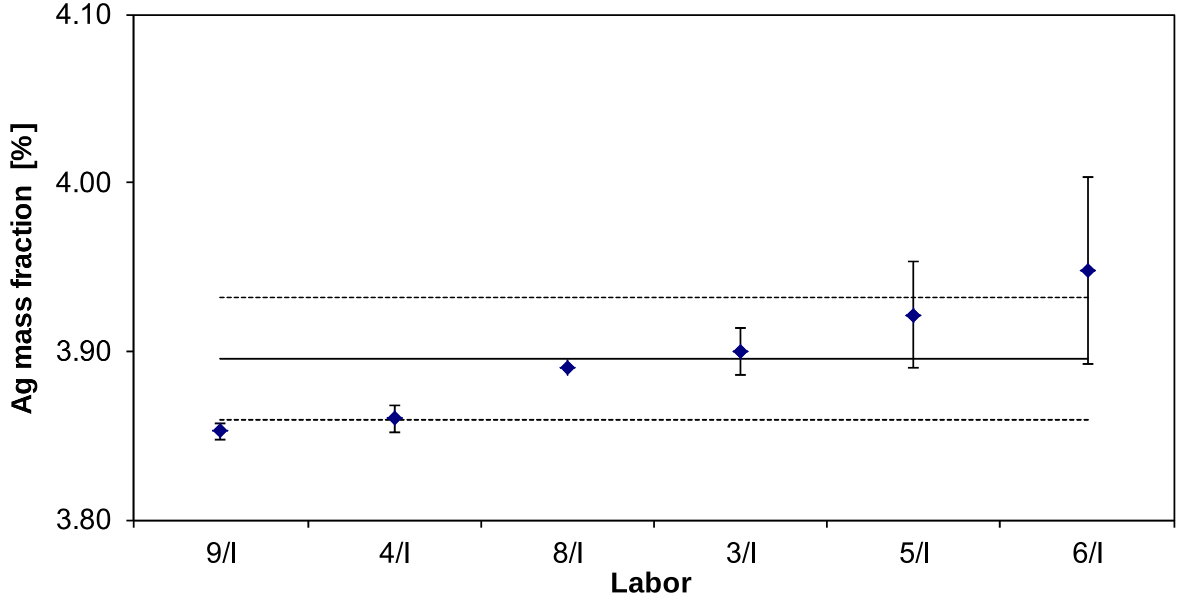

Table 12: Results for Ag in ERM-EB506

Lab./Meth.	8/I	6/I	5/I	3/I	4/I	9/I		Ges.
M_i [%]	35.6	35.52	35.67	35.7	35.6	35.7		N
	35.6	35.61	35.77	35.7	35.8	35.7		6
	35.6	35.58	35.64	35.7	35.7	35.7		
	35.6	35.68	35.50	35.7	35.7	35.8		
			35.56					
			35.69					
M [%]	**35.595**	**35.598**	**35.638**	**35.673**	**35.690**	**35.708**		**35.650**
s [%]	0.025	0.067	0.096	0.015	0.078	0.046	s_M [%]	0.0476
							$\bar{s}_i$ [%]	0.0615
s_{rel}	0.001	0.002	0.003	0.000	0.002	0.001		0.001

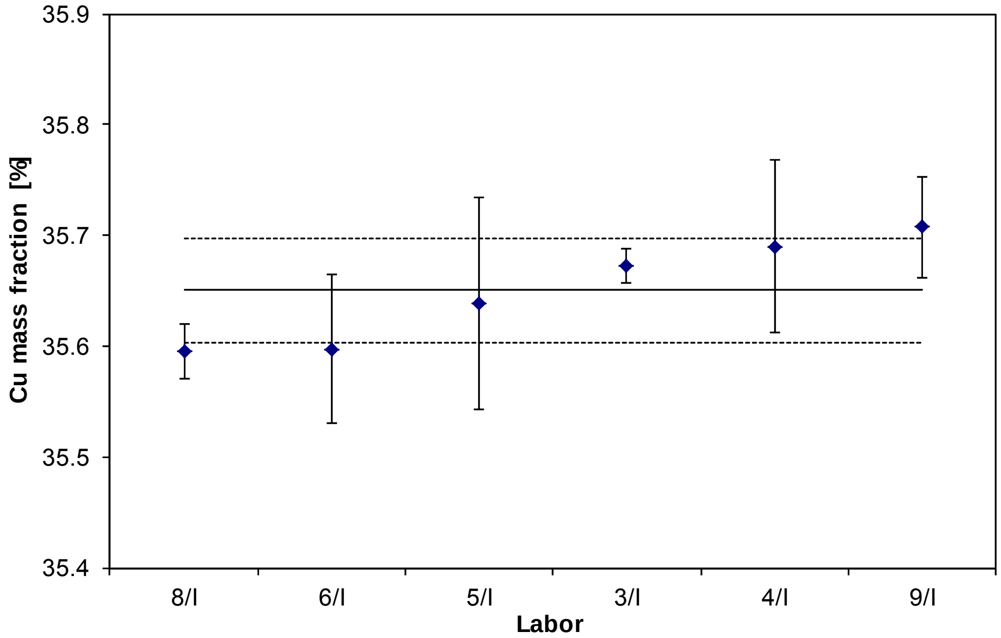

Table 13: Results for Cu in ERM-EB506

Lab./Meth.	6/I	4/I	3/I	9/I	8/I	5/I		Ges.
M_i [%]	1.86	1.87	1.88	1.90	1.90	1.91		N
	1.89	1.88	1.88	1.90	1.90	1.92		6
	1.86	1.87	1.89	1.89	1.91	1.91		
	1.88	1.89	1.88	1.88	1.90	1.92		
						1.92		
						1.92		
***M* [%]**	**1.87**	**1.88**	**1.88**	**1.89**	**1.90**	**1.92**		**1.891**
s [%]	0.015	0.010	0.005	0.010	0.005	0.005	s_M [%]	0.0167
							$\bar{s}_i$ [%]	0.0090
s_{rel}	0.008	0.005	0.003	0.005	0.003	0.003		0.009

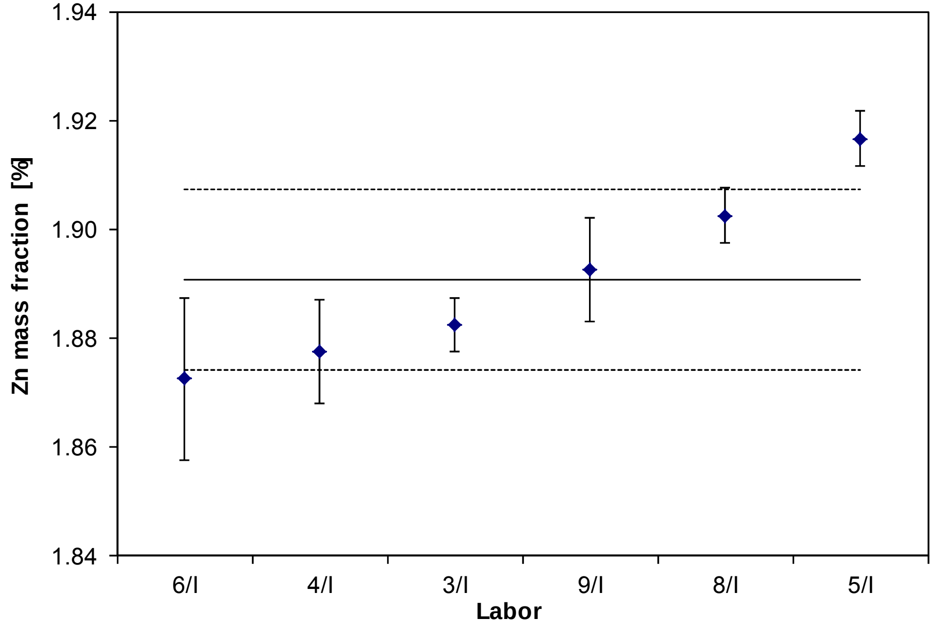

Table 14: Results for Zn in ERM-EB506

Lab./Meth.	1/Pb-Dok.	7/Dok.	4/Dok.	3/Dok.	8/Dok.	2/Pb-Dok.	6/I	5/Dok.		Ges.
M_i [%]	75.059	75.030	75.107	75.110	75.120	75.102	75.330	75.185		N
	75.058	75.090	75.096	75.100	75.100	75.119	75.070	75.174		8
	75.056	75.020		75.100	75.110	75.103	75.000	75.185		
	75.054	75.100		75.100		75.132	75.060	75.109		
								75.108		
								75.149		
M [%]	**75.0568**	**75.0600**	**75.1015**	**75.1025**	**75.1100**	**75.1140**	**75.1150**	**75.1517**		**75.1014**
s [%]	0.0022	0.0408	0.0078	0.0050	0.0100	0.0143	0.1466	0.0359	s_M [%]	0.0308
									$\bar{s}_i$ [%]	0.0557
s_{rel}	0.00003	0.00054	0.00010	0.00007	0.00013	0.00019	0.00195	0.00048		0.00041

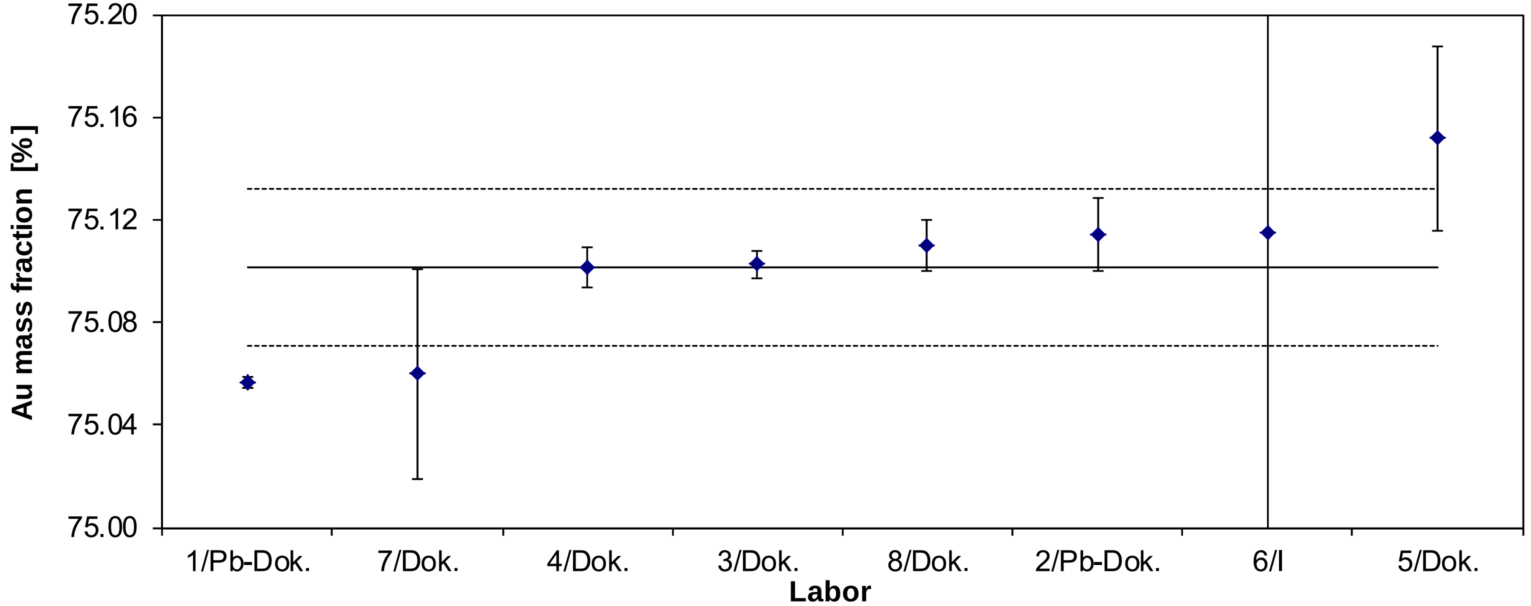

Table 15: Results for Au in ERM-EB507

Lab./Meth.	4/I	9/I	8/I	6/I	3/I	5/I		Ges.
M_i [%]	2.94	2.99	3.01	3.02	3.05	3.09		N
	2.93	3.01	3.00	3.07	3.05	3.06		6
	2.96	3.00	3.01	3.01	3.04	3.07		
	2.94	3.00	3.01	3.09	3.05	3.04		
						3.05		
						3.07		
M [%]	**2.9425**	**3.0000**	**3.0075**	**3.0475**	**3.0475**	**3.0632**		**3.0180**
s [%]	0.0126	0.0082	0.0050	0.0386	0.0050	0.0165	s_M [%]	0.0445
							$\bar{s}_i$ [%]	0.0184
s_{rel}	0.00428	0.00272	0.00166	0.01267	0.00164	0.00539		0.01476

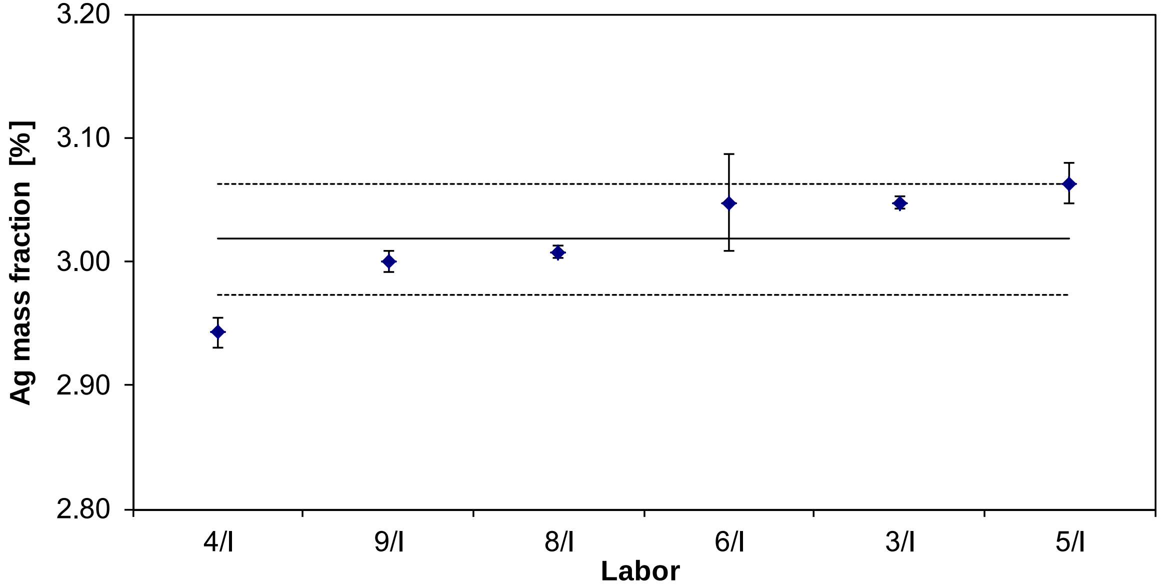

Table 16: Results for Ag in ERM-EB507

Lab./Meth.	9/I	3/I	8/I	5/I	4/I	6/I		Ges.
M_i [%]	14.66 14.61 14.64 14.63	14.65 14.68 14.66 14.67	14.70 14.66 14.68 14.69	14.78 14.78 14.70 14.69 14.69 14.62	14.71 14.70 14.73 14.71	14.58 14.71 14.95 14.70		N 6
***M* [%]**	**14.635**	**14.665**	**14.683**	**14.710**	**14.713**	**14.735**		**14.690**
s [%]	0.021	0.013	0.017	0.061	0.013	0.155	s_M [%] $\bar{s}_i$ [%]	0.0365 0.0693
s_{rel}	0.001	0.001	0.001	0.004	0.001	0.011		0.002

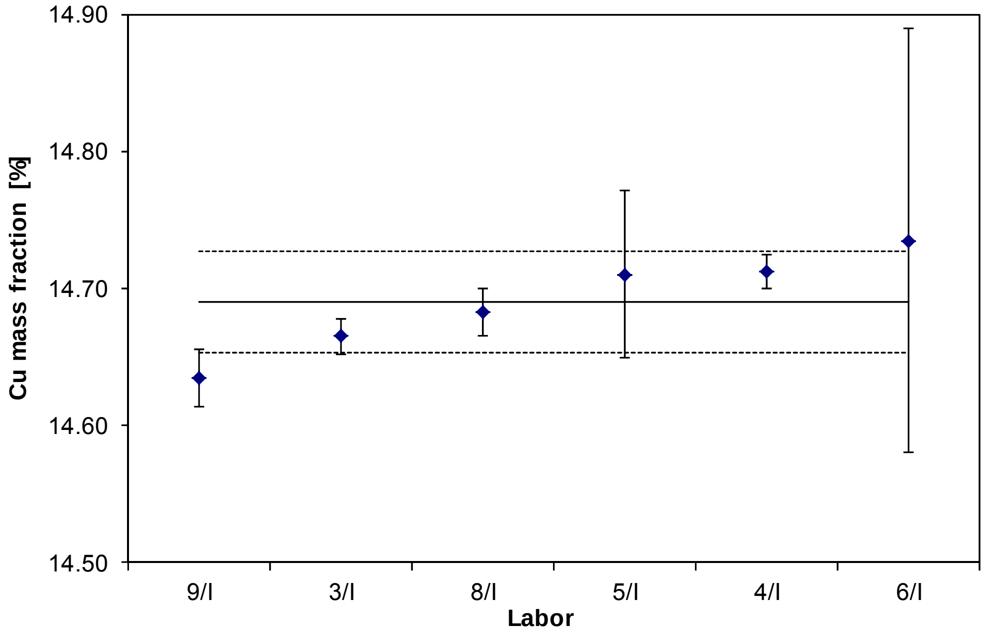

Table 18: Results for Cu in ERM-EB507

Lab./Meth.	4/I	5/I	8/I	3/I	9/I	6/I		Ges.
M_i [%]	4.95	4.99	5.00	5.00	5.02	4.99		N
	4.95	4.95	5.00	5.01	5.00	5.04		6
	4.95	4.92	5.01	5.00	4.99	4.97		
	4.93	5.02	5.00	5.01	5.01	5.04		
		5.02						
		5.01						
***M* [%]**	**4.945**	**4.985**	**5.003**	**5.005**	**5.005**	**5.010**		**4.992**
s [%]	0.010	0.041	0.005	0.006	0.013	0.036	s_M [%]	0.0246
							$\bar{s}_i$ [%]	0.0234
s_{rel}	0.002	0.008	0.001	0.001	0.003	0.007		0.005

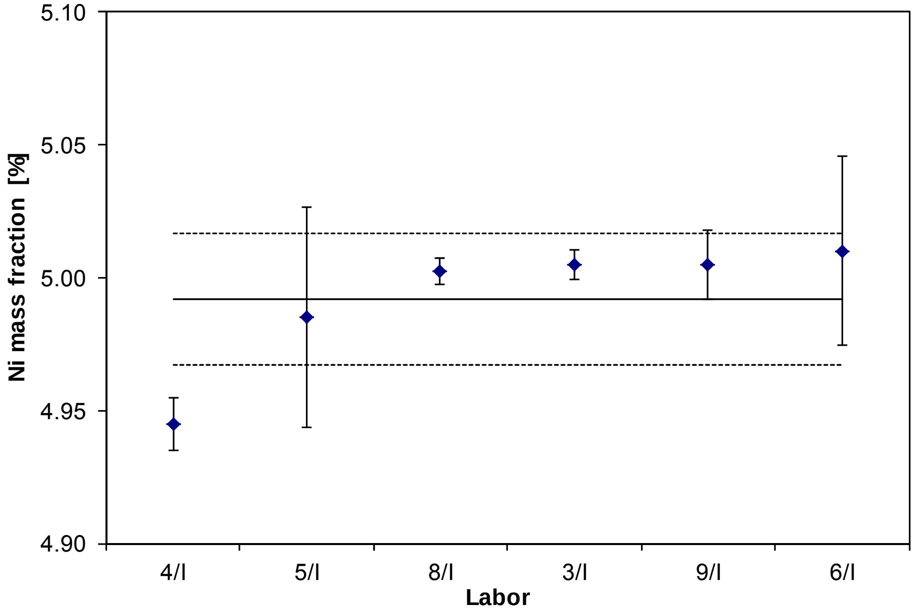

Table 19: Results for Ni in ERM-EB507

Lab./Meth.	6/I	4/I	3/I	9/I	8/I	5/I		Ges.
M_i [%]	2.07 2.09 2.07 2.10	2.11 2.11 2.10 2.09	2.11 2.11 2.11 2.11	2.11 2.10 2.12 2.11	2.12 2.11 2.12 2.12	2.10 2.09 2.08 2.15 2.15 2.15		N 6
***M* [%]**	**2.083**	**2.103**	**2.110**	**2.110**	**2.118**	**2.120**		**2.107**
s [%]	0.015	0.010	0.000	0.008	0.005	0.035	s_M [%] $\bar{s}_i$ [%]	0.0136 0.0164
s_{rel}	0.007	0.005	0.000	0.004	0.002	0.016		0.006

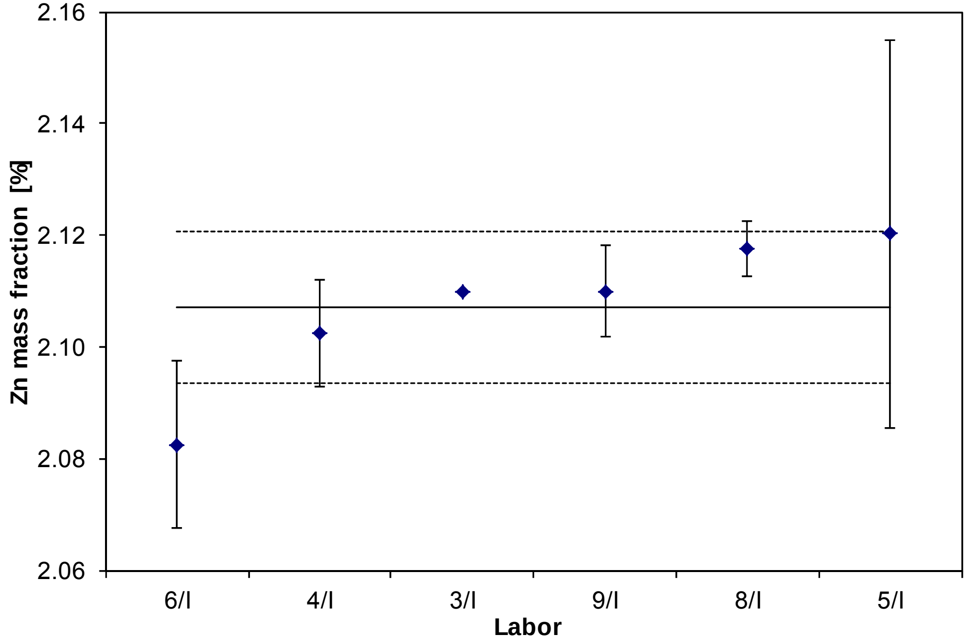

Table 20: Results for Zn in ERM-EB507

Lab./Meth.	7/Dok.	3/Dok.	2/Pb-Dok.	4/Dok.	6/I	8/Dok.	1/Pb-Dok	5/Dok.		Ges.
M_i [%]	75.080	75.110	75.101	75.126	75.060	75.100	75.136	75.154		N
	75.100	75.080	75.105	75.133	75.180	75.130	75.140	75.157		8
	75.030	75.120	75.133	75.101	75.100	75.170	75.130	75.155		
	74.990	75.110	75.135		75.190		75.138	75.129		
								75.115		
								75.134		
***M* [%]**	**75.0500**	**75.1050**	**75.1185**	**75.1200**	**75.1325**	**75.1333**	**75.1362**	**75.1407**		**75.1170**
s [%]	0.0497	0.0173	0.0180	0.0168	0.0629	0.0351	0.0042	0.0173	s_M [%]	0.0295
									$\bar{s}_i$ [%]	0.0333
s_{rel}	0.00066	0.00023	0.00024	0.00022	0.00084	0.00047	0.00006	0.00023		0.00039

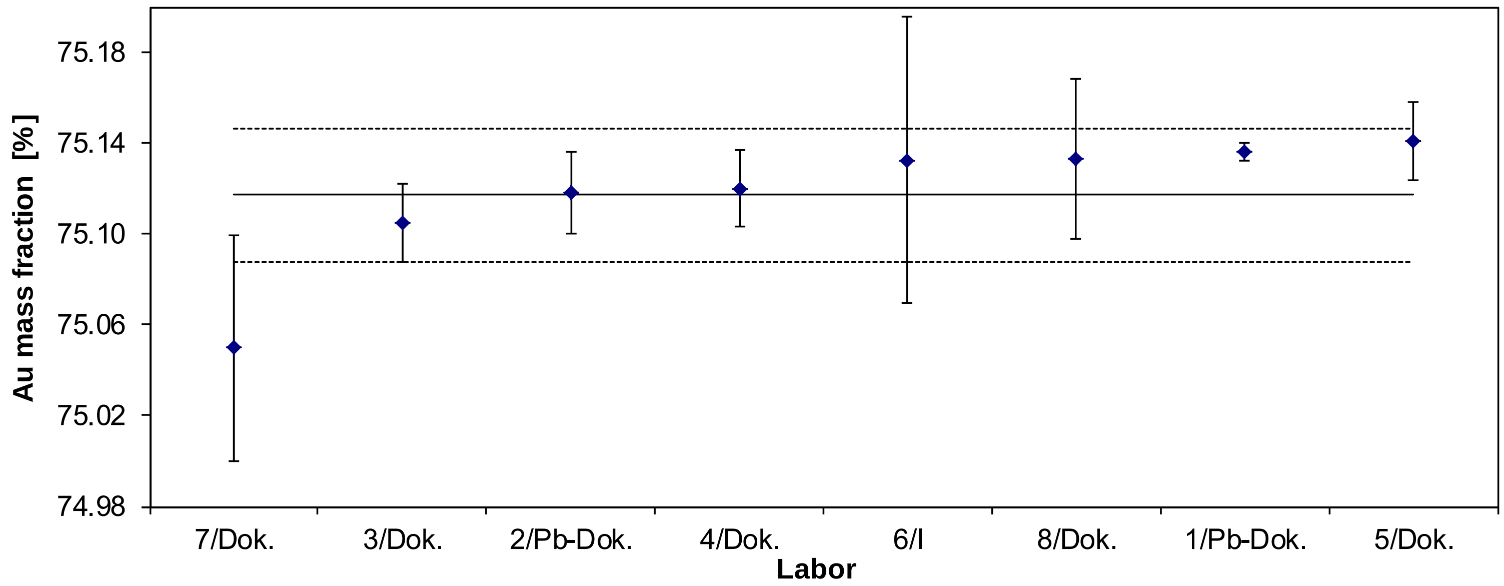

Table 21: Results for Au in ERM-EB508

Lab./Meth.	6/I	4/I	3/I	9/I	8/I	5/I		Ges.
M_i [%]	24.93	24.91	24.90	24.8900	24.92	24.97		N
	24.81	24.88	24.83	24.8800	24.92	24.98		6
	24.89	24.88	24.95	24.9100	24.89	24.96		
	24.80	24.85	24.93	24.9300	24.89	24.99		
						24.97		
						24.96		
***M* [%]**	**24.8575**	**24.8800**	**24.9025**	**24.9025**	**24.9050**	**24.9713**		**24.9031**
s [%]	0.0629	0.0245	0.0525	0.0222	0.0173	0.0090	s_M [%]	0.0381
							$\bar{s}_i$ [%]	0.0369
s_{rel}	0.00253	0.00098	0.00211	0.00089	0.00070	0.00036		0.00153

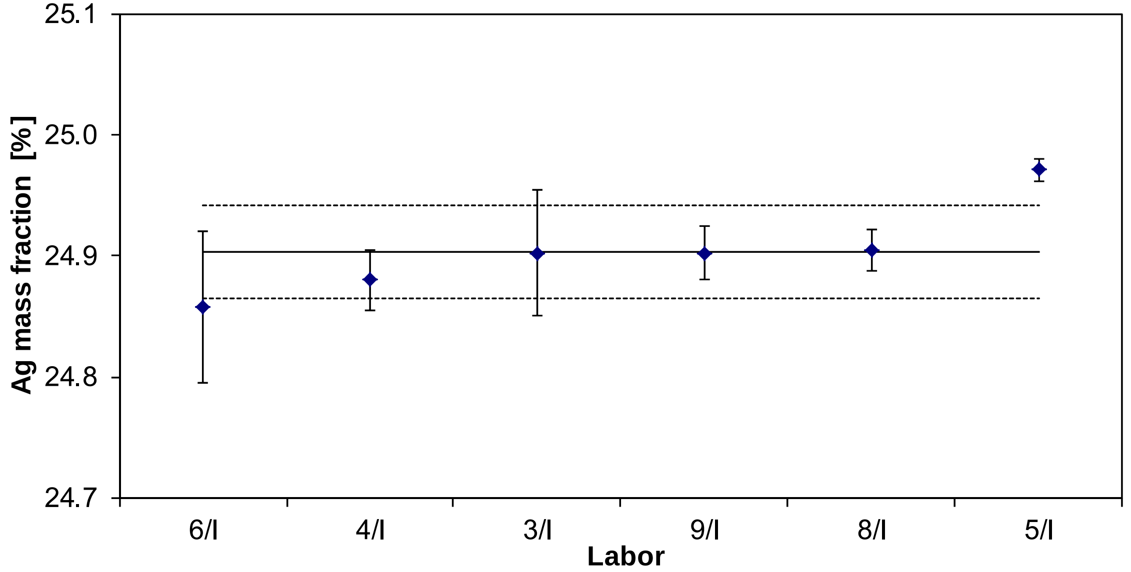

Table 22: Results for Ag in ERM-EB508

6. Instructions for users and stability

The certified reference materials ERM®-EB506, -507 and -508 are intended for the calibration and quality control of X-ray fluorescence spectrometers, especially hand held instruments used for the analysis of similar materials.
Normally the surface of the material need not be cleaned before analysis. However cleaning with alcohol is possible in case of dirt on the surface.
The material will remain stable provided that it is not subjected to excessive heat or mechanical treatment.

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, 2009

[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

[7] ISO/IEC Guide 98-1:2009, Uncertainty of measurement -- Part 1: Introduction to the expression of uncertainty in measurement

8. Information on and purchase of the CRM

Information and purchase is done by

BAM Bundesanstalt für Materialforschung und -prüfung
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, 12489 Berlin
Phone +49 (0)30 - 8104 2061 or 1119
Fax: +49 (0)30 - 8104 1117
E-Mail: sales.crm@bam.de

Each unit of ERM®-EB506, -507 and -508 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,

http://www.bam.de/en/fachthemen/referenzmaterialien/index.htm
www.webshop.bam.de

Annex: Homogeneity measurements and calculation of uncertainty

ERM-EB 506

	Ag	Au	Zn	Cu
	Intensity	Intensity	Intensity	Intensity
EB506 1	2.983	69.609	8.118	100.148
EB506 2	2.977	69.570	8.125	100.328
EB506 3	2.968	69.665	8.129	100.338
EB506 4	2.966	69.636	8.113	100.359
EB506 5	2.959	69.624	8.101	100.362
EB506 6	2.976	69.598	8.123	100.306
EB506 7	2.984	69.644	8.138	100.308
EB506 8	2.994	69.669	8.129	100.235
EB506 9	2.975	69.561	8.114	100.225
EB506 10	2.982	69.641	8.130	100.182
Drift	*3.009*	*69.627*	*8.150*	*100.039*
EB506 11	2.956	69.557	8.095	100.465
EB506 12	2.972	69.536	8.120	100.282
EB506 13	2.980	69.645	8.136	100.338
EB506 14	2.973	69.637	8.119	100.264
EB506 15	2.986	69.692	8.136	100.254
EB506 16	2.972	69.627	8.114	100.301
EB506 17	2.975	69.679	8.137	100.231
EB506 18	2.979	69.632	8.118	100.275
EB506 19	2.973	69.564	8.099	100.258
EB506 20	2.967	69.636	8.116	100.243
Drift	*3.004*	*69.711*	*8.161*	*100.140*
EB506 21	2.957	69.535	8.105	100.381
EB506 22	2.974	69.642	8.138	100.199
EB506 23	2.970	69.582	8.118	100.355
EB506 24	2.987	69.655	8.148	100.222
EB506 25	2.972	69.576	8.105	100.228
EB506 26	2.971	69.625	8.078	100.262
EB506 27	2.993	69.599	8.128	100.173
EB506 28	2.988	69.573	8.115	100.136
EB506 29	2.981	69.610	8.121	100.207
EB506 30	2.957	69.546	8.097	100.269
Drift	*3.010*	*69.663*	*8.141*	*99.983*
Drift	*3.002*	*69.766*	*8.132*	*99.988*
Drift	*3.005*	*69.658*	*8.130*	*100.073*
Drift	*3.002*	*69.734*	*8.148*	*99.912*
Drift	*3.008*	*69.691*	*8.141*	*100.006*
M	**2.9748**	**69.6121**	**8.1187**	**100.2711**
s	**0.0100**	**0.0437**	**0.0154**	**0.0742**
s_{rel}	0.3353	0.0628	0.1895	0.0740

	Ag	Au	Zn	Cu
	Intensity	Intensity	Intensity	Intensity
EB506 drift	2.998	69.658	8.111	99.845
EB506 drift	3.006	69.734	8.140	100.007
EB506 drift	2.999	69.611	8.123	99.910
EB506 drift	3.008	69.702	8.139	99.992
EB506 drift	3.006	69.691	8.151	100.028
EB506 drift	3.006	69.667	8.133	99.951
EB506 drift	3.004	69.709	8.135	99.949
EB506 drift	3.003	69.680	8.142	100.070
EB506 drift	3.002	69.714	8.154	99.996
EB506 drift	3.009	69.651	8.148	100.049
M	**3.0042**	**69.6816**	**8.1376**	**99.9798**
s	**0.0035**	**0.0362**	**0.0131**	**0.0678**
s_{rel}	0.1174	0.0519	0.1612	0.0678

s_{eff}	0.01229	0.02060	0.00189	0.01078
s_{ilc}	0.03620	0.02660	0.01670	0.04760
n	6	8	6	6
$u_{combined}$	0.01922	0.02265	0.00708	0.02222
U	0.04805	0.05662	0.01769	0.05556

ERM-EB507

	Ag	Au	Zn	Cu	Ni
	Intensity	Intensity	Intensity	Intensity	Intensity
EB507 1	2.059	94.889	7.926	39.128	11.628
EB507 2	2.053	94.961	7.945	39.190	11.655
EB507 3	2.059	95.006	7.966	39.099	11.627
EB507 4	2.062	95.014	7.954	39.125	11.583
EB507 5	2.063	94.998	7.960	39.086	11.570
EB507 6	2.061	94.782	7.960	39.071	11.598
EB507 7	2.064	94.942	7.957	39.067	11.598
EB507 8	2.067	94.930	7.960	39.089	11.597
EB507 9	2.053	94.946	7.956	39.112	11.628
EB507 10	2.062	94.949	7.963	39.009	11.608
Drift	*2.075*	*94.901*	*8.012*	*38.990*	*11.476*
EB507 11	2.067	94.972	7.973	39.116	11.619
EB507 12	2.061	94.942	7.926	39.041	11.619
EB507 13	2.070	94.960	7.968	39.103	11.617
EB507 14	2.062	94.900	7.953	39.131	11.607
EB507 15	2.060	94.936	7.960	39.118	11.623
EB507 16	2.058	94.929	7.931	39.104	11.675
EB507 17	2.056	94.813	7.953	39.114	11.633
EB507 18	2.064	94.890	7.957	39.115	11.609
EB507 19	2.067	94.964	7.945	39.110	11.590
EB507 20	2.058	94.944	7.947	39.163	11.632
Drift	*2.076*	*94.885*	*8.032*	*39.046*	*11.456*
EB507 21	2.065	94.821	7.956	39.088	11.640
EB507 22	2.056	94.926	7.937	39.182	11.663
EB507 23	2.070	94.946	7.973	39.004	11.538
EB507 24	2.048	94.795	7.924	39.147	11.650
EB507 25	2.062	94.822	7.973	39.150	11.633
EB507 26	2.058	94.935	7.960	39.183	11.666
EB507 27	2.061	94.977	7.942	39.131	11.625
EB507 28	2.061	94.882	7.970	39.217	11.642
EB507 29	2.056	94.996	7.971	39.185	11.648
Drift	*2.080*	*95.041*	*8.020*	*39.007*	*11.464*
Drift	*2.076*	*94.927*	*8.026*	*39.056*	*11.472*
Drift	*2.077*	*94.954*	*8.036*	*39.015*	*11.453*
M	**2.061**	**94.923**	**7.954**	**39.116**	**11.621**
s	**0.005**	**0.063**	**0.014**	**0.050**	**0.030**
s_{rel}	0.240	0.067	0.182	0.129	0.256

	Ag	Au	Zn	Cu	Ni
	Intensity	Intensity	Intensity	Intensity	Intensity
EB507 drift	2.072	94.927	8.010	38.955	11.427
EB507 drift	2.078	94.954	7.997	38.948	11.440
EB507 drift	2.079	94.922	8.017	39.013	11.472
EB507 drift	2.077	94.940	8.020	38.991	11.459
EB507 drift	2.076	94.927	8.026	39.064	11.456
EB507 drift	2.079	94.999	8.027	39.022	11.444
EB507 drift	2.077	95.027	8.016	38.992	11.481
EB507 drift	2.075	94.943	8.026	38.955	11.456
EB507 drift	2.078	94.900	8.030	39.032	11.479
EB507 drift	2.082	94.957	8.014	39.031	11.479
M	**2.077**	**94.949**	**8.018**	**39.000**	**11.459**
s	**0.003**	**0.038**	**0.010**	**0.039**	**0.018**
s_{rel}	0.1279	0.0399	0.1238	0.0999	0.1607

s_{eff}	0.00416	0.05084	0.01054	0.03208	0.02344
s_{ilc}	0.04550	0.03080	0.01360	0.03650	0.02460
n	6	8	6	6	6
$u_{combined}$	0.01904	0.05199	0.01191	0.03537	0.02550
U	0.04759	0.12998	0.02978	0.08842	0.06376

ERM-EB508

	Ag	Au
	Intensity	Intensity
EB508 1	4.158	110.336
EB508 2	4.152	110.192
EB508 3	4.162	110.239
EB508 4	4.165	110.336
EB508 5	4.149	110.196
EB508 6	4.159	110.194
EB508 7	4.152	110.261
EB508 8	4.168	110.303
EB508 9	4.161	110.308
EB508 10	4.161	110.263
DRIFT	*4.153*	*110.230*
EB508 11	4.160	110.316
EB508 12	4.156	110.360
EB508 13	4.160	110.217
EB508 14	4.165	110.275
EB508 15	4.163	110.214
EB508 16	4.153	110.232
EB508 17	4.170	110.397
EB508 18	4.164	110.225
EB508 19	4.164	110.301
EB508 20	4.155	110.321
DRIFT	*4.152*	*110.209*
EB508 21	4.160	110.244
EB508 22	4.166	110.270
EB508 23	4.157	110.261
EB508 24	4.146	110.140
EB508 25	4.150	110.297
EB508 26	4.164	110.346
EB508 27	4.166	110.333
EB508 28	4.161	110.235
EB508 29	4.162	110.253
EB508 30	4.169	110.219
DRIFT	*4.155*	*110.163*
M	**4.1599**	**110.2695**
s	**0.0061**	**0.0591**
s_{rel}	0.1477	0.0536

	Ag	Au
	Intensity	Intensity
EB508 drift	4.152	110.104
EB508 drift	4.152	110.104
EB508 drift	4.156	110.140
EB508 drift	4.156	110.140
EB508 drift	4.158	110.147
EB508 drift	4.158	110.147
EB508 drift	4.155	110.065
EB508 drift	4.155	110.065
EB508 drift	4.157	110.144
EB508 drift	4.157	110.144
M	**4.1556**	**110.1201**
s	**0.0021**	**0.0336**
s_{rel}	0.0505	0.0305

s_{eff}	0.03469	0.03320
s_{ilc}	0.03620	0.02960
n	6	8
$u_{combined}$	0.02046	0.04153
U	0.05116	0.10382