DLA
Dienstleistung
Lebensmittel
Analytik GbR

Evaluation Report
proficiency test

DLA 41/2014

Finger Paint:
Heavy Metals (As,Ba,Cd,Cr,Hg,Pb,Sb,Se)

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1. Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the validity of the particular testing method.
The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.
Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009.

2. Realisation

2.1 Test material

The finger paint consists of water, colorants, fillers, binding agents, humectants, preservatives, surfactans and bitter substances. These products are examined according to DIN EN 71-7 (16) for their suitability and safety. These bitter substances have been added in order to protect children from putting fingers in there mouth.

The test material was a mixture of a number of colour tones (red, black, green, white) from commercial water soluble finger paints and additionally a heavy metal standard solution (Sb: 4,0 mg/kg; As: 6,0 mg/kg; Ba: 40 mg/kg; Cd: 8,0 mg/kg; Cr: 6,0 mg/kg; Pb: 10 mg/kg; Hg: 6,0 mg/kg; Se: 8,0 mg/kg). It should be determined the migration (according to EN 71) and the total content of the heavy metals arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), antimony (Sb) and selenium (Se).

Approximately 0,5 kg of the material were homogenized and then packaged in portions to approximately 5 g. The portions were numbered chronologically.

2.1.1 Homogeneity

The calculation of the repeatability standard deviation of the participants for chromium (total) was used as an indicator of homogeneity. The result is similar to the repeatability standard deviation of the German official method ASU § 64 LFGB L00.00-135 (11). The repeatability standard deviation of the participants is given in the documentation.

In the documentation the portion numbers are graphically assigned to the results of mercury (x5). There is no trend recognizable in the results which could suggest inhomogeneity.

2.2 Test

Two portions of test material were sent to every participating laboratory in the 39th week of 2014. The testing method was optional, the migration tests should be carried out according to EN 71 (15). The tests should be finished at 7th November 2014 the latest.

2.3 Results

The participants submitted their results in standard forms, which have been handed out with the samples. The finally calculated concentrations of As, Ba, Cd, Cr, Pb, Hg, Sb and Se (migration according to EN 71-3 and total content) as average of duplicate determinations of both numbered samples was used for the statistical evaluation.
Queried and documented were single results, recovery and the testing method used. One participants have not submitted any results.

3. Evaluation

3.1 Assigned value

Because the analysed material was no certified reference material the robust mean of the submitted results was used as assigned value X (6).
The distribution of submitted results showed no hint for bimodal distribution or other reasons for a higher variability.

3.2 Standard deviation

For comparison to the target standard deviation a robust standard deviation (S_x) was calculated (6).

3.3 Outliers

Statistical outliers were determined by Mandel´s-h-Statistic (5). Detected outliers were stated for information only, when z-score was < -2 or > 2.

3.4 Target standard deviation

The target standard deviation of the assigned value is determined according to the following methods.

3.4.1 General model (Horwitz)

The relative target standard deviation in % of the assigned value is calculated according to the following equation.

$$\hat{\sigma} \ (\%) = 2^{(1-0,5 \log X)}$$

Out of this is calculated the target standard deviation in mg/kg

$$\hat{\sigma} = X * \hat{\sigma} \ (\%) / 100.$$

3.4.2 Precision experiment

Using the reproducibility standard deviation σ_R and the repeatability standard deviation σ_r of a precision experiment the between-laboratories standard deviation (σ_L) can be calculated :

$$\sigma_L = \sqrt{(\sigma_R^2 - \sigma_r^2)} \quad .$$

And then, using the number of replicate measurements n, each participant is to perform, the standard deviation for proficiency assessment is calculated :

$$\hat{\sigma} = \sqrt{(\sigma_L^2 + (\sigma_r^2/n))} \quad .$$

The relevant ISO standards for the multi element determination with ICP-MS used in this PT are not specific with respect to statistical characteristics of the method. Therefore the statistical evaluation of the total content of the heavy metals was realised with the target standard deviation according to Horwitz.

The specific requirements of the EN 71 (determination of the migration of the elements) have the consequence that the migration results showed a considerable uncertainty. As shown in EN 71 the results of an identical element varies between the laboratories at least 25 %. On this account we have defined the target standard deviation for this PT to 25%. This target standard deviation was used for the statistical evaluation of the results with z-score.

3.5 z-Score

To assess the results of the participants the z-score is used. It indicates about which multiple of the target standard deviation ($\hat{\sigma}$) the result (x) of the participant is deviating from the assigned value (X)(6).

Participants' z-scores were derived as:

$$z = (x - X) / \hat{\sigma} \quad ;$$

the requirements for the analytical performance are generally considered as fulfilled if

$$-2 \leq z \leq 2$$

3.6 Quotient $S^x/\hat{\sigma}$

Following the Horrat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation and target standard deviation does not exceed the value of 2.
A value > 2 means an insufficient precision, i.e. the analytical method is too variable, or the variation between the test participants is higher than estimated. Thus the comparability of the results is not given.

For this PT the results for antimony (total content) showed a limited comparability.

3.7 Standard uncertainty

The assigned value X has a standard uncertainty u_X that depends on the analytical method, differences between the analytical methods used, the test material, the number of participant laboratories and perhaps on other factors. The standard uncertainty (u_X) for this PT is calculated as follows (6).

$$u_X = 1{,}25 * S^x / \sqrt{(p)}$$

If $u_X \leq 0{,}3 * \hat{\sigma}$ the standard uncertainty of the assigned value needs not be included in the interpretation of the results of the PT (6). The Quotient $u_X/\hat{\sigma}$ is reported in the characteristics of the test.

4. Results

All following tables are anonymized. With the delivering of the evaluation-report the participants are informed about their individual evaluation-number.

For the elements chromium, mercury and lead we had based on an very small number of participants a relatively large variance. For this reason we refused on a statistical evaluation for these elements.

In the upper table – test - the characteristics are listed:

Number of results	
Number of outliers	
Mean	
Median	
Robust mean (X)	
Robust standard deviation (S^x)	
Target standard deviation($\hat{\sigma}$)	
Lower limit of target range	
Upper limit of target range	
Quotient $S^x/\hat{\sigma}$	
Standard uncertainty u_x	
Quotient $u_X/\hat{\sigma}$	
Number of results in the target range	

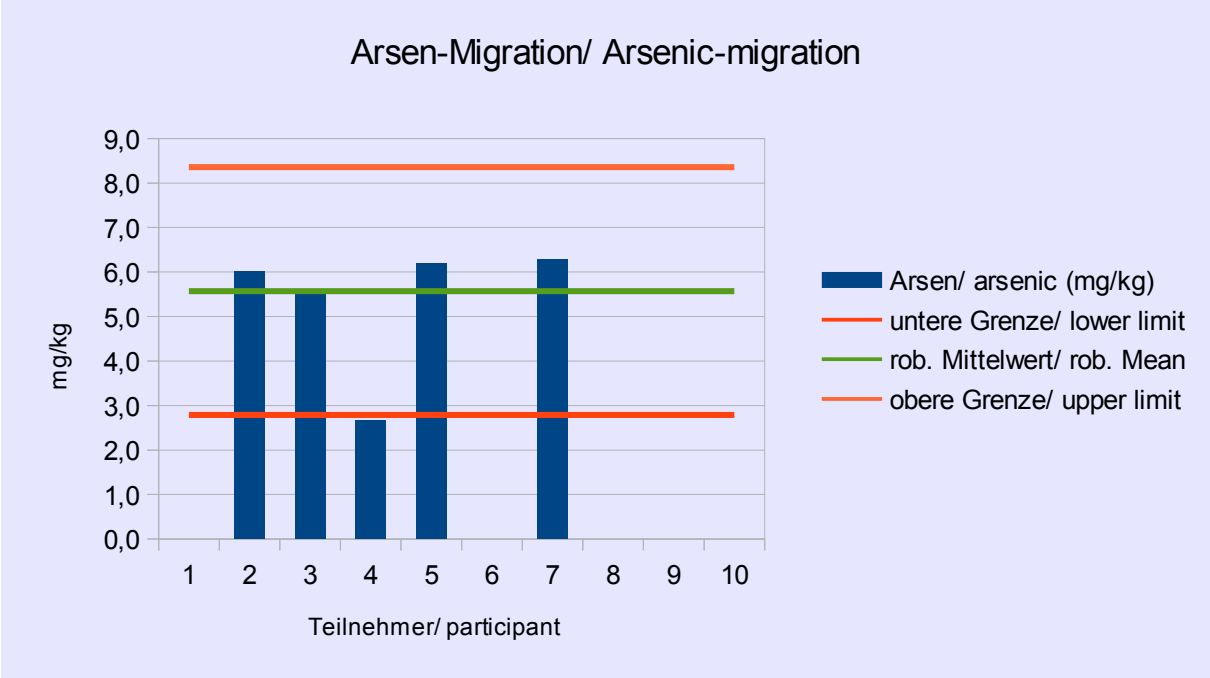
In the lower table - Laboratories - the individual results of the participating laboratories are listed:

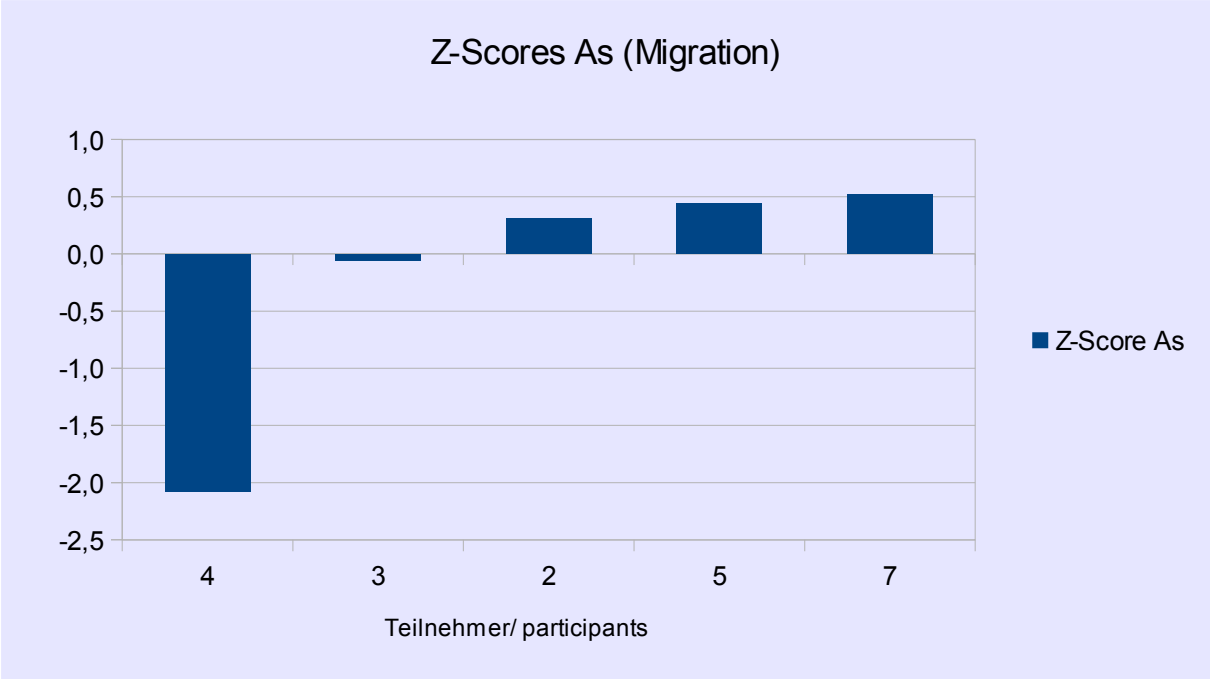
Evaluation number	Result	Deviation	z-Score	Remarks

4.1.1 Arsenic

4.1.1 Arsenic migration in mg/kg

Characteristics	
Number of results	5
Number of outliers	1
Mean	5,3
Median	6,0
Robust mean (X)	5,6
Robust standard deviation (S^x)	1,1
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	1,4
Lower limit of target range (X - 2 $\hat{\sigma}$)	2,8
Upper limit of target range (X + 2 $\hat{\sigma}$)	8,3
Quotient $S^x/\hat{\sigma}$	0,8
standard uncertainty u_x	0,62
Quotient $u_X/\hat{\sigma}$	0,45
Number of results in the target range	4 (80%)



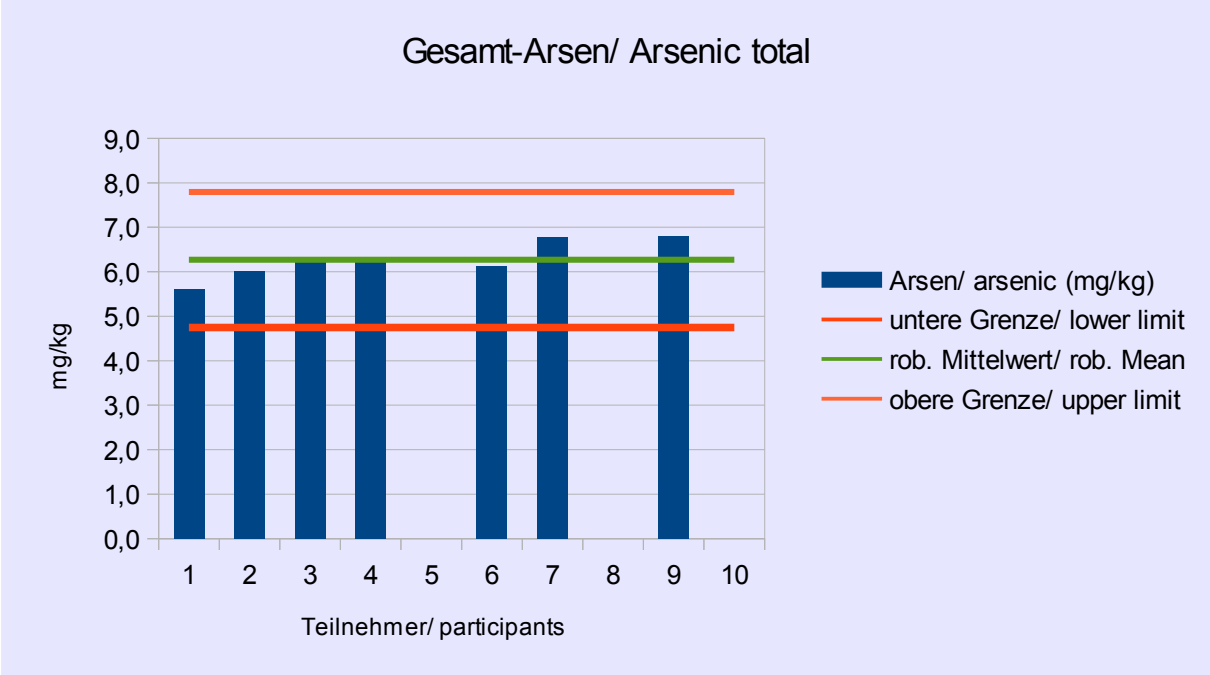


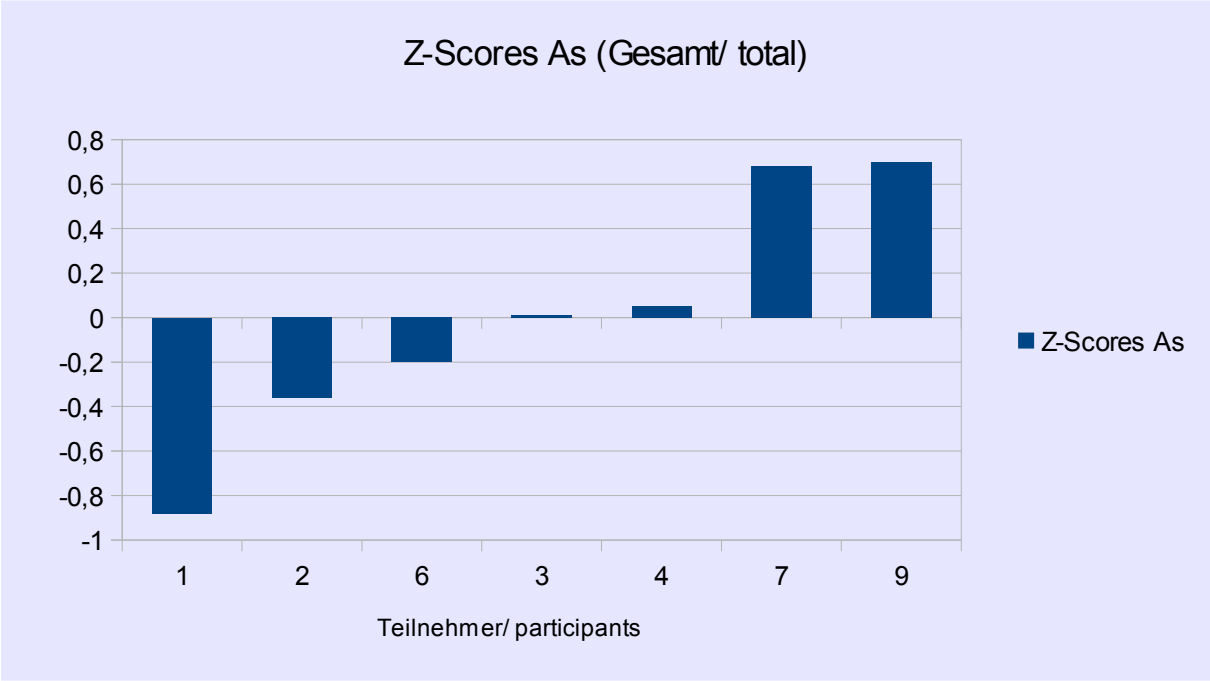
Laboratories

Teilnehmer/ participant	Arsen/ arsenic	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	6	0,43	0,3	
3	5,49	-0,08	-0,1	
4	2,67	-2,90	**-2,1**	**Ausreißer/ outlier**
5	6,18	0,61	0,4	
7	6,29	0,72	0,5	

4.1.2 Arsenic total in mg/kg

Characteristics	
Number of results	7
Number of outliers	0
Mean	6,3
Median	6,3
Robust mean (X)	6,3
Robust standard deviation (S^x)	0,49
Target standard deviation($\hat{\sigma}$)(Horwitz)	0,76
Lower limit of target range (X - 2 $\hat{\sigma}$)	4,7
Upper limit of target range (X + 2 $\hat{\sigma}$)	7,8
Quotient $S^x/\hat{\sigma}$	0,6
standard uncertainty u_x	0,23
Quotient $u_X/\hat{\sigma}$	0,3
Number of results in the target range	7 (100%)





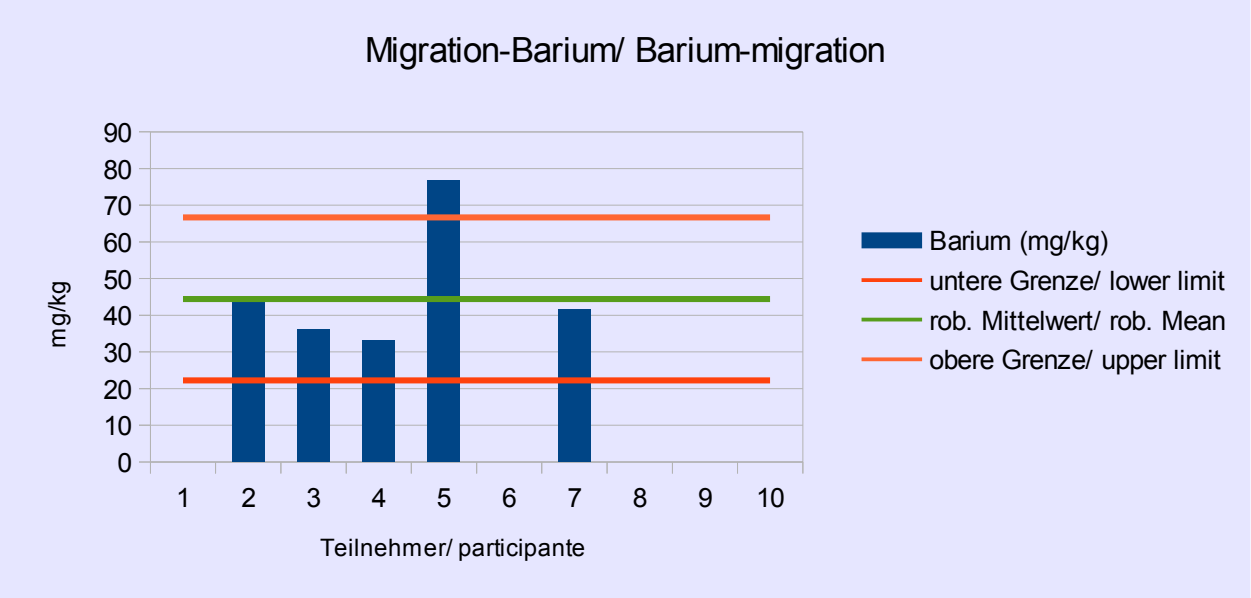
Laboratories

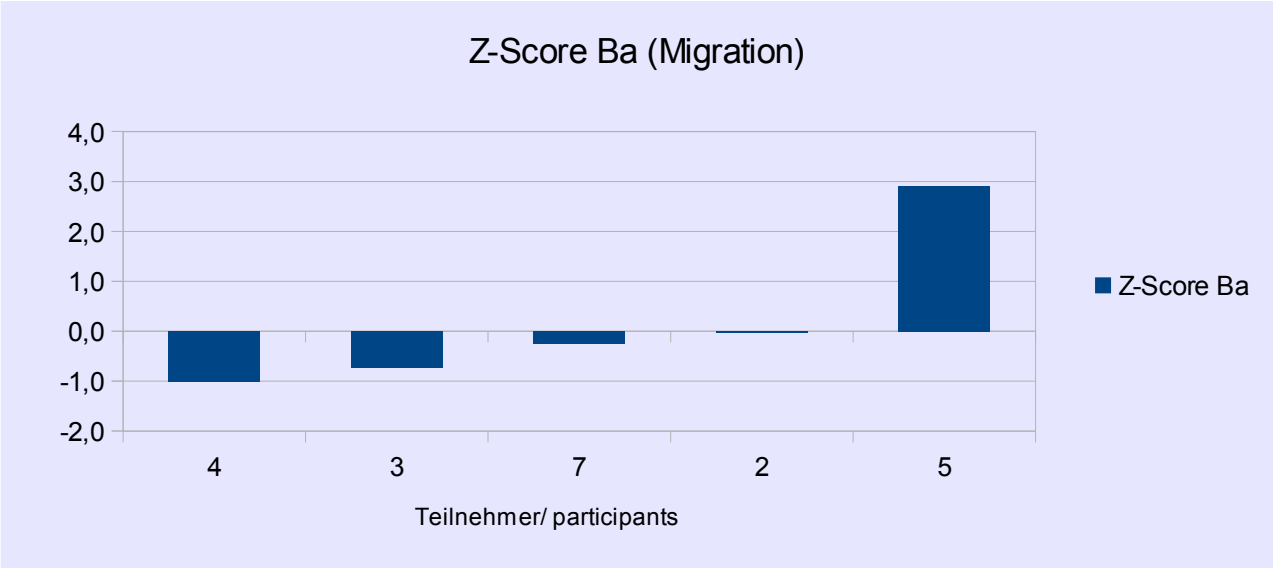
Teilnehmer/ participants	Arsen/ Arsenic	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
1	5,60	-0,67	-0,9	
2	6,00	-0,27	-0,36	
3	6,28	0,01	0,01	
4	6,31	0,04	0,05	
6	6,12	-0,16	-0,20	
7	6,79	0,52	0,68	
9	6,80	0,53	0,7	

4.2 Barium

4.2.1 Barium-migration in mg/kg

Characteristics	
Number of results	5
Number of outliers	1
Mean	46,4
Median	41,7
Robust mean (X)	44,4
Robust standard deviation (S^x)	15,2
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	11,1
Lower limit of target range (X - 2 $\hat{\sigma}$)	22,2
Upper limit of target range (X + 2 $\hat{\sigma}$)	66,7
Quotient $S^x/\hat{\sigma}$	1,4
standard uncertainty u_x	8,5
Quotient $u_X/\hat{\sigma}$	0,76
Number of results in the target range	4 (80%)



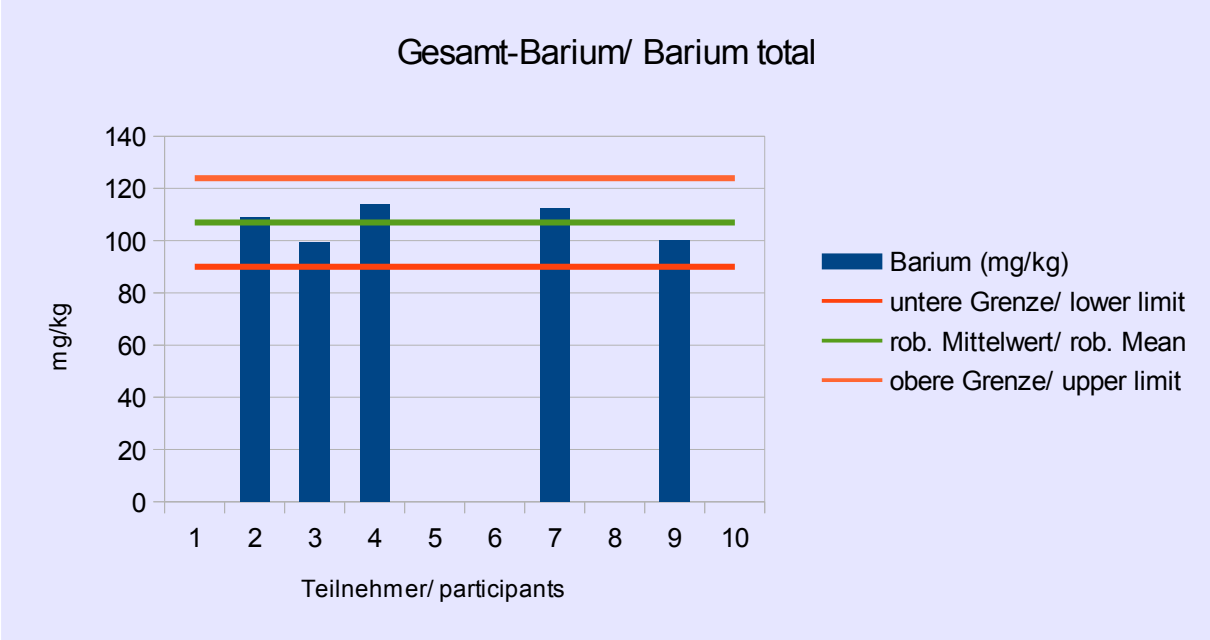


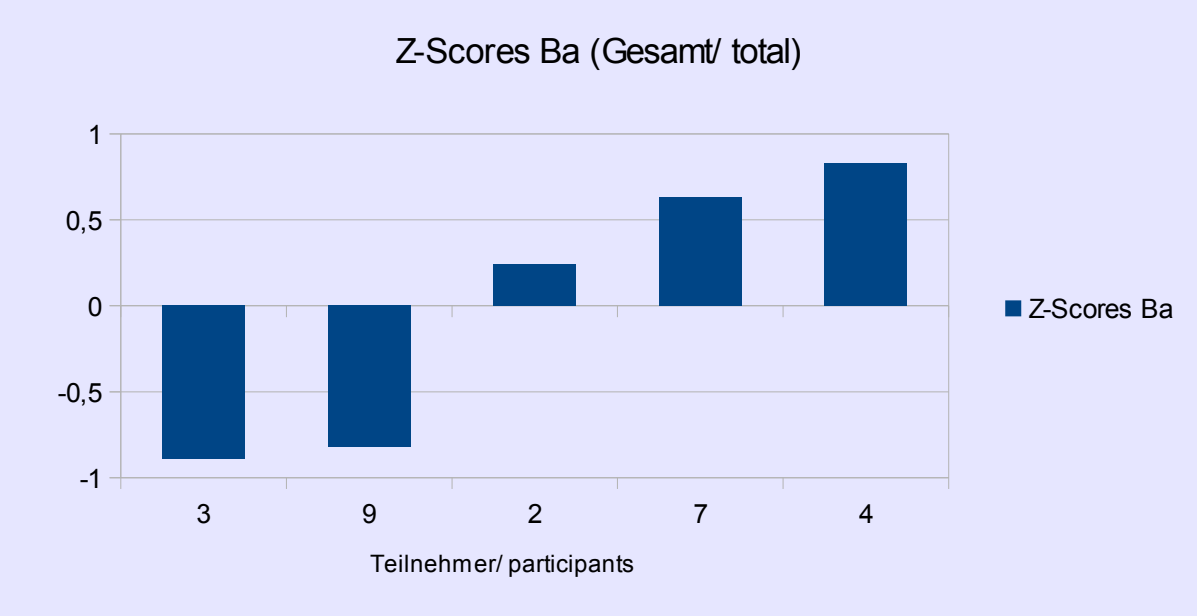
Laboratories

Teilnehmer/ participants	Barium	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	44,00	-0,45	0,0	
3	36,20	-8,25	-0,7	
4	33,20	-11,25	-1,0	
5	76,78	32,33	**2,9**	**Ausreißer/ outlier**
7	41,70	-2,75	-0,2	

4.2.2 Barium total in mg/kg

Characteristics	
Number of results	5
Number of outliers	0
Mean	107
Median	109
Robust mean (X)	107
Robust standard deviation (S^x)	7,8
Target standard deviation($\hat{\sigma}$)(Horwitz)	8,5
Lower limit of target range (X - 2 $\hat{\sigma}$)	90,0
Upper limit of target range (X + 2 $\hat{\sigma}$)	124
Quotient $S^x/\hat{\sigma}$	0,9
standard uncertainty u_x	4,3
Quotient $u_X/\hat{\sigma}$	0,5
Number of results in the target range	5 (100%)





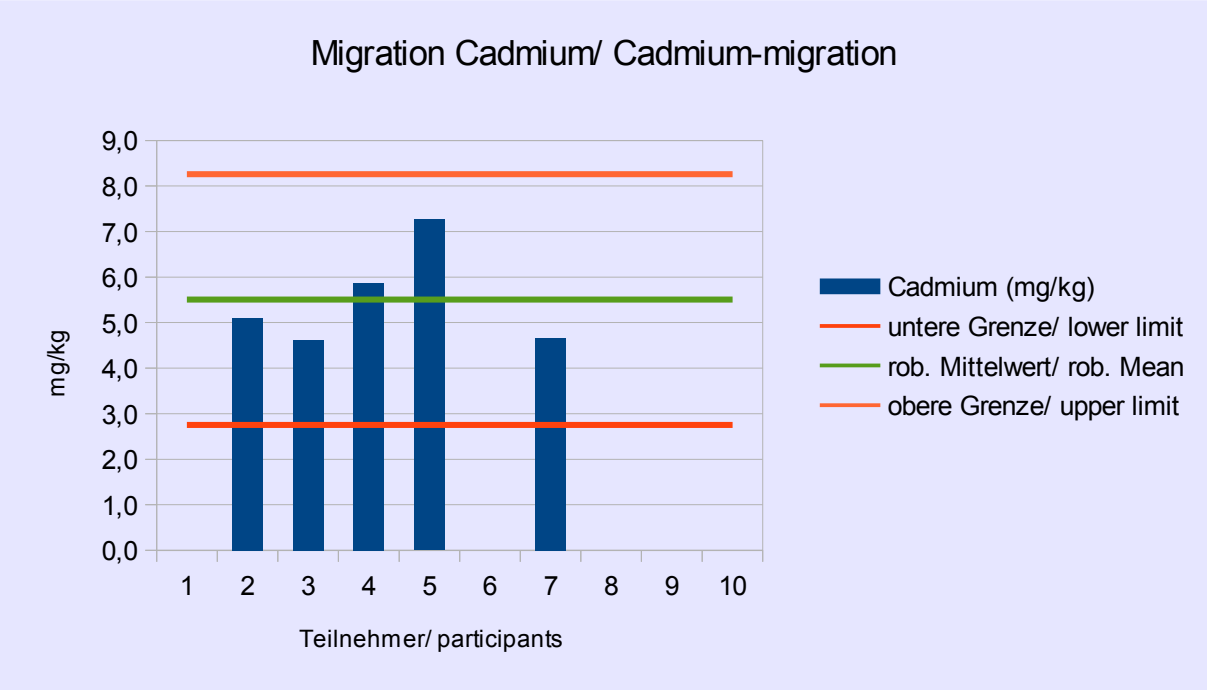
Laboratories

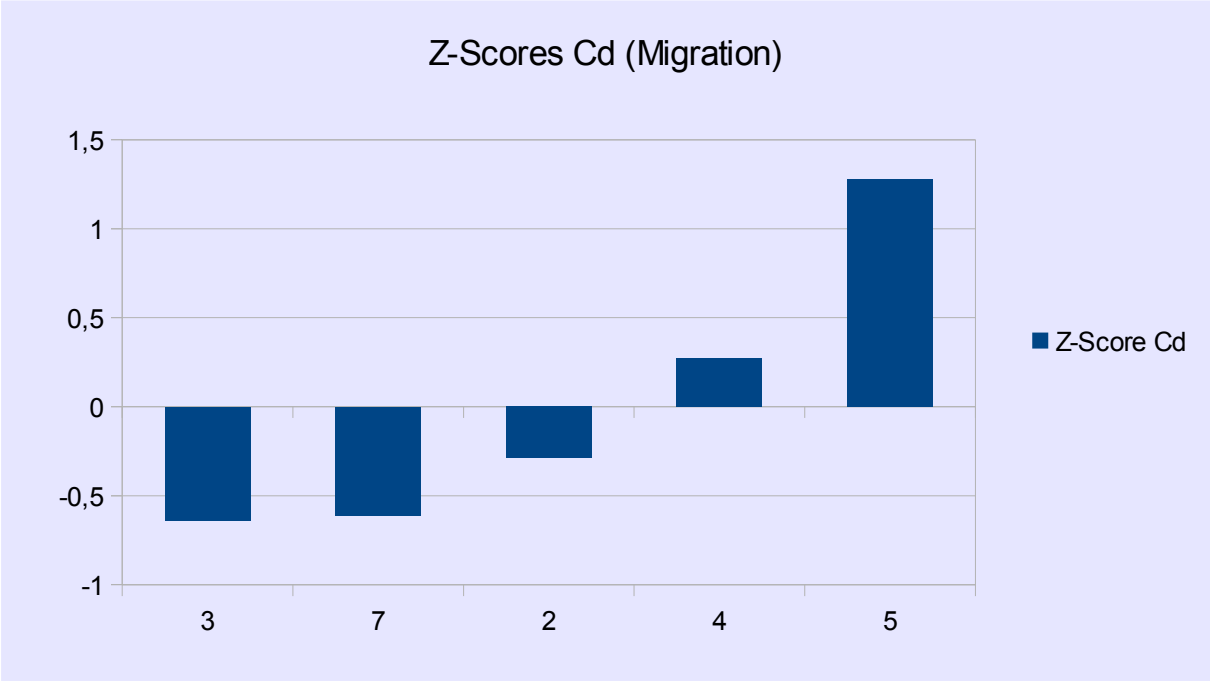
Teilnehmer/ participants	Barium	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	109	2,06	0,24	
3	99,4	-7,54	-0,89	
4	114	7,06	0,83	
7	112,3	5,36	0,63	
9	100	-6,94	-0,8	

4.3 Cadmium

4.3.1 Cadmium-migration in mg/kg

Characteristics	
Number of results	5
Number of outliers	0
Mean	5,5
Median	5,1
Robust mean (X)	5,5
Robust standard deviation (S^x)	1,3
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	1,4
Lower limit of target range (X - 2 $\hat{\sigma}$)	2,75
Upper limit of target range (X + 2 $\hat{\sigma}$)	8,26
Quotient $S^x/\hat{\sigma}$	0,9
standard uncertainty u_x	0,70
Quotient $u_X/\hat{\sigma}$	0,5
Number of results in the target range	5 (100%)



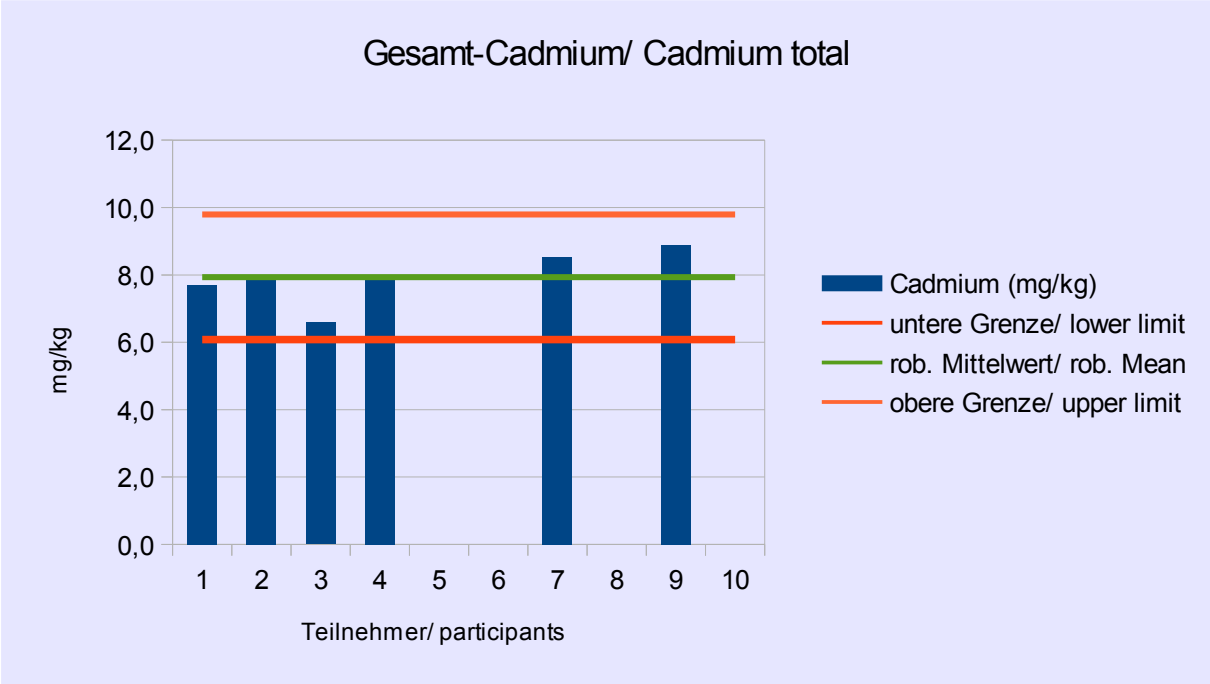


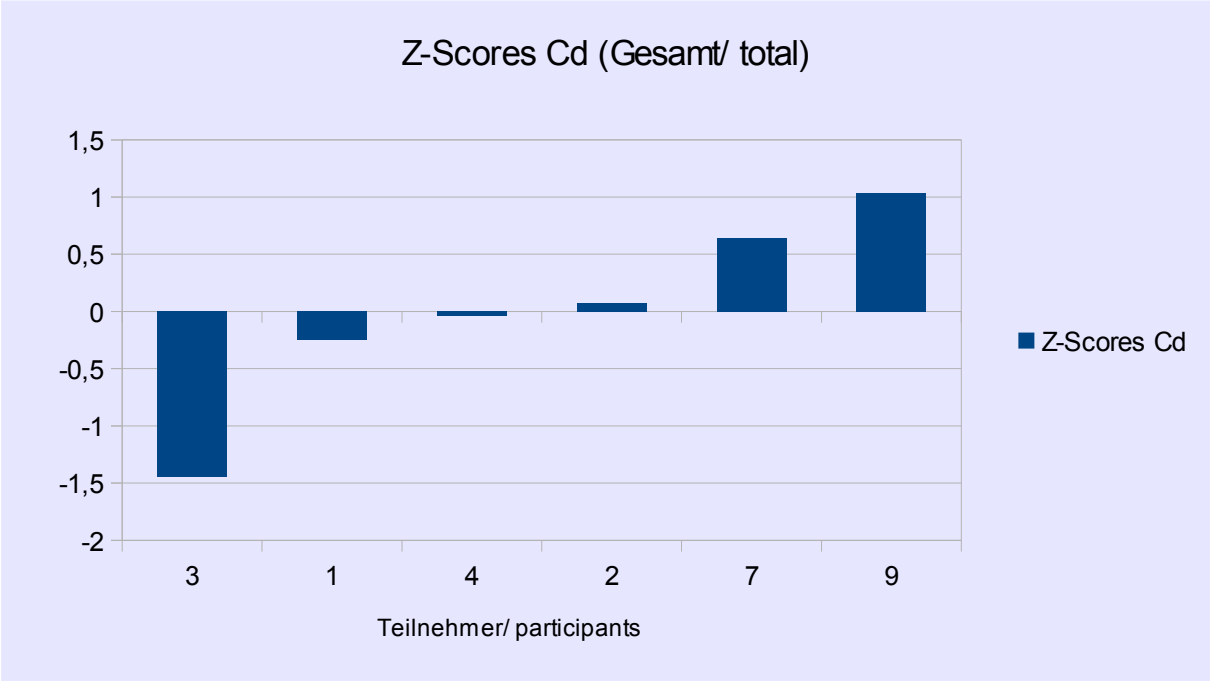
Laboratories

Teilnehmer/ participants	Cadmium	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	5,10	-0,40	-0,3	
3	4,62	-0,88	-0,6	
4	5,87	0,37	0,3	
5	7,26	1,76	1,3	
7	4,67	-0,83	-0,6	

4.3.2 Cadmium total in mg/kg

Characteristics	
Number of results	6
Number of outliers	0
Mean	7,9
Median	8,0
Robust mean (X)	7,9
Robust standard deviation (S^x)	0,9
Target standard deviation($\hat{\sigma}$)(Horwitz)	0,9
Lower limit of target range (X - 2 $\hat{\sigma}$)	6,1
Upper limit of target range (X + 2 $\hat{\sigma}$)	9,8
Quotient $S^x/\hat{\sigma}$	1,0
standard uncertainty u_x	0,50
Quotient $u_X/\hat{\sigma}$	0,5
Number of results in the target range	6 (100%)





Laboratories

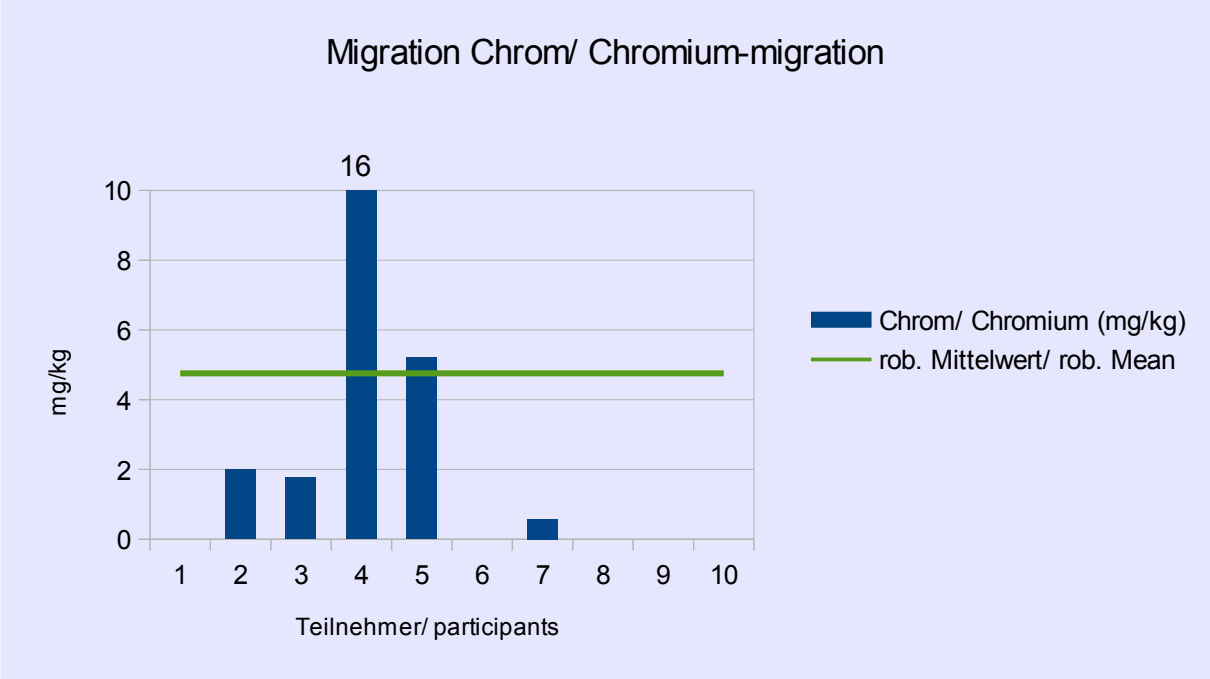
Teilnehmer/ participants	Cadmium	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
1	7,70	-0,24	-0,3	
2	8,00	0,06	0,07	
3	6,59	-1,35	-1,4	
4	7,90	-0,04	0,0	
7	8,53	0,59	0,6	
9	8,90	0,96	1,0	

4.4 Chromium

4.4.1 Chromium-migration in mg/kg

There were only 5 results showing a high variance. The results are only given for information and without an evaluation.

Characteristics	
Number of results	5
Number of outliers	-
Mean	5,1
Median	2,0
Robust mean (X)	4,7
Robust standard deviation (S^x)	6,3
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	1,2
Lower limit of target range (X - 2 $\hat{\sigma}$)	-
Upper limit of target range (X + 2 $\hat{\sigma}$)	-
Quotient $S^x/\hat{\sigma}$	-
standard uncertainty u_x	-
Quotient $u_X/\hat{\sigma}$	-
Number of results in the target range	-

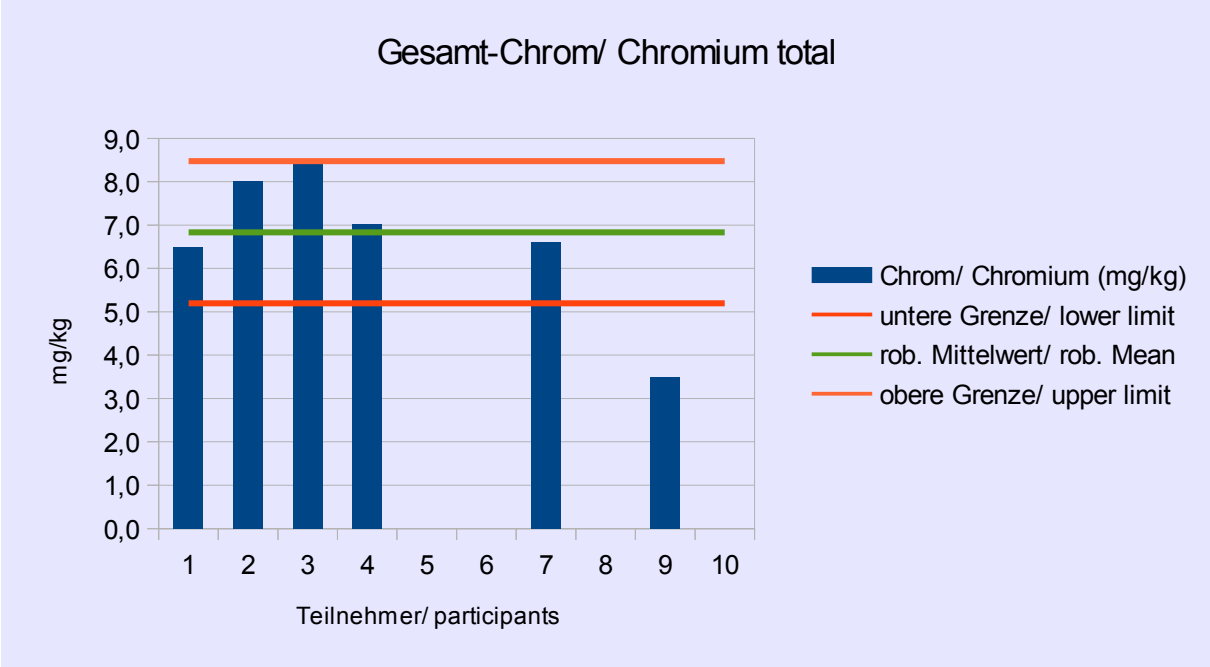


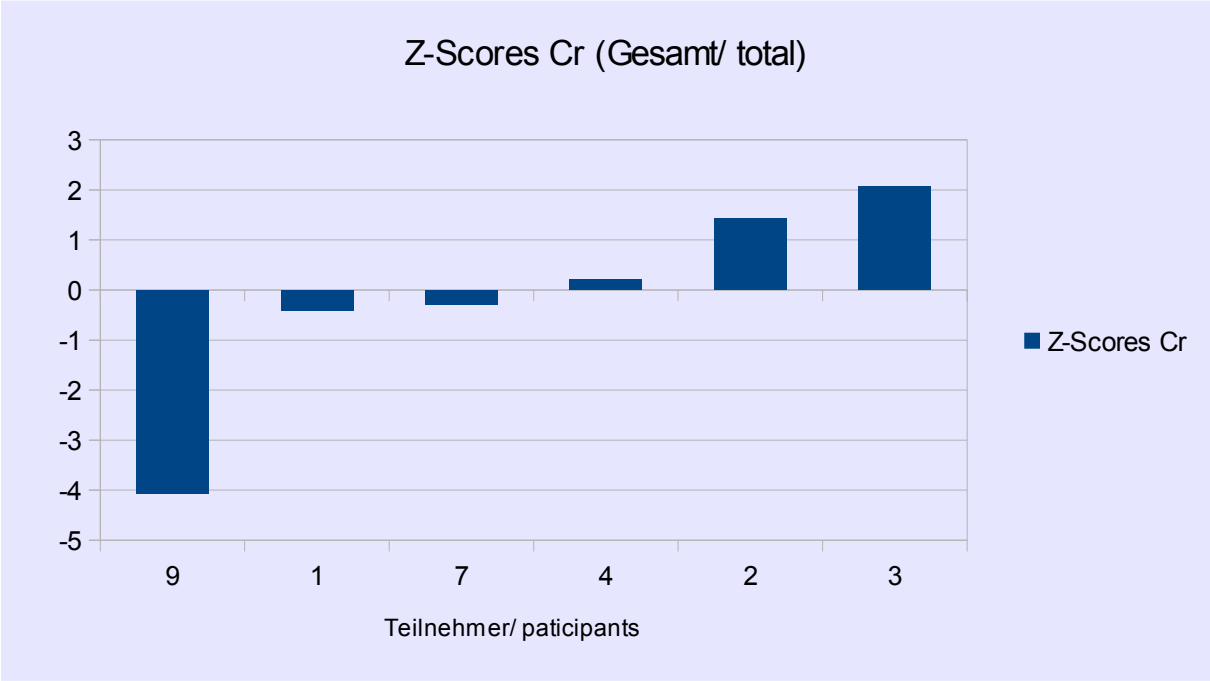
Laboratories

Teilnehmer/ participant	Chrom/ Chromium	Abweichung/ deviation	Z-Score	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	2,00	-2,75	-	
3	1,77	-2,98	-	
4	16,00	11,30	-	
5	5,22	0,47	-	
7	0,57	-4,18	-	

4.4.2 Chromium total in mg/kg

Characteristics	
Number of results	6
Number of outliers	1
Mean	6,7
Median	6,8
Robust mean (X)	6,8
Robust standard deviation (S^x)	1,6
Target standard deviation($\hat{\sigma}$)(Horwitz)	0,82
Lower limit of target range (X - 2 $\hat{\sigma}$)	5,2
Upper limit of target range (X + 2 $\hat{\sigma}$)	8,5
Quotient $S^x/\hat{\sigma}$	2,0
standard uncertainty u_x	0,83
Quotient $u_X/\hat{\sigma}$	1,0
Number of results in the target range	4 (67%)





Laboratories

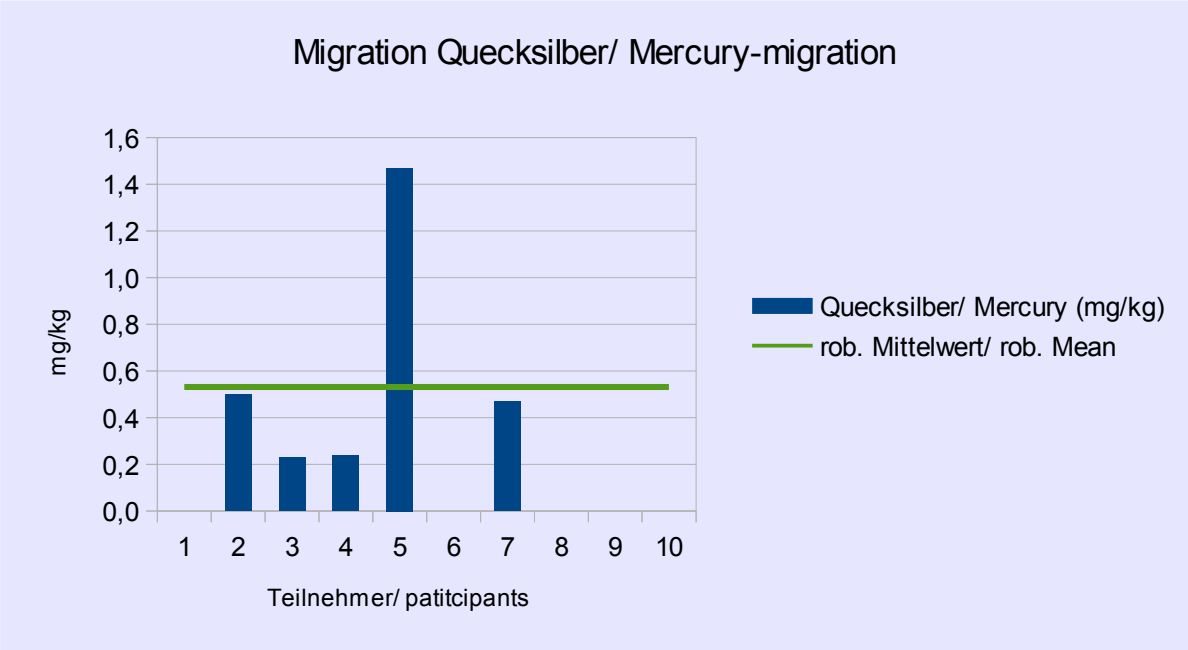
Teilnehmer/ participant	Chrom/ Chromium	Abweichung/ deviation	Z-Scores	Bermerkungen/ remarks
	mg/kg	mg/kg		
1	6,50	-0,33	-0,4	
2	8,00	1,17	1,4	
3	8,52	1,69	**2,1**	
4	7,01	0,18	0,2	
7	6,60	-0,23	-0,3	
9	3,50	-3,33	**-4,1**	**Ausreißer/ outlier**

4.5 Mercury

4.5.1 Mercury-migration in mg/kg

There were only 5 results showing a high variance. The results are only given for information and without an evaluation.

Characteristics	
Number of results	5
Number of outliers	-
Mean	0,58
Median	0,47
Robust mean (X)	0,53
Robust standard deviation (S^x)	0,46
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	0,13
Lower limit of target range (X - 2 $\hat{\sigma}$)	-
Upper limit of target range (X + 2 $\hat{\sigma}$)	-
Quotient $S^x/\hat{\sigma}$	-
standard uncertainty u_x	-
Quotient $u_X/\hat{\sigma}$	-
Number of results in the target range	-

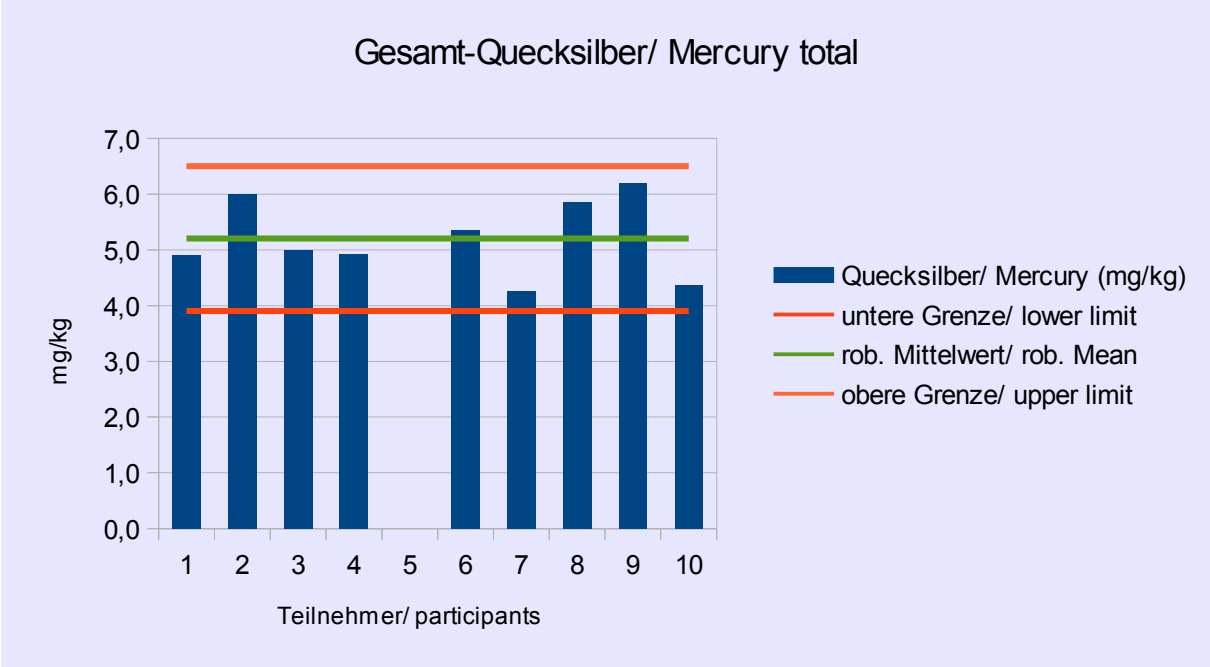


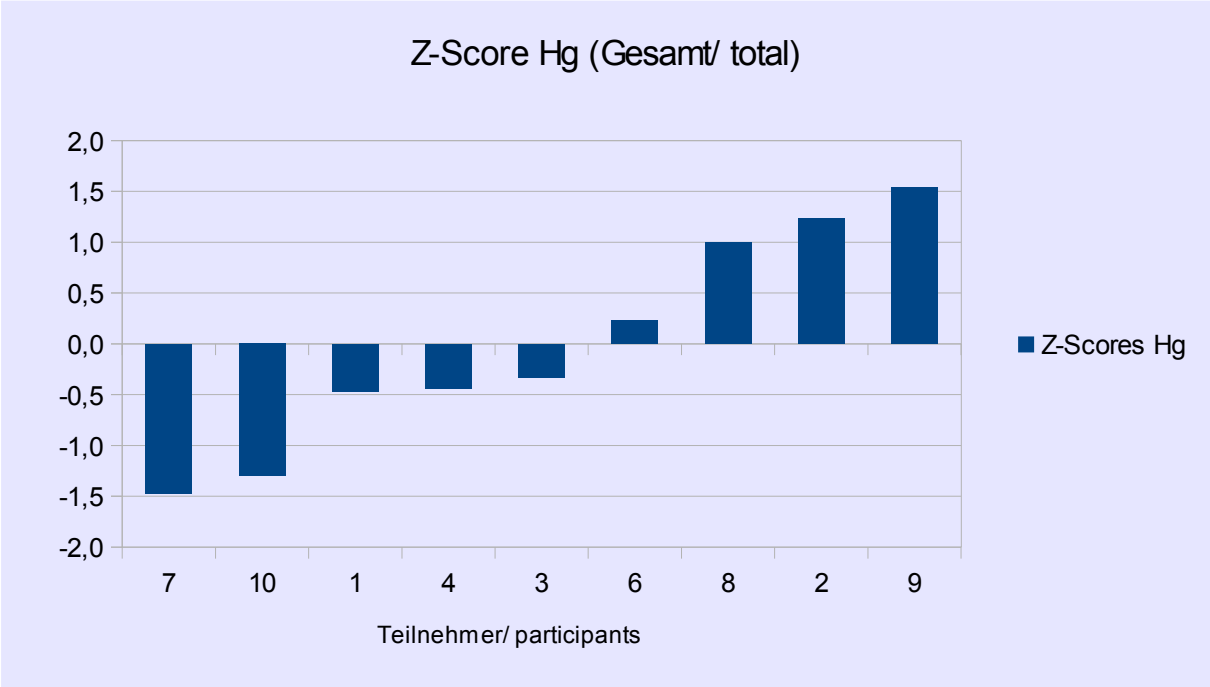
Laboratories

Teilnehmer/ participant	Quecksilber/ Mercury	Abweichung/ deviatin	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	0,50	-0,03	-	
3	0,23	-0,30	-	
4	0,24	-0,29	-	
5	1,47	0,94	-	
7	0,47	-0,06	-	

4.5.2 Mercury total in mg/kg

Characteristics	
Number of results	9
Number of outliers	0
Mean	5,2
Median	5,0
Robust mean (X)	5,2
Robust standard deviation (S^x)	0,79
Target standard deviation($\hat{\sigma}$)(Horwitz)	0,65
Lower limit of target range (X - 2 $\hat{\sigma}$)	3,9
Upper limit of target range (X + 2 $\hat{\sigma}$)	6,5
Quotient $S^x/\hat{\sigma}$	1,2
standard uncertainty u_x	0,33
Quotient $u_X/\hat{\sigma}$	0,51
Number of results in the target range	9 (100%)





Laboratories

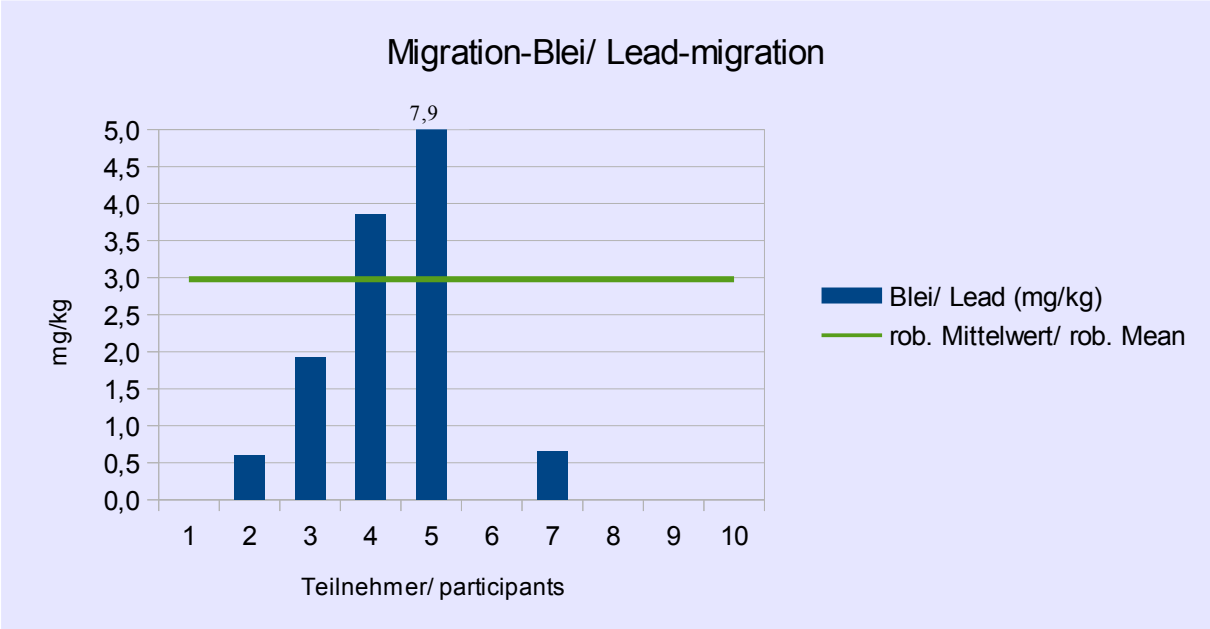
Teilnehmer/ participant	Quecksilber/ Mercury	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
1	4,90	-0,30	-0,5	
2	6,00	0,80	1,23	
3	4,99	-0,21	-0,33	
4	4,92	-0,28	-0,44	
6	5,36	0,15	0,23	
7	4,25	-0,95	-1,47	
8	5,85	0,65	1,00	
9	6,20	1,00	1,5	
10	4,36	-0,84	-1,3	

4.6 Lead

4.6.1 Lead-migration in mg/kg

There were only 5 results showing a high variance. The results are only given for information and without an evaluation.

Characteristics	
Number of results	5
Number of outliers	-
Mean	3,0
Median	1,9
Robust mean (X)	3,0
Robust standard deviation (S^x)	3,4
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	0,7
Lower limit of target range (X - 2 $\hat{\sigma}$)	-
Upper limit of target range (X + 2 $\hat{\sigma}$)	-
Quotient $S^x/\hat{\sigma}$	-
standard uncertainty u_x	-
Quotient $u_X/\hat{\sigma}$	-
Number of results in the target range	-

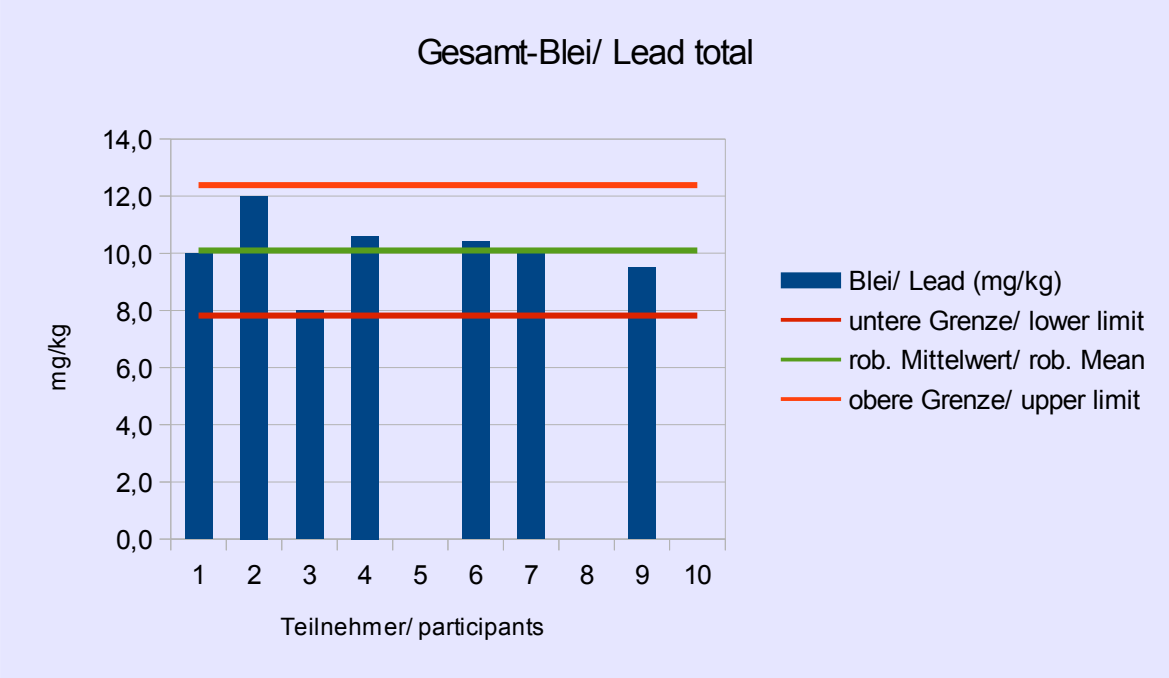


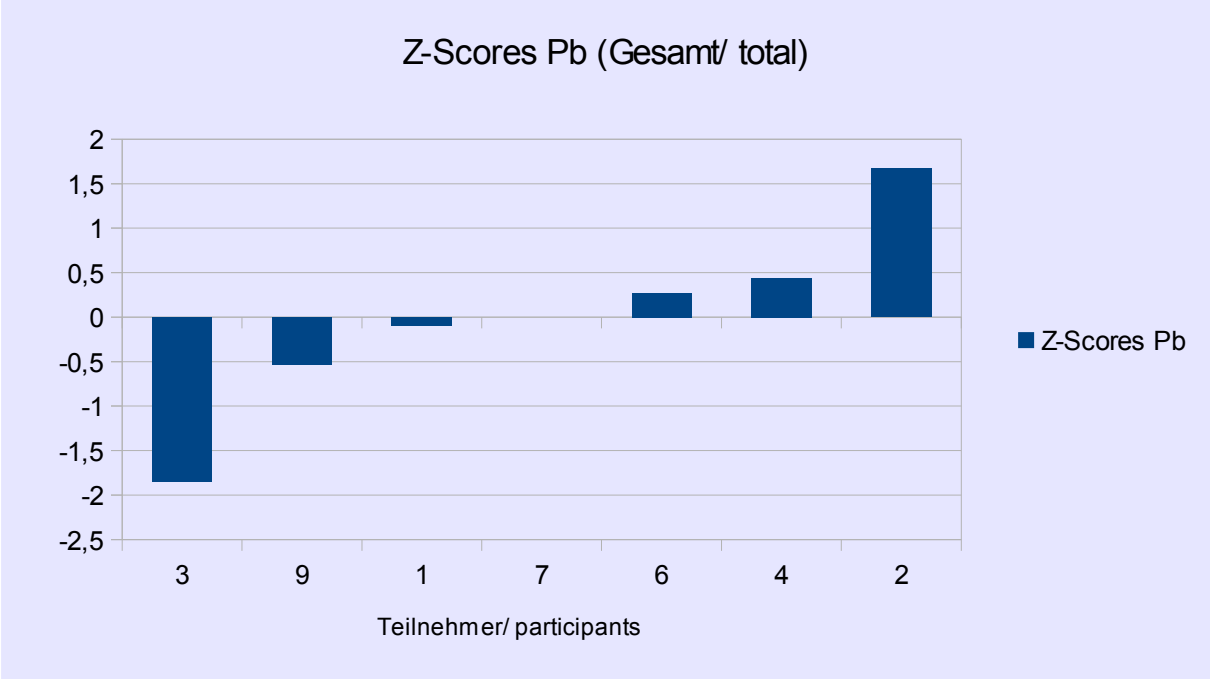
Laboratories

Teilnehmer/ participant	Blei/ Lead	Abweichung/ deviation	Z-Scores	Bemer- kungen/ remarks
	mg/kg	mg/kg		
2	0,6	-2,38	-	
3	1,92	-1,06	-	
4	3,86	0,88	-	
5	7,86	4,88	-	
7	0,65	-2,33	-	

4.6.2 Lead total in mg/kg

Characteristics	
Number of results	7
Number of outliers	0
Mean	10,1
Median	10,1
Robust mean (X)	10,1
Robust standard deviation (S^x)	1,3
Target standard deviation($\hat{\sigma}$)(Horwitz)	1,1
Lower limit of target range (X - 2 $\hat{\sigma}$)	7,8
Upper limit of target range (X + 2 $\hat{\sigma}$)	12,4
Quotient $S^x/\hat{\sigma}$	1,2
standard uncertainty u_x	0,63
Quotient $u_X/\hat{\sigma}$	0,55
Number of results in the target range	7 (100%)





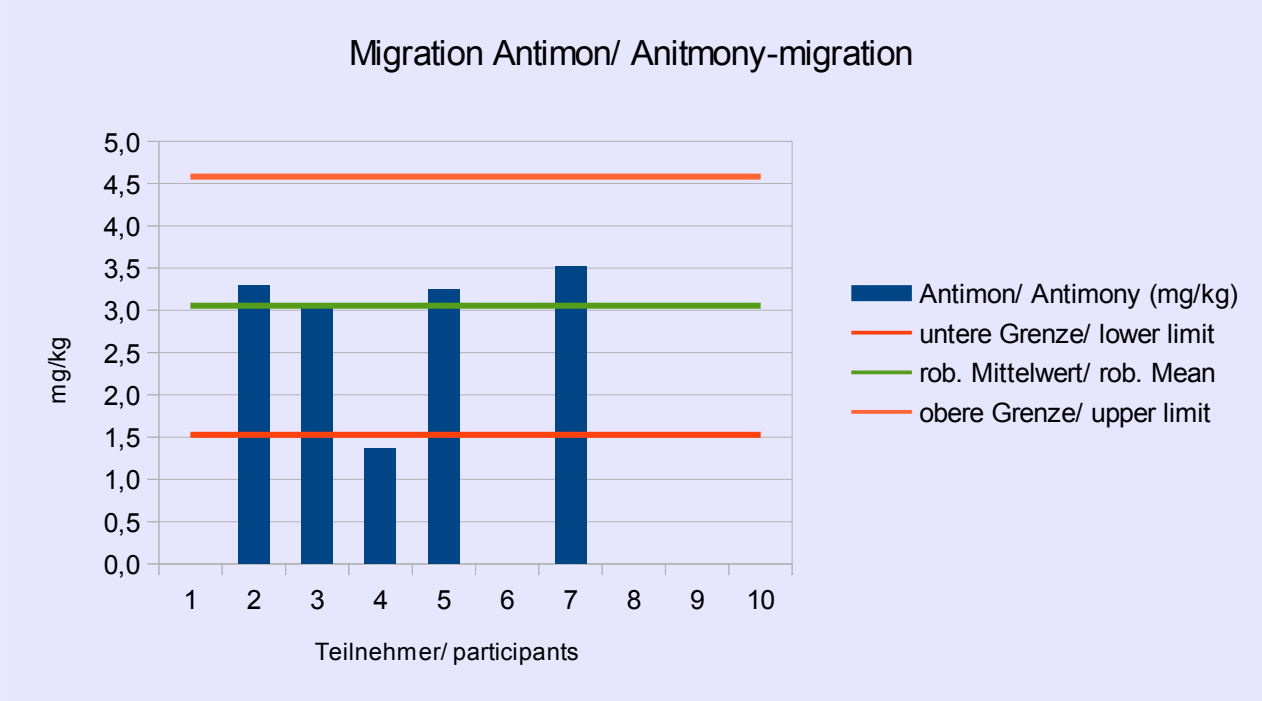
Laboratories

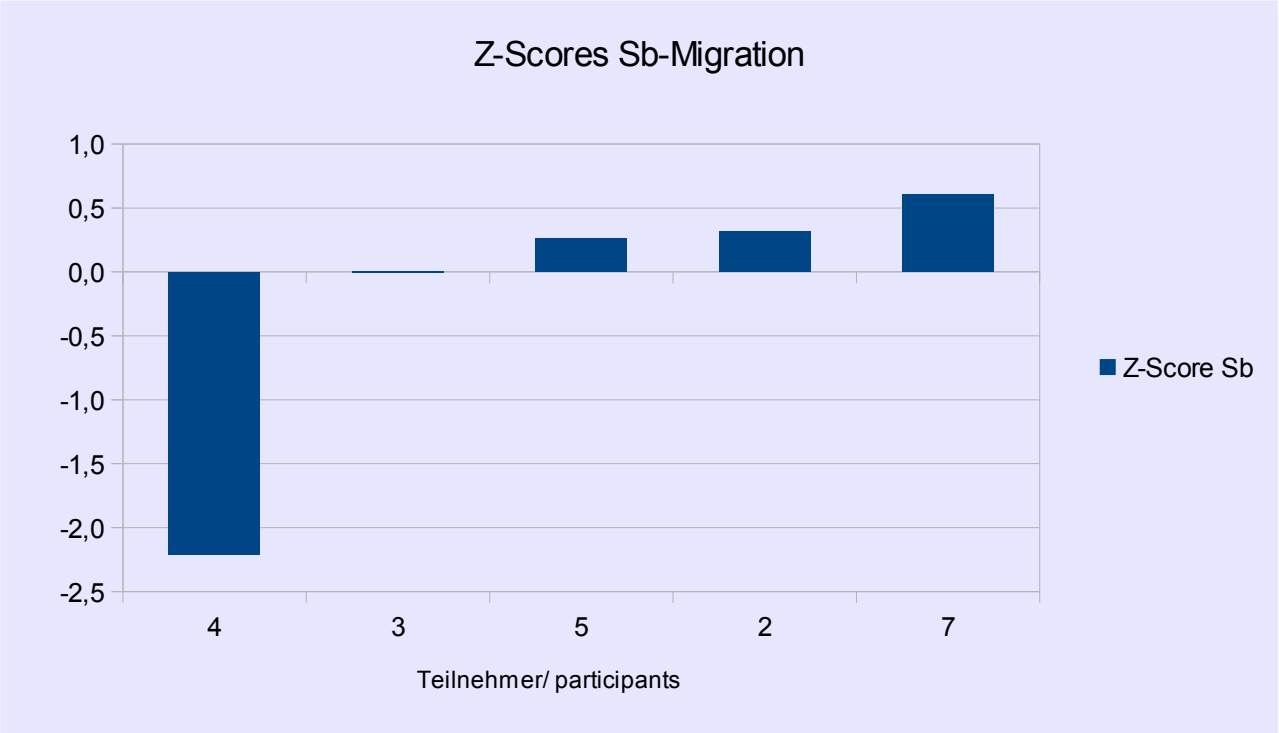
Teilnehmer/ participant	Blei/ Lead	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
1	10,0	-0,10	-0,1	
2	12,0	1,90	1,67	
3	8,0	-2,11	-1,85	
4	10,6	0,50	0,44	
6	10,4	0,31	0,27	
7	10,1	0,00	0,00	
9	9,5	-0,60	-0,53	

4.7 Antimony

4.7.1 Antimony-migration in mg/kg

Characteristics	
Number of results	5
Number of outliers	1
Mean	2,9
Median	3,3
Robust mean (X)	3,1
Robust standard deviation (S^x)	0,60
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	0,76
Lower limit of target range (X - 2 $\hat{\sigma}$)	1,5
Upper limit of target range (X + 2 $\hat{\sigma}$)	4,6
Quotient $S^x/\hat{\sigma}$	0,8
standard uncertainty u_x	0,34
Quotient $u_X/\hat{\sigma}$	0,44
Number of results in the target range	4 (80%)



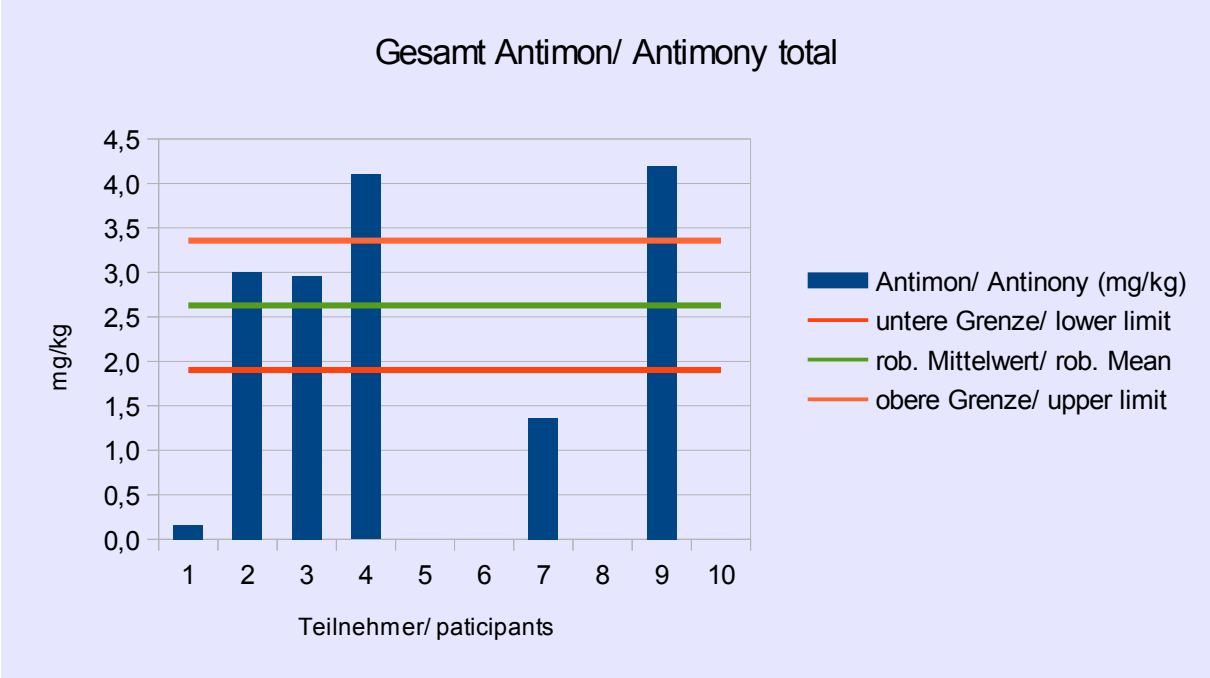


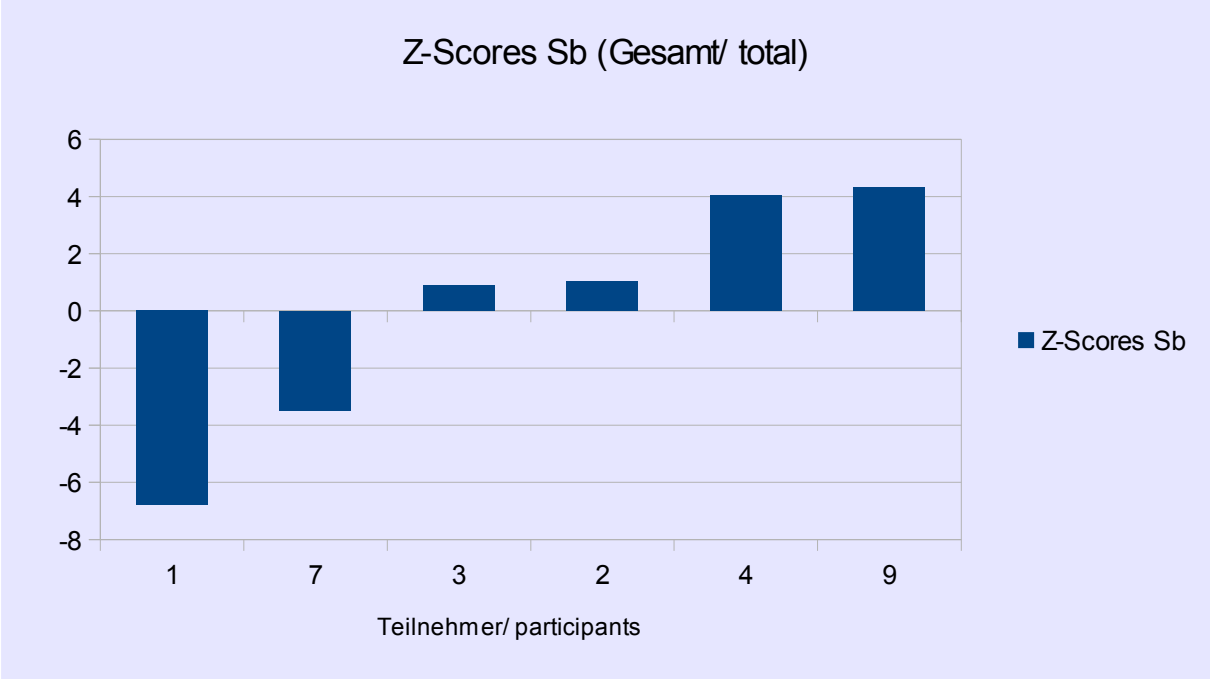
Laboratories

Teilnehmer/ participant	Antimon/ Antimony	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	3,30	0,25	0,3	
3	3,05	0,00	0,0	
4	1,37	-1,68	**-2,2**	**Ausreißer/ outlier**
5	3,25	0,20	0,3	
7	3,52	0,47	0,6	

4.7.2 Antimony total in mg/kg

Characteristics	
Number of results	6
Number of outliers	0
Mean	2,6
Median	3,0
Robust mean (X)	2,6
Robust standard deviation (S^x)	2,0
Target standard deviation($\hat{\sigma}$)(Horwitz)	0,36
Lower limit of target range (X - 2 $\hat{\sigma}$)	1,9
Upper limit of target range (X + 2 $\hat{\sigma}$)	3,4
Quotient $S^x/\hat{\sigma}$	4,9
standard uncertainty u_x	0,92
Quotient $u_X/\hat{\sigma}$	2,5
Number of results in the target range	2 (33%)





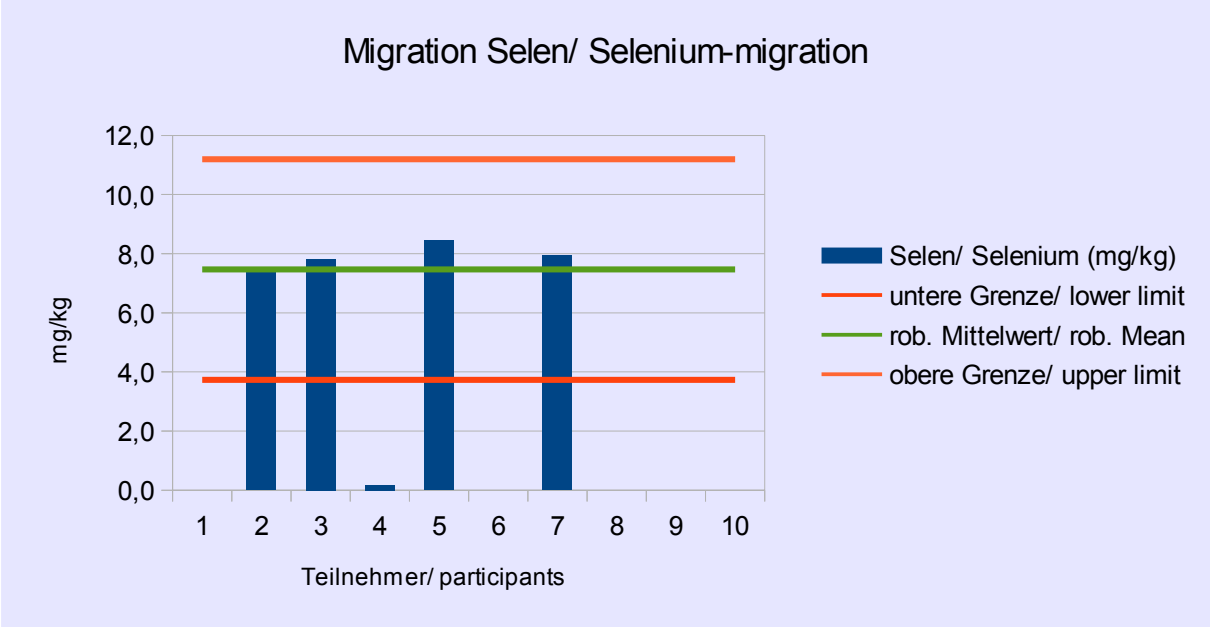
Laboratories

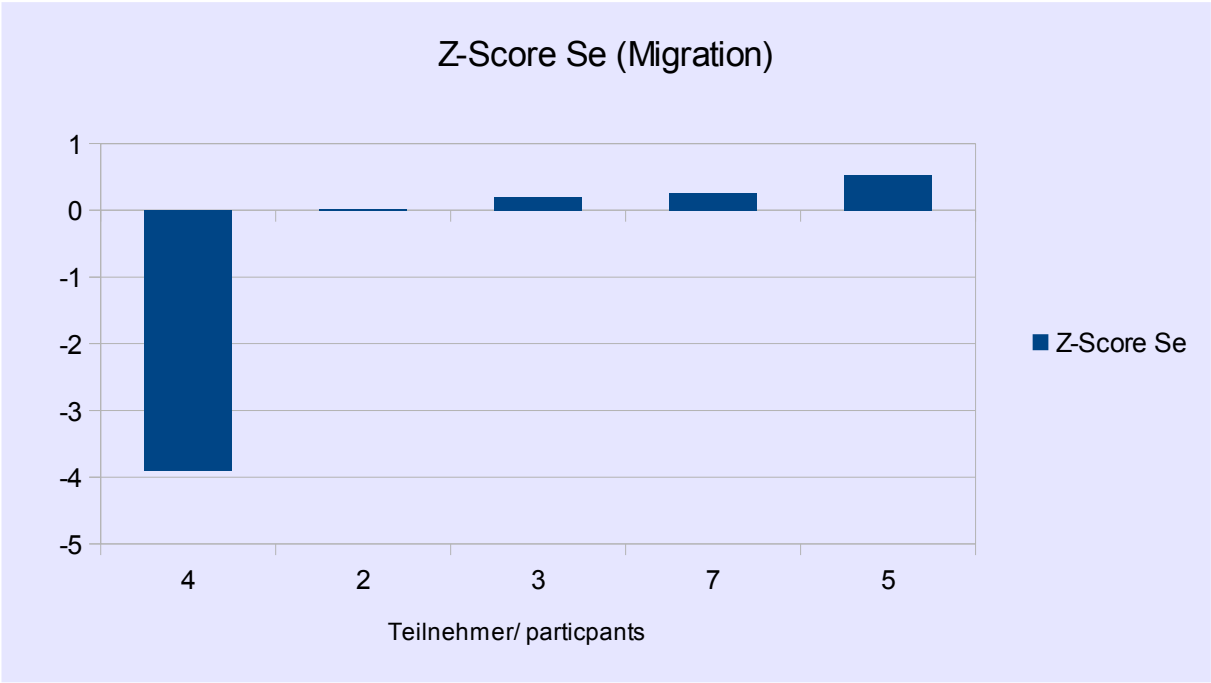
Teilnehmer/ participant	Antimon/ Antinony	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
1	0,16	-2,47	**-6,8**	
2	3,00	0,37	1,02	
3	2,96	0,33	0,9	
4	4,10	1,47	**4,0**	
7	1,36	-1,27	**-3,5**	
9	4,20	1,57	**4,3**	

4.8 Selenium

4.8.1 Selenium-migration in mg/kg

Characteristics	
Number of results	5
Number of outliers	1
Mean	6,4
Median	7,8
Robust mean (X)	7,5
Robust standard deviation (S^x)	1,2
Target standard deviation($\hat{\sigma}$)(according to EN 71-3)	1,9
Lower limit of target range (X - 2 $\hat{\sigma}$)	3,7
Upper limit of target range (X + 2 $\hat{\sigma}$)	11,2
Quotient $S^x/\hat{\sigma}$	0,7
standard uncertainty u_x	0,70
Quotient $u_X/\hat{\sigma}$	0,37
Number of results in the target range	4 (80%)



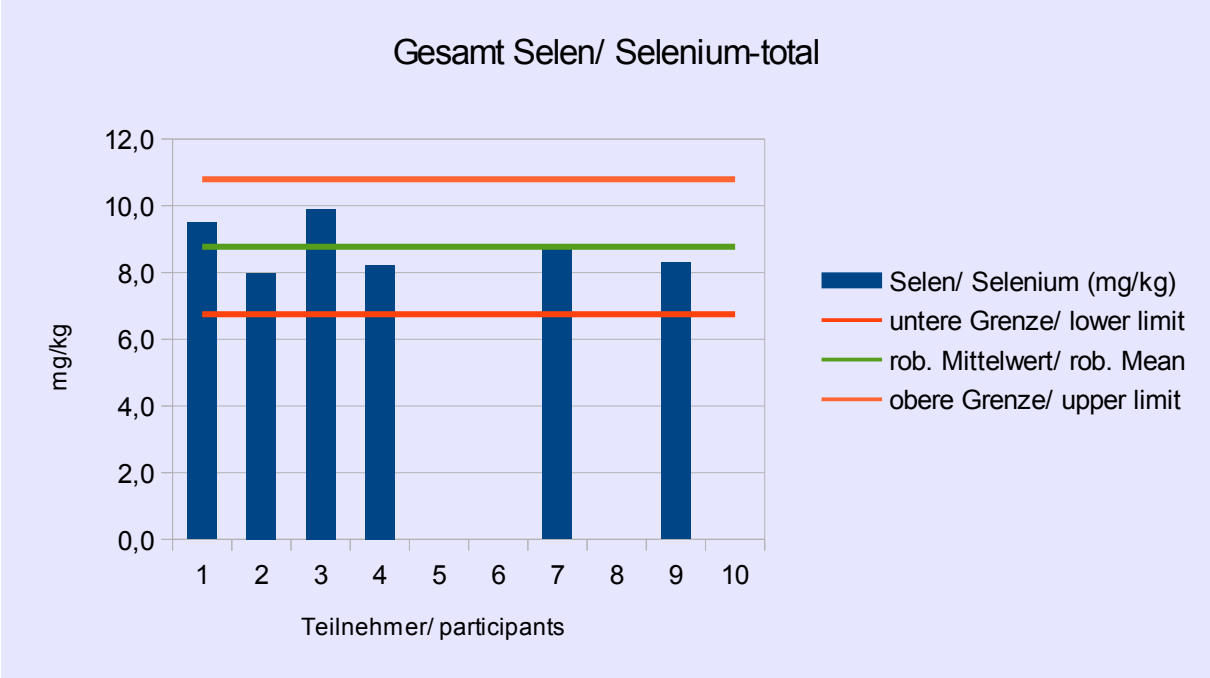


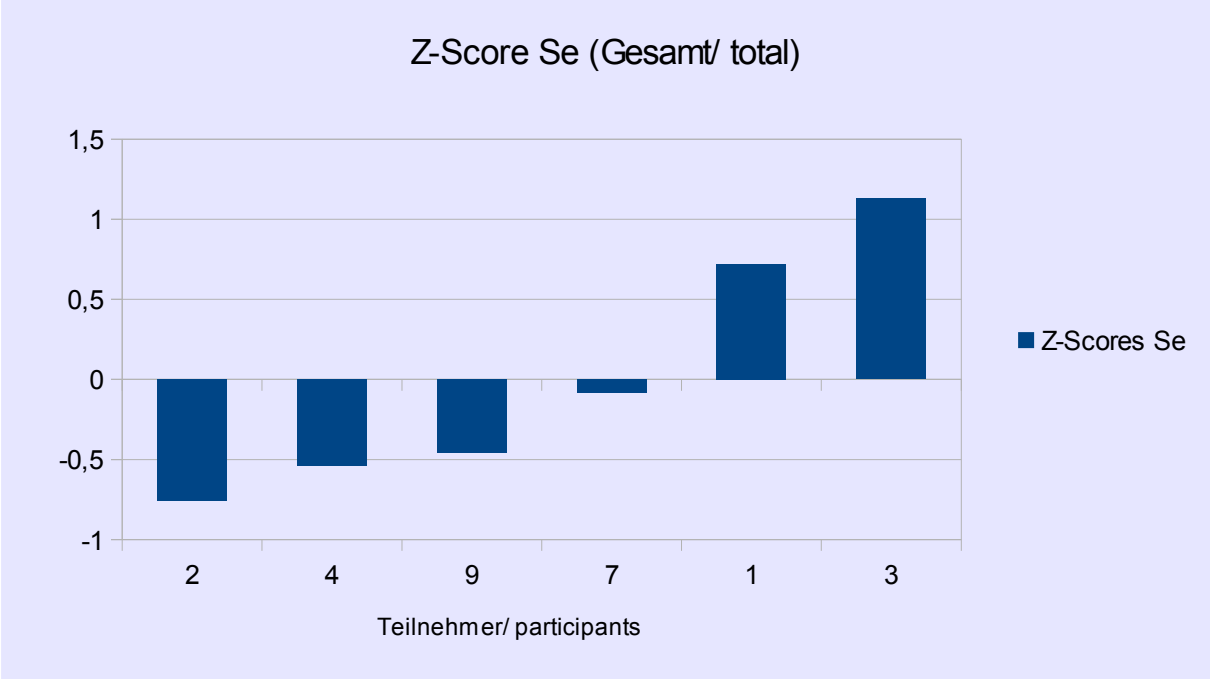
Laboratories

Teilnehmer/ participant	Selen/ Selenium	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
2	7,50	0,04	0,0	
3	7,83	0,37	0,2	
4	0,17	-7,29	**-3,9**	**Ausreißer/ outlier**
5	8,45	0,99	0,5	
7	7,94	0,48	0,3	

4.8.2 Selenium total in mg/kg

Characteristics	
Number of results	6
Number of outliers	0
Mean	8,8
Median	8,5
Robust mean (X)	8,8
Robust standard deviation (S^x)	0,87
Target standard deviation($\hat{\sigma}$)(Horwitz)	1,0
Lower limit of target range (X - 2 $\hat{\sigma}$)	6,7
Upper limit of target range (X + 2 $\hat{\sigma}$)	10,8
Quotient $S^x/\hat{\sigma}$	0,9
standard uncertainty u_x	0,44
Quotient $u_X/\hat{\sigma}$	0,44
Number of results in the target range	6 (100%)





Laboratories

Teilnehmer/ participant	Selen/ Selenium	Abweichung/ deviation	Z-Scores	Bemerkungen/ remarks
	mg/kg	mg/kg		
1	9,50	0,73	0,7	
2	8,00	-0,77	-0,76	
3	9,91	1,14	1,13	
4	8,22	-0,55	-0,54	
7	8,69	-0,08	-0,08	
9	8,30	-0,47	-0,46	

5. Documentation

5.1 Primary data in mg/kg

5.1.1a Arsen/ Arsenic (Migration)

Teilnehmer/ participants	DLA Probe Nr. A/ sample no. A	DLA Probe Nr. B/ sample no.B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	6	6	6	
3	15	46	5,49	5,56	5,42	
4	2	38	2,67	2,64	2,69	100
5	16	31	6,18	6,42	5,95	100
6						
7	25	6	6,29	6,28	6,3	
8						
9						
10						

5.1.1b Arsen/ Arsenic (Gesamt/ total)

Teilnehmer/ participants	DLA Probe Nr. A/ sample no. A	DLA Probe Nr.B/ sample no.B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	5,6	6,7	6,2	
2	26	44	6	6	6	
3	15	46	6,28	6,37	6,19	
4	2	38	6,31	6,27	6,35	100
5	16	31				
6	10	39	6,115	6,042	6,188	
7	25	6	6,79	6,75	6,82	
8						
9	9	34	6,8	6,67	6,91	
10	29	50				

5.1.2a Barium (Migration)

Teilnehmer/ participants	DLA Probe Nr. A/ sample no. A	DLA Probe Nr.B/ sample no. B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	44	44	45	
3	15	46	36,2	38,5	33,8	
4	2	38	33,2	33,5	32,9	125
5	16	31	76,78	73,58	79,98	100
6						
7	25	6	41,7	42,45	40,56	
8						
9						
10						

5.1.2b Barium (Gesamt/ total)

Teilnehmer/ participants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21				
2	26	44	109	110	108	
3	15	46	99,4	100,4	98,3	
4	2	38	114	112	115	110
5						
6						
7	25	6	112,3	112,8	111,8	
8						
9	9	34	100	105,7	95,2	
10						

5.1.3a Cadmium (Migration)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample no. A	DLA Probe Nr.B/ sample no.B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	5,1	5,3	4,9	
3	15	46	4,62	4,66	4,58	
4	2	38	5,87	5,82	5,91	100
5	16	31	7,26	7,57	6,95	100
6						
7	25	6	4,67	4,53	4,8	
8						
9						
10						

5.1.3b Cadmium (Gesamt/ total)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	7,7	8,2	7,2	
2	26	44	8	8	8	
3	15	46	6,59	6,73	6,45	
4	2	38	7,9	7,79	8	105
5						
6						
7	25	6	8,53	8,52	8,54	
8						
9	9	34	8,9	8,59	9,30	
10						

5.1.4a Chrom/ Chromium (Migration)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	2	2	2	
3	15	46	1,77	1,9	1,64	
4	2	38	16	13,4	18,5	110
5	16	31	5,22	5,28	5,15	100
6						
7	25	6	0,571	0,577	0,564	
8						
9						
10						

5.1.4b Chrom/ Chromium (Gesamt/ total)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	6,5	6,9	6,1	
2	26	44	8	8	8	
3	15	46	8,52	8,19	8,86	
4	2	38	7,01	6,99	7,03	100
5						
6						
7	25	6	6,6	6,58	6,61	
8						
9	9	34	3,5	4,70	2,37	
10						

5.1.5a Quecksilber/ Mercury (Migration)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	0,5	0,47	0,54	
3	15	46	0,23	0,2	0,26	
4	2	38	0,239	0,234	0,243	95
5	16	31	1,47	1,42	1,52	100
6						
7	25	6	0,47	0,45	0,49	
8						
9						
10						

5.1.5b Quecksilber/ Mercury (Gesamt/ total)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	4,9	5,1	4,7	
2	26	44	6	6,5	5,5	
3	15	46	4,99	5,06	4,93	
4	2	38	4,92	5	4,83	95
5						
6	10	39	5,355	5	5,71	
7	25	6	4,25	4,23	4,26	
8	12	35	5,85	5,87	5,84	
9	9	34	6,2	6,15	6,17	
10	29	50	4,36	4,39	4,34	

5.2.6a Blei/ Lead (Migration)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	0,6	0,7	0,5	
3	15	46	1,92	1,78	2,06	
4	2	38	3,86	4,45	3,27	125
5	16	31	7,86	8,31	7,40	100
6						
7	25	6	0,648	0,551	0,745	
8						
9						
10						

5.2.6b Blei/ Lead (Gesamt/ total)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	10	10,9	9,9	
2	26	44	12	12	12	
3	15	46	7,99	8,21	7,77	
4	2	38	10,6	10,4	10,8	110
5						
6	10	39	10,405	10,332	10,479	
7	25	6	10,1	10,1	10,1	
8						
9	9	34	9,5	9,86	9,11	
10						

5.1.7a Antimon/ Antimony (Migration)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs -rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	3,3	3,3	3,3	
3	15	46	3,05	3,07	3,02	
4	2	38	1,37	1,35	1,39	120
5	16	31	3,25	3,80	2,70	100
6						
7	25	6	3,52	3,5	3,57	
8						
9						
10						

5.1.7b Antimon/ Antimony (Gesamt/ total)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs- rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	0,16	0,23	0,083	
2	26	44	3	3	3	
3	15	46	2,96	3,11	2,8	
4	2	38	4,1	4,04	4,15	110
5						
6						
7	25	6	1,36	1,37	1,34	
8						
9	9	34	4,2	4,00	4,47	
10						

5.1.8a Selen/ Selenium (Migration)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1						
2	26	44	7,5	8	7	
3	15	46	7,83	7,94	7,71	
4	2	38	0,172	0,177	0,166	95
5	16	31	8,45	8,60	8,31	100
6						
7	25	6	7,94	7,92	7,97	
8						
9						
10						

5.1.8b Selen/ Selenium (Gesamt/ total)

Teilnehmer/ paticipants	DLA Probe Nr. A/ sample A	DLA Probe Nr.B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfindungs-rate/ recovery
			mg/kg	mg/kg	mg/kg	in %
1	43	21	9,5	8,9	10,1	
2	26	44	8	8	8	
3	15	46	9,91	10	9,82	
4	2	38	8,22	8,26	8,17	95
5						
6						
7	25	6	8,69	8,59	8,79	
8						
9	9	34	8,3	7,71	8,80	
10						

5.2 DLA-portion-numbers and homogeneity

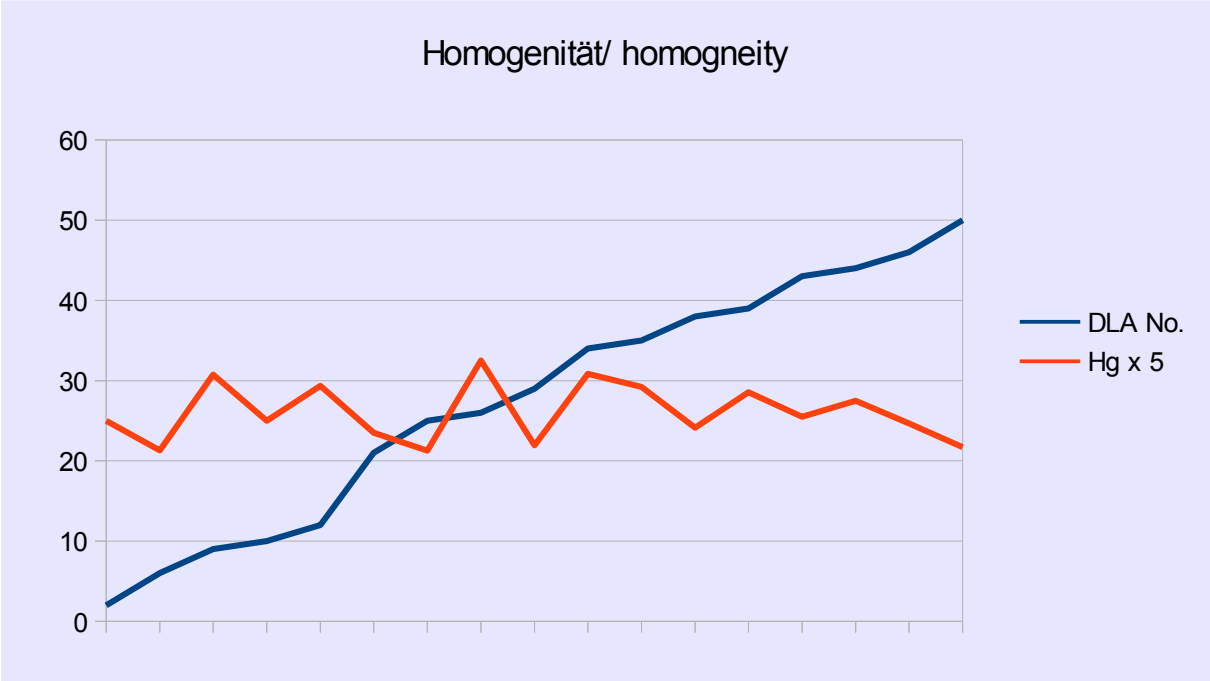
5.2.1 Repeatability standard deviation of participants

The repeatability standard deviation was calculated like under 5.1 documented.
It is 1,04 mg/kg = 15,3 % of X (= 6,8 mg/kg) for Chromium total.

For comparison ASU § 64 LFGB L00.00-135 (11):
For chromium (White cabbage): 0,145 mg/kg = 15 % of X (= 0,97 mg/kg)

5.2.2 Comparison of sample number/test result

The comparison of the rising sample-numbers and measured mercury-concentrations (total/ x5) shows a sufficient homogeneity.



5.3 Analytical methods

Teil-nehmer/ parti-cipant	Methode/ method	Details	Akkredi-tiert/ accredited
1	Total content: acid digestion, Detection with ICP-MS	1. no 2. - 3. 0,236 g 4. - 5. with calibration	yes
2	Migration: Eluate according to EN 71; measurement ICP-MS.	1. no 2. - 3. 400 mg 4. - 5. -	yes
	Total content: Microwave digestion with HNO3 / measurement ICP-MS.	1. no 2. - 3. 200 mg 4. - 5. -	yes
3	Migration: DIN EN 71-3	1. yes 2. - 3. 0,5 g 4. - 5. external	yes
	Total content: ICP-OES Hg: CV-AAS	1. yes 2. microwave HNO3/HCl for As, otherwise no details 3. - 4. 0,2 -0,3 g 5. External	yes
4	Migration: As § 64 LFGB L 00.00-19 (HG-AAS)	1. yes 2. EN-71-3 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 6-point-calibration 6. with correction factor from EN 71-3 cleared	yes
	Migration: Ba. Pb, Sb DIN EN ISO 17294-2 (ICP-MS)	1. yes 2. EN-71-3 3. 0,1 g 4. TM-15,2 (water) 5. 1-point-calibration 6. with correction factor from EN 71-3 cleared; for lead: results disperse.	
	Migration: Cd, Cr § 64 LFGB L 00.00-19 (GF-AAS)	1. yes 2. EN-71-3 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 5-point-calibration 6. with correction factor from EN 71-3 cleared. For Chromium: results implausible but confirmed with ICP-MS.	

Teil-nehmer/ parti-cipant	Methode/ method	Details	Akkredi-tiert/ accredited
	Migration: Hg DIN EN 12338 (Amalgam-AAS)	1. yes 2. EN-71-3 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 5-point-calibration 6. with correction factor from EN 71-3 cleared	
	Migration: Se DIN 38405-23 (HG-GF-AAS)	1. yes 2. EN-71-3 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 3-point-calibration 6. with correction factor from EN 71-3 cleared	
	Total content: As § 64 LFGB L 00.00-19 (HG-AAS)	1. yes 2. HNO3/H2O/HF 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 6-point-calibration	
	Total content: Ba, Cd, Cr, Pb, Sb DIN EN ISO 17294-2 (ICP-MS)	1. yes 2. HNO3/H2O/HF 3. 0,1 g 4. TM-15,2(water) 5. 1-point-calibration	
	Total content: Hg DIN EN 12338 (Amalgam-AAS)	1. yes 2. HNO3/H2O/HF 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 5-point-calibration	
	Total content: Se DIN 38405-23 (HG-GF-AAS)	1. yes 2. HNO3/H2O/HF 3. 0,1 g 4. NIST 1515 (apple leaves) 5. 3-point-calibration	
5	Migration: - According to EN-71-3 (2005-11), §. 8.7.3 - 8.7.4 - Weight 1 g, in 50 ml HCl 0.05 mol/L - Correction pH to <1.5 with approx. 60 drops HCl 2 mol/L - Migration 1h/ 37±2°C in the dark while stirring. - than 1h/ 37±2°C in darkness - stabilize with HCl 2 mol/L and dilute to 100 ml - Measurement direct with ICP-OES (Ba, Cd, Cr, Pb) - Measurement with VGA-AAS (As, Se, Sb) and CVAAS (Hg)	1. no 2. Migration according to EN-71-3 3. 1 g 4. As: Fluka TraceCERT Art. 01969-100ML-F; Ba, Cd, Cr, Pb, : Merk Certipur Art. 1.113550100 ICP multi-element sol. IV; Hg, Sb, Se: Fluka TraceCERT Art. 28941-100ML; 5. external calibration	yes
6	Total content: As, Hg, Pb Microwave/ ICPMS	1. - 2. - 3. 0,2 g 4. DLA 40-2013 5. - 6.without recovery	yes

Teil-nehmer/ parti-cipant	Methode/ method	Details	Akkredi-tiert/ accredited
7	Migration: DIN EN 71-3, ICP-MS	1. yes 2. - 3. 0,5 g 4. - 5. -	yes
	Total content: -	1. yes 2. - 3. 0,2 g 4. - 5. Calibration standard	no
8	Total content: Hg heat digestion	1. - 2. - 3. < 0,1 g 4. - 5. -	yes
9	Total content: Acid-digestion, ICP-MS	1. 2. - 3. 200 mg 4. - 5. -	no
10	Total content: Hg Analysed with direct mercury analyser	1. - 2. - 3. 0,02 g 4. SMR 2586 5. -	yes

1. = Homogenization
2. = Hydrolysis/ digestion
3. = Sample weight
4. = Reference material
5. = Calibration
6. = Remarks

6. Index of participant laboratories

Teilnehmer/ participnat	Ort/ location
	Germany
	Hong Kong
	USA
	Denmark
	Singapur
	Germany
	Switzerland
	Germany
	Germany
	Germany

[The address data of the participants were deleted for publication of the evaluation report.]

6. Index of literature

1. DIN EN ISO/IEC 17043:2010; Konformitätsbewertung – Allgemeine Anforderungen an Eignungsprüfungen / Conformity assessment – General requirements for proficiency testing
2. Verordnung / Regulation 882/2004/EU; Verordnung über amtliche Kontrollen / Regulation on official controls
3. DIN EN ISO/IEC 17025:2005; Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien / General requirements for the competence of testing and calibration laboratories
4. Richtlinie / Directive 1993/99/EU; über zusätzliche Maßnahmen im Bereich der amtlichen Lebensmittelüberwachung / on additional measures concerning the official control of foodstuffs
5. ASU §64 LFGB : Planung und statistische Auswertung von Ringversuchen zur Methodenvalidierung
6. ISO 13528:2005; Statistische Verfahren für Eignungsprüfungen durch Ringversuche
7. The International Harmonised Protocol for the Proficiency Testing of Ananlytical Laboratories ; J.AOAC Int., 76(4), 926 – 940 (1993)
8. The International Harmonised Protocol for the Proficiency Testing of Ananlytical Chemistry Laboratories ; Pure Appl Chem, 78, 145 – 196 (2006)
9. Evaluation of analytical methods used for regulation of food and drugs;W. Horwitz; Analytical Chemistry, 54, 67-76 (1982)
10. A Horwitz-like funktion describes precision in proficiency test; M. Thompson, P.J. Lowthian; Analyst, 120, 271-272 (1995)
11. ASU §64 LFGB : L00.00-135; Bestimmung von Arsen, Cadmium, Quecksilber und Blei in Lebensmitteln (Jan. 2011)
12. ASU §64 LFGB : L00.00-19/3; Bestimmung von Blei, Cadmium, Chrom und Molybdän in Lebensmitteln (Juli 2004)
13. ASU §64 LFGB : L00.00-19/4; Bestimmung von Quecksilber in Lebensmitteln (Dezember 2003)
14. ASU §64 LFGB : L00.00-19/6; Bestimmung von Gesamtarsen in Lebensmitteln (Juli 2001)
15. Norm EN 71-3 Sicherheit von Spielzeug Teil 3: Migration bestimmter Elemente (Oktober 2000)
16. Norm EN 71-7 Sicherheit von Spielzeug Teil 7: Fingermalfarben, Anforderungen und Prüfverfahren (November 2002)

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