DLA
Dienstleistung
Lebensmittel
Analytik GbR

Evaluation Report
proficiency test

35/2014

Cosmetic Products II:

Preservatives
(Benzylalcohol, Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben and Isopropylparaben)

in Skin Cream (Bodylotion)

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Content

1. Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. 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 (6).

2. Realisation

2.1 Test material

The test material is a mixture of three common in commerce skin creams (bodylotions) with different perfumes and colour additives but the same basic formulations from European suppliers. The materials were mixed and homogenized. Afterwards the samples were packaged lightproof in portions to approximately 20 g. The portions were numbered chronologically.

The composition (list of ingredients) is given in table 1.

Table 1: Composition of DLA-Sample

Mixture of Bodylotions:
List of Ingredients (INCI): Aqua, Cocoglycerides, Dicaprylyl Ether, Cetearyl Alcohol, Propylene Glycol, Sorbitol, Pentaerythryl Distearate, Theobroma Cacao (Cocoa) Seed Butter, Prunus Amygdalus Dulcis (Sweet Almond) Oil, Dimethicone, Butyrospermum Parkeri (Shea) Butter, Polyglyceryl-3 Diisostearate, Sodium Stearoyl Glutamate, Fructose, Xanthan Gum, **Benzylalcohol**, Tocopherylacetate, **Phenoxyethanol**, Parfum, Panthenol, Acrylates/C10-30 Alkyl Acrylate Crosspolymer-Carbomer, Niacinamide, Sodium Polyacrylate, Citric Acid, Sodium Hydroxide, **Methylparaben, Ethylparaben**, **Butylparaben, Isobutylparaben, Propylparaben**, Citrus Aurantium Dulcis (Orange) Peel Extract / Prunus Cerasus (Bitter Cherry) Fruit Extract / Passiflora Incarnata Fruit Extract, CI 15985, CI 47005 (without naming of allergenic substances)

2.1.1 Homogeneity

The calculation of the repeatability standard deviation of the participants was also used as an indicator of homogeneity. For methylparaben it was 4,7% and in the range of common relative repeatability standard deviations of official methods (AUS §64) (14). The repeatability standard deviation of the participants for methylparaben is given in the documentation.

Additionally in the documentation the portion numbers are graphically assigned to the results of methylparaben. 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 38th week of 2014. The testing method was optional. The tests should be finished at 31st october 2014.

2.3 Submission of results

The participants submitted their results in standard forms, which have been handed out with the samples.
The finally calculated concentration of the preservatives benzylalcohol, phenoxyethanol, methylparaben, ethylparaben, butylparaben, propylparaben and isobutylparaben as an average of a duplicate determination of both numbered samples was used for each statistical evaluation. By mistake on the result standard forms iso*propyl*paraben was written instead of iso*butyl*paraben. Isopropylparaben was not contained in the recipe of the formulation.
Queried and documented were single results, recovery and the testing methods used.
All other participants submitted the results in time.

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 for 95% significance niveau (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.

In general the Horwitz target standard deviation is suitable for the statistical evaluation of interlaboratory tests where different analytical methods are applied. The standard deviation from precision experiments are derived from proficiency tests where a specific analytical method is mandatory.

For all analytes the target standard deviation according to the general model (Horwitz) was applied.

3.4.1 General model (Horwitz)

The relative target standard deviation in % of the assigned value is derived from following equation (Horwitz)

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

From the result the target standard deviation is calculated

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

3.4.2 Value by 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 can be calculated σ_L :

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

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

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

The German official ASU §64 method for the determination of benzylalcohol as well as for phenoxyethanol and the parabens in cosmetic products (K 84.00-21 and -23) gives a maximum deviation of 10% for the repeatability determination (13, 14). Reproducibility standard deviation and repeatability standard deviation are not reported.

3.4.3 Value by perception

The target standard deviation for proficiency assessment can be set at a value that corresponds to the level of performance that the coordinator would wish laboratories to be able to achieve (6).
For methylchloroisothiazolone and methylisothiazolone no suitable data were available.

For the evaluation in the present proficiency testing the model according to Horwitz was applied.

For ***phenoxyethanol*** *and* ***butylparaben*** the suitability of the model of Horwitz with the normal relative target standard deviations was limited (quotients $S^x/\hat{\sigma} > 2$ and $u_X/\hat{\sigma} > 0{,}3$)). **Therefore the evaluation of participants' results was done using z'-values and the target standard deviation $\hat{\sigma}$'** (s. 3.6 and 3.8).

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:

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

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

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

3.6 z'-Score

The z'-score can be used for the valuation of the results of the participants, in cases the standard uncertainty has to be considered (s. 3.8). The z'-score represents the relation of the deviation of the result (x) of the participant from the respective assigned value (X) to the square root of quadrat sum of the target standard deviation ($\hat{\sigma}$) and the standard uncertainty (Ux) (6).

Participants' z'-scores are derived as:

$$z' = (x - X) / \sqrt{\hat{\sigma}^2 + u_X^2}$$

In the following we define the denominator $\sqrt{\hat{\sigma}^2 + u_X^2}$ as the target standard deviation $\hat{\sigma}'$.

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

$$-2 \leq z' \leq 2 \ .$$

3.7 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 (11).
In the present proficiency tests the quotients $S^x/\hat{\sigma}$ were

In the present proficiency tests the quotients $S^x/\hat{\sigma}$ for phenoxyethanol and butylparaben were 4,3 and 4,6 respectively. Therefore the evaluation was done according to 3.6 z'-scores. For the other parameters the quotients were satisfactory in the range of 0,6 to 2,2.

3.8 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 to be included in the interpretation of the results of the PT (6).

In the present proficiency test for phenoxyethanol and butylparaben the quotients $U_x/\hat{\sigma}$ were 1,8 each. Therefore for the valuation of the participants' results the z'-Score considering the standard uncertainty was used (s. 3.6).

4. Results

All following tables are anonymized. With the delivering of the evaluation-report the participants are informed about their individual evaluation-number.
In the upper table the characteristics are listed:

Statistic Data
Number of results
Number of outliers
Mean
Median
Robust mean (X)
Robust standard deviation (S^x)
Target range:
Target standard deviation for information
Target standard deviation $\hat{\sigma}$ '
lower limit of target range (X - 2 $\hat{\sigma}$) or (X - 2 $\hat{\sigma}$ ') *
upper limit of target range (X + 2 $\hat{\sigma}$) or (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

* Target range is calculated with z-score or z'-score

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

evaluation number	test result	deviation from assigned value	Z-Score Horwitz	Z'-Score Horwitz	Remarks

4.1 Benzylalcohol (in g/100 g)

Statistic Data	
Number of results	*9*
Number of outliers	*1*
Mean	0,332
Median	0,336
Robust mean (X)	0,334
Robust standard deviation (S^x)	0,0292
Target range:	
Target standard deviation $\hat{\sigma}$ (Horwitz)	0,0157
lower limit of target range (X - 2 $\hat{\sigma}$)	0,302
upper limit of target range (X + 2 $\hat{\sigma}$)	0,365
Quotient $S^x/\hat{\sigma}$	*1,9*
Standard uncertainty u_X	*0,0122*
Quotient $u_X/\hat{\sigma}$	*0,77*
Number of results in the target range	*7 (78%)*

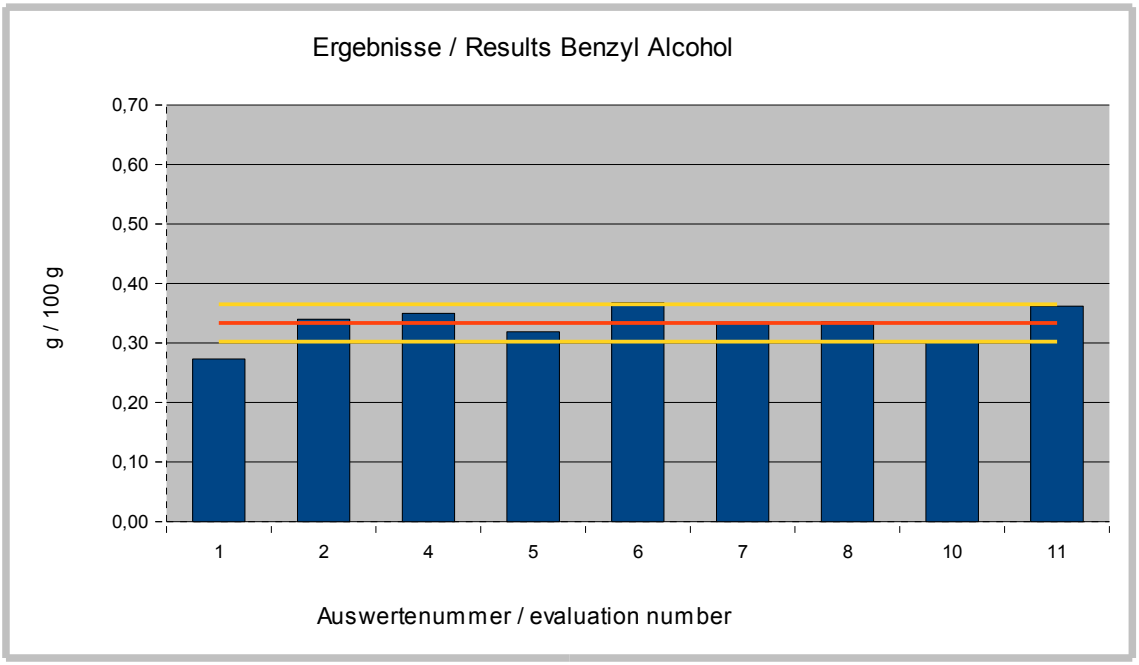


Fig. 1: Results Benzylalcohol
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score $\hat{\sigma}$	Remarks
	[g/100g]	X rob. Mean	Horwitz	
1	0,2733	-0,060	-3,8	Ausreißer
2	0,34	0,006	0,4	
4	0,35	0,016	1,0	
5	0,319	-0,015	-0,9	
6	0,368	0,034	2,2	
7	0,335	0,001	0,1	
8	0,336	0,002	0,1	
10	0,304	-0,030	-1,9	
11	0,362	0,028	1,8	

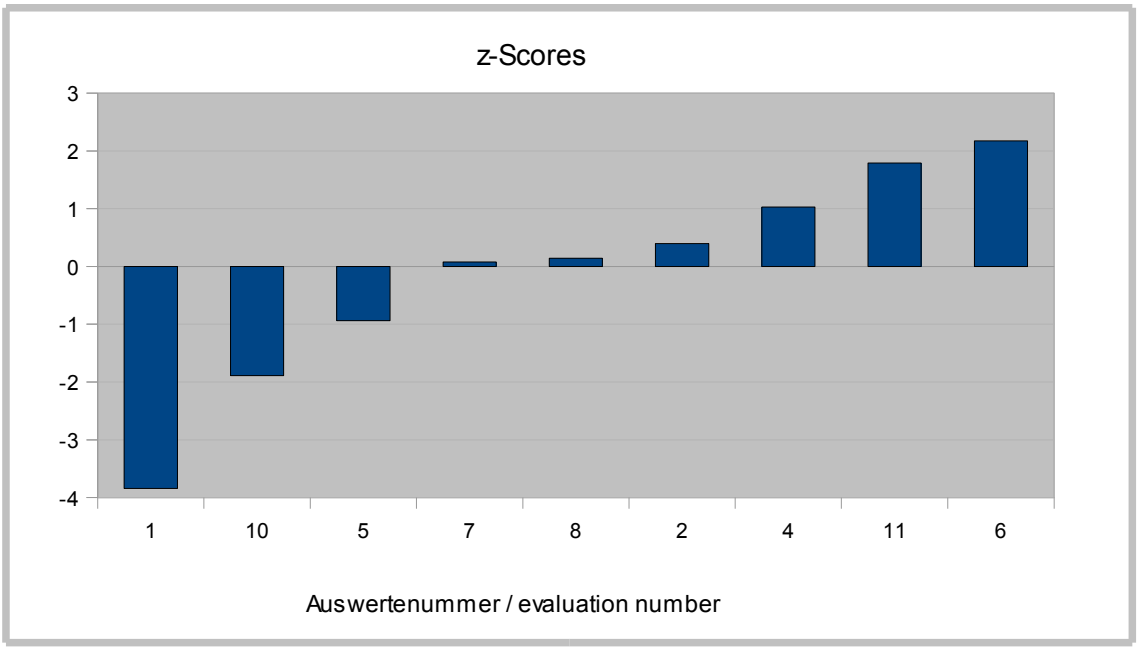


Fig. 2: Z-Scores Benzylalcohol

4.2 Phenoxyethanol (in g/100 g)

Statistic Data	
Number of results	*9*
Number of outliers	*1*
Mean	0,630
Median	0,567
Robust mean (X)	0,606
Robust standard deviation (S^x)	0,112
Target range:	
Target standard deviation $\hat{\sigma}'$	0,0534
lower limit of target range *	0,499
upper limit of target range *	0,713
Quotient $S^x/\hat{\sigma}'$	*2,1*
Standard uncertainty u_X	*0,047*
Quotient $u_X/\hat{\sigma}'$	*0,87*
Number of results in the target range	*7 (78%)*

** target range calculated from z'-score*

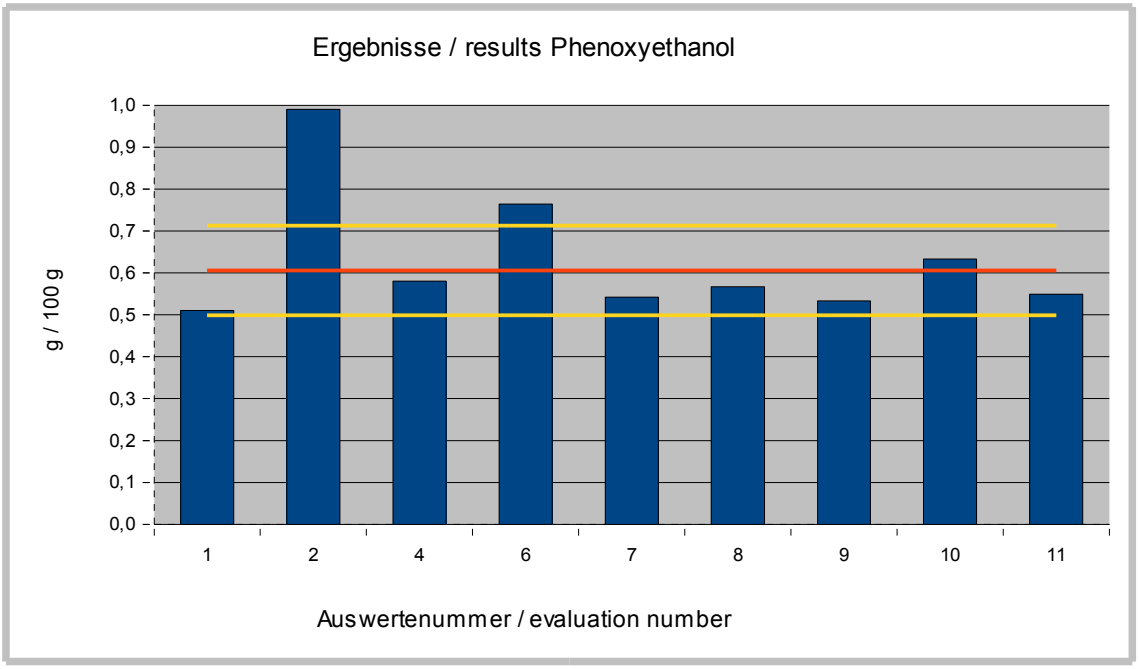


Fig. 3: Results Phenoxyethanol
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score	Z'-Score	Remarks
	[g/100g]	X rob. Mean	Horwitz	Horwitz	
1	0,51	-0,096	-3,7	-1,8	
2	0,99	0,384	14,7	7,2	outlier
4	0,58	-0,026	-1,0	-0,5	
6	0,764	0,158	6,1	3,0	
7	0,542	-0,064	-2,4	-1,2	
8	0,567	-0,039	-1,5	-0,7	
9	0,533	-0,073	-2,8	-1,4	
10	0,633	0,027	1,0	0,5	
11	0,549	-0,057	-2,2	-1,1	

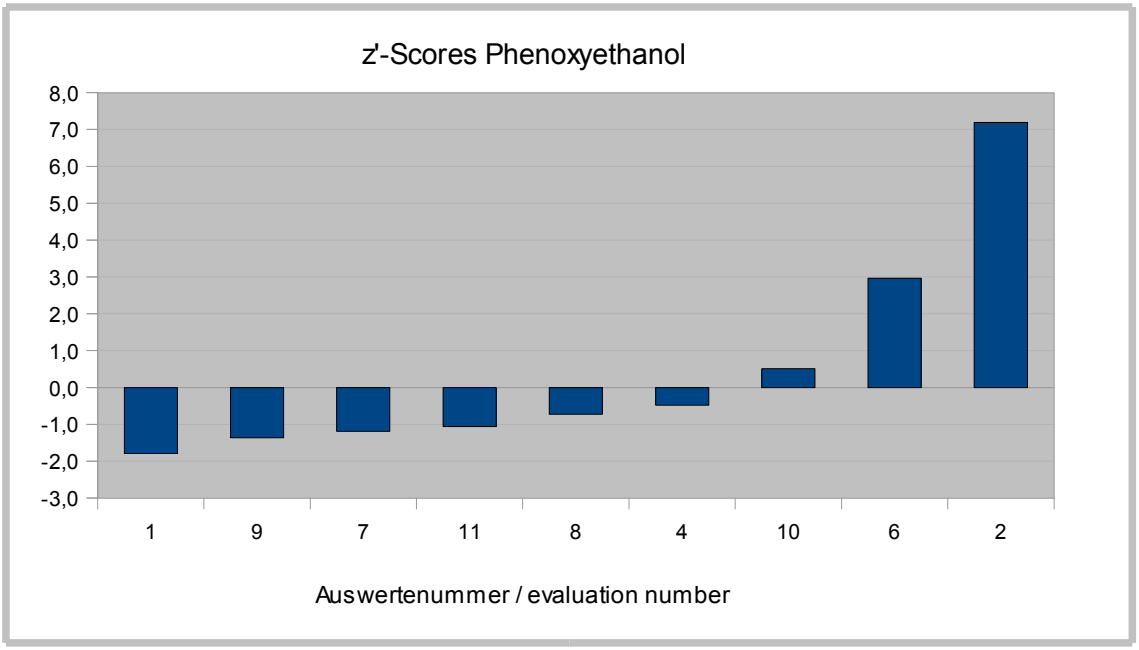


Fig. 4: Z'-Scores Phenoxyethanol

4.3 Methylparaben (in g/100 g)

Statistic Data	
Number of results	*11*
Number of outliers	*1*
Mean	0,106
Median	0,101
Robust mean (X)	0,101
Robust standard deviation (S^x)	0,0032
Target range:	
Target standard deviation $\hat{\sigma}$ (Horwitz)	0,0057
lower limit of target range (X - 2 $\hat{\sigma}$)	0,090
upper limit of target range (X + 2 $\hat{\sigma}$)	0,113
Quotient $S^x/\hat{\sigma}$	*0,56*
Standard uncertainty u_X	*0,0012*
Quotient $u_X/\hat{\sigma}$	*0,21*
Number of results in the target range	*10 (91%)*

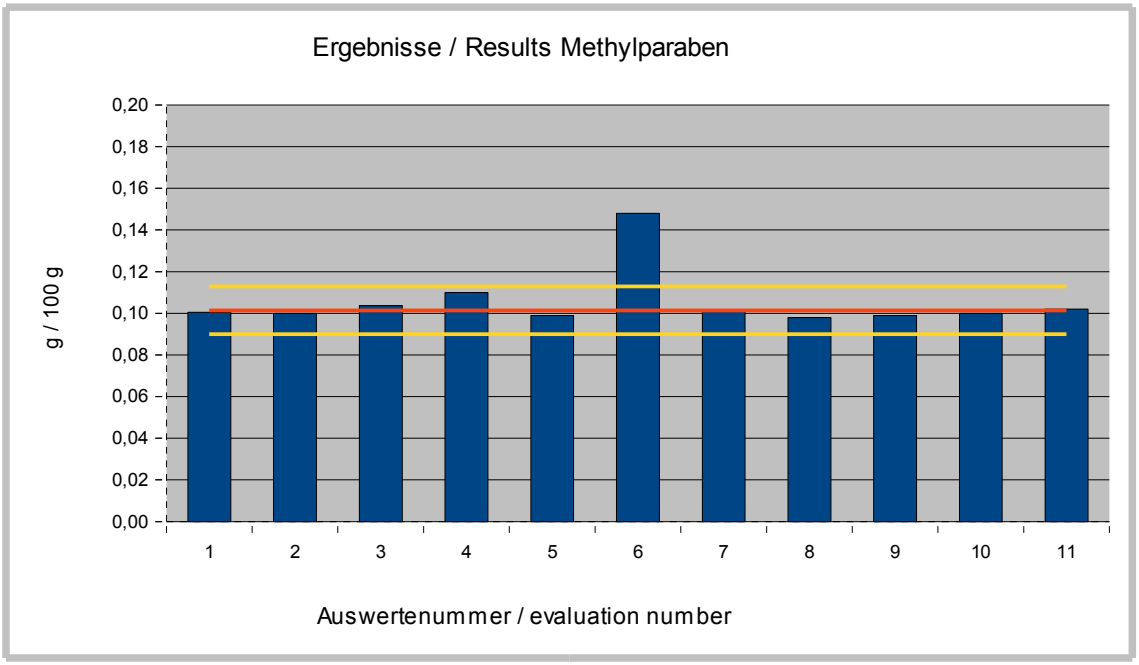


Fig. 5: Results Methylparaben
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score $\hat{\sigma}$	Remarks
	[g/100g]	X rob. Mean	Horwitz	
1	0,1005	-0,001	-0,2	
2	0,10	-0,001	-0,2	
3	0,104	0,002	0,4	
4	0,11	0,009	1,5	
5	0,099	-0,002	-0,4	
6	0,148	0,047	8,1	outlier
7	0,101	0,000	-0,1	
8	0,098	-0,003	-0,6	
9	0,099	-0,002	-0,4	
10	0,1	-0,001	-0,2	
11	0,102	0,001	0,1	

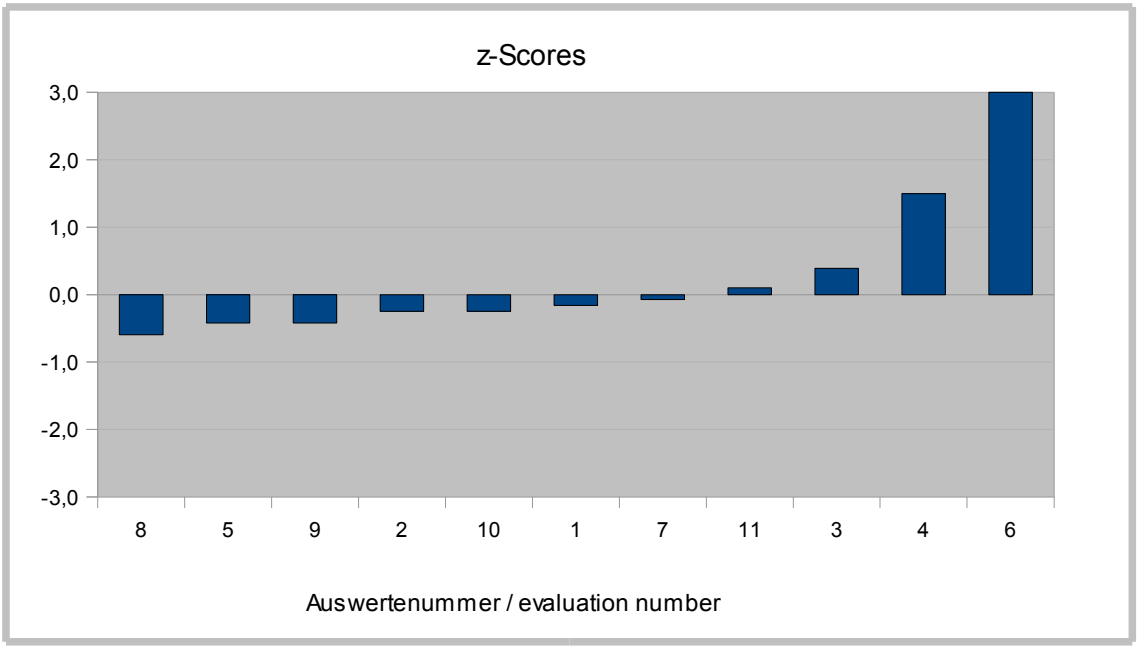


Fig. 6: Z-Scores Methylparaben

4.4 Ethylparaben (in g/100 g)

Statistic Data	
Number of results	*10 **
Number of outliers	*1*
Mean	0,0246
Median	0,0250
Robust mean (X)	0,0244
Robust standard deviation (S^x)	0,0018
Target range:	
Target standard deviation $\hat{\sigma}$ (Horwitz)	0,017
lower limit of target range (X - 2 $\hat{\sigma}$)	0,0210
upper limit of target range (X + 2 $\hat{\sigma}$)	0,0278
Quotient $S^x/\hat{\sigma}$	*1,0*
Standard uncertainty u_X	*0,0007*
Quotient $u_X/\hat{\sigma}$	*0,41*
Number of results in the target range	*9 (90%)*

** result 4 not considered*

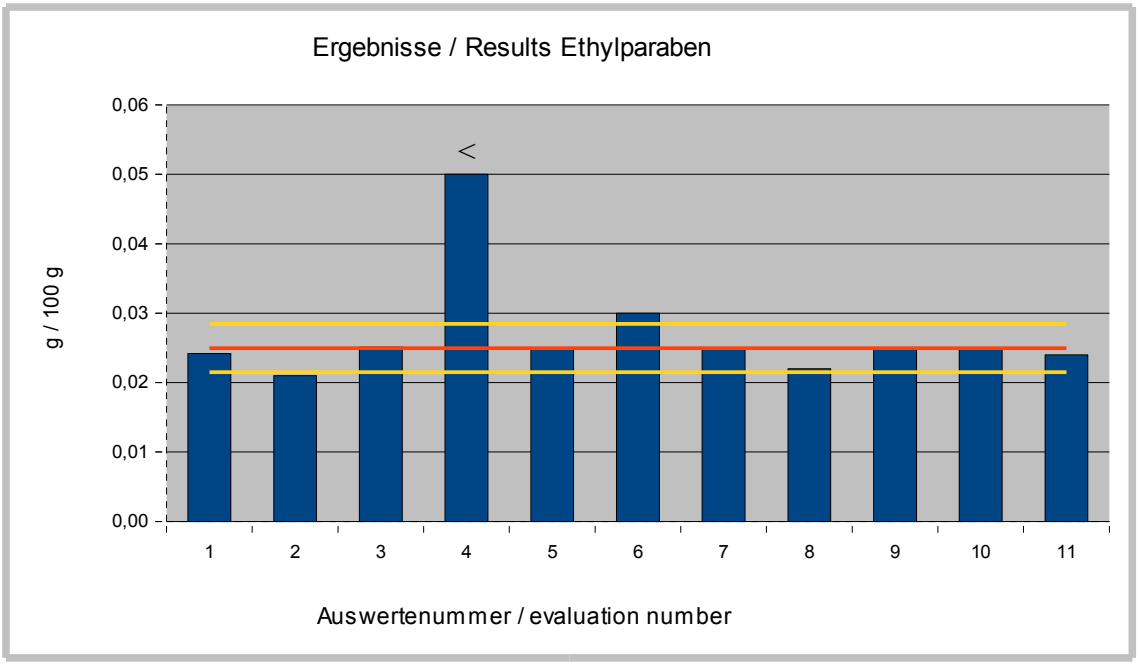


Fig. 7: Results Ethylparaben
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score $\hat{\sigma}$	Remarks
	[g/100g]	X rob. Mean	Horwitz	
1	0,0242	-0,0002	-0,1	
2	0,021	-0,0034	-2,0	
3	0,025	0,0007	0,4	
4	< 0,05			not considered
5	0,025	0,0006	0,3	
6	0,03	0,0056	3,3	
7	0,025	0,0006	0,3	
8	0,022	-0,0024	-1,4	
9	0,025	0,0006	0,3	
10	0,025	0,0006	0,3	
11	0,024	-0,0004	-0,2	

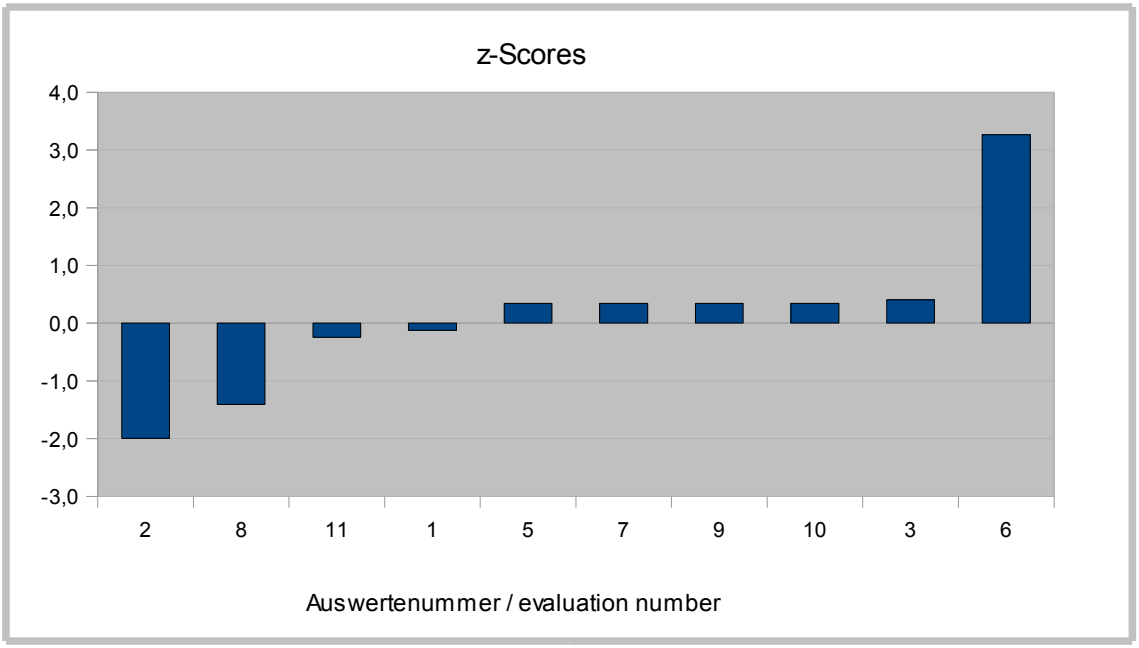


Fig. 8: Z-Scores Ethylparaben

4.5 Butylparaben (in g/100 g)

Statistic Data	
Number of results	*10 **
Number of outliers	*0*
Mean	0,0220
Median	0,0247
Robust mean (X)	0,0222
Robust standard deviation (S^x)	0,0072
Target range:	
Target standard deviation $\hat{\sigma}'$	0,0033
lower limit of target range *	0,0157
upper limit of target range *	0,0288
Quotient $S^x/\hat{\sigma}'$	*2,2*
Standard uncertainty u_X	*0,0029*
Quotient $u_X/\hat{\sigma}'$	*0,88*
Number of results in the target range	*8 (80%)*

** result 4 not considered*
*** target range calculated from z'-score*

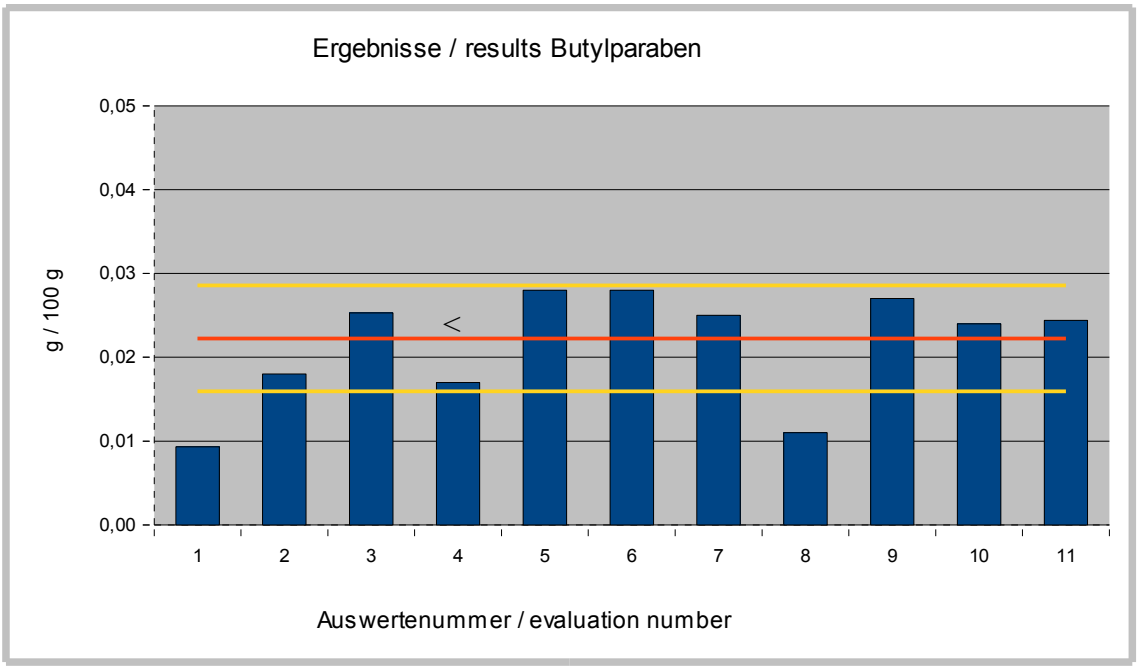


Fig. 9: Results Butylparaben
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score	Z'-Score	Remarks
	[g/100g]	X rob. Mean	Horwitz	Horwitz	
1	0,0093	-0,013	-8,2	-4,1	
2	0,018	-0,004	-2,7	-1,3	
3	0,025	0,003	1,9	1,0	
4	< 0,017				not considered
5	0,028	0,006	3,6	1,8	
6	0,028	0,006	3,6	1,8	
7	0,025	0,003	1,7	0,9	
8	0,011	-0,011	-7,1	-3,6	
9	0,027	0,005	3,0	1,5	
10	0,024	0,002	1,1	0,6	
11	0,0244	0,002	1,4	0,7	

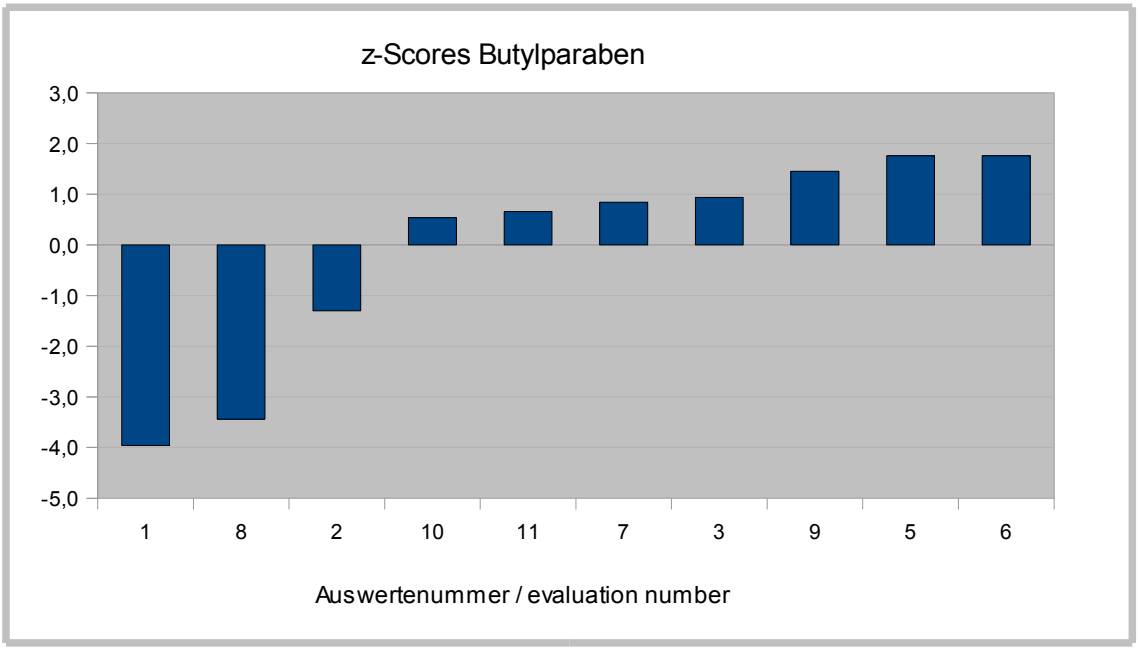


Fig. 10: Z'-Scores Butylparaben

4.6 Propylparaben (in g/100 g)

Statistic Data	
Number of results	*10 **
Number of outliers	*1*
Mean	0,0119
Median	0,0126
Robust mean (X)	0,0122
Robust standard deviation (S^x)	0,0021
Target range:	
Target standard deviation $\hat{\sigma}$ (Horwitz)	0,00094
lower limit of target range (X - 2 $\hat{\sigma}$)	0,0103
upper limit of target range (X + 2 $\hat{\sigma}$)	0,0140
Quotient $S^x/\hat{\sigma}$	*2,2*
Standard uncertainty u_X	*0,0008*
Quotient $u_X/\hat{\sigma}$	*0,87*
Number of results in the target range	*7 (70%)*

* result 4 not considered

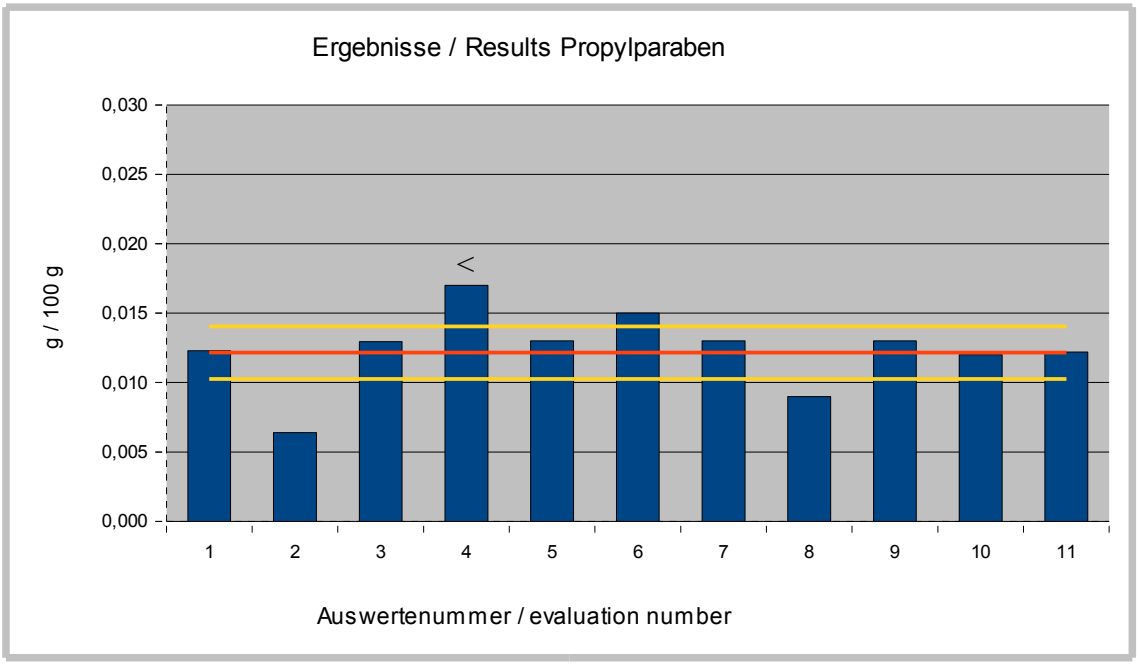


Fig. 11: Results Propylparaben
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score $\hat{\sigma}$	Remarks
	[g/100g]	X rob. Mean	Horwitz	
1	0,0123	0,0001	0,1	
2	0,0064	-0,0058	-6,1	outlier
3	0,013	0,0008	0,8	
4	< 0,017			not considered
5	0,013	0,0008	0,9	
6	0,015	0,0028	3,0	
7	0,013	0,0008	0,9	
8	0,009	-0,0032	-3,3	
9	0,013	0,0008	0,9	
10	0,012	-0,0002	-0,2	
11	0,0122	0,0000	0,0	

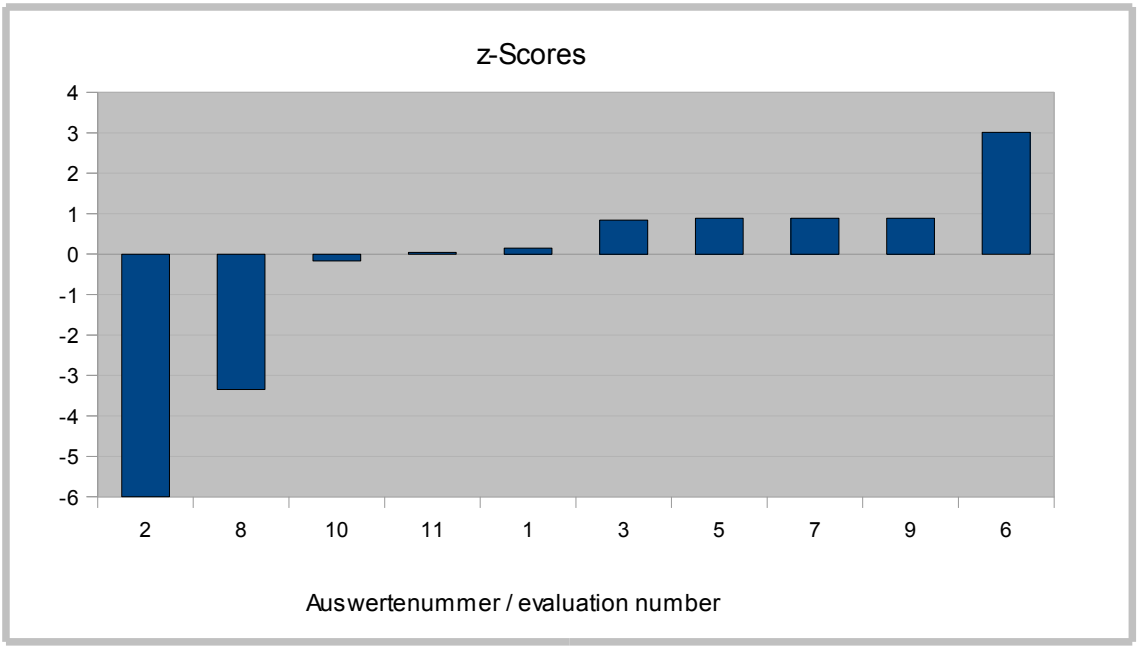


Fig. 12: Z-Scores Propylparaben

4.7 Isobutylparaben (in g/100 g)

Statistic Data	
Number of results	*5*
Number of outliers	*0*
Mean	0,0122
Median	0,0129
Robust mean (X)	0,0122
Robust standard deviation (S^x)	0,0014
Target range:	
Target standard deviation $\hat{\sigma}$ (Horwitz)	0,00095
lower limit of target range (X - 2 $\hat{\sigma}$)	0,0103
upper limit of target range (X + 2 $\hat{\sigma}$)	0,0141
Quotient $S^x/\hat{\sigma}$	*1,5*
Standard uncertainty u_X	*0,0008*
Quotient $u_X/\hat{\sigma}$	*0,84*
Number of results in the target range	*4 (80%)*

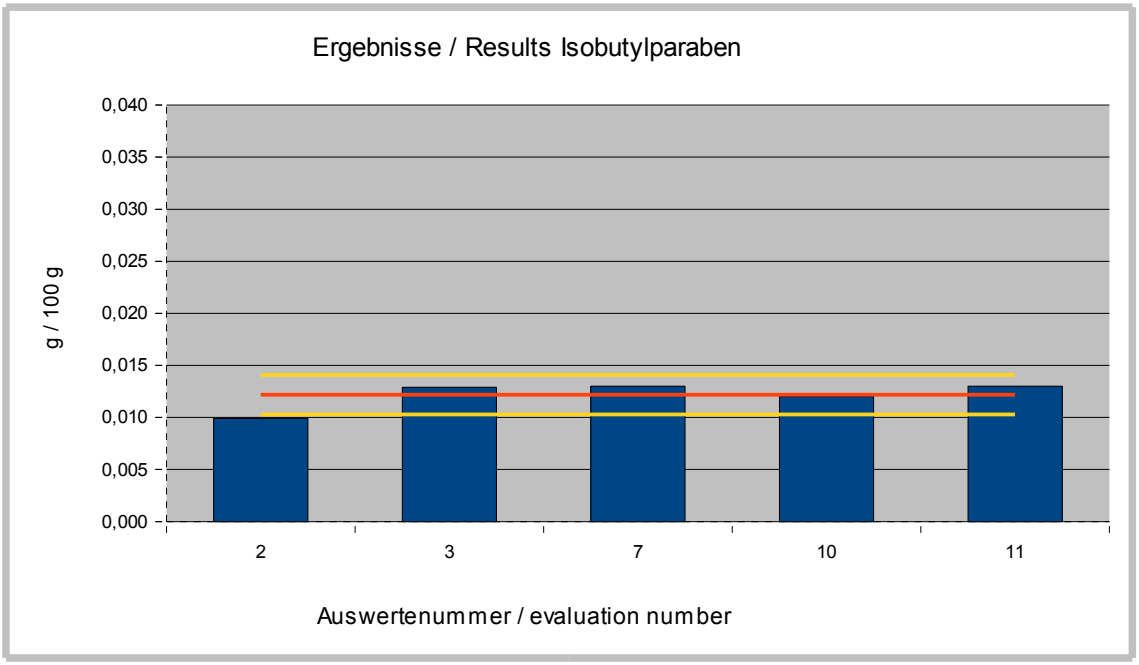


Fig. 13: Results Isobutylparaben
(red line = robust mean, yellow lines = target range)

Results of participants

Evaluation number	Result	Deviation	Z-Score $\hat{\sigma}$	Remarks
	[g/100g]	X rob. Mean	Horwitz	
2	0,0099	-0,0023	-2,4	
3	0,013	0,0007	0,7	
7	0,013	0,0008	0,9	
10	0,012	-0,0002	-0,2	
11	0,013	0,0008	0,9	

Fig. 14: Z-Scores Isobutylparaben

4.8 Isopropylparaben (in g/100 g)

Results of participants

Evaluation number	Result	Deviation	Z-Score $\hat{\sigma}$	Remarks
	[g/100g]	X rob. Mean	Horwitz	
1	0,0264			
4	< 0,017			
6	< 0,010			
8	< 0,0005			
10	< 0,0005			

not valuated.

5. Documentation

5.1 Primary data

5.1.1 Benzylalcohol

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,2733	11	30	0,27	0,2776	-
2	0,34	17; 39	17; 39	0,30	0,30	117
3		4; 25	4; 25			
4	0,35	16; 35	16; 35	0,35	0,36	"--"
5	0,319	7; 38	7; 38	0,319	0,319	n.b.
6	0,368	15; 32	15; 32	0,368	0,368	101
7	0,335	9	22	0,340	0,330	100
8	0,336	10; 23	10; 23	0,342	0,33	
9		13; 24	13; 24			
10	0,304	27	41	0,297	0,311	103
11	0,362	2; 19	2; 19	0,372	0,359	99

5.1.2 Phenoxyethanol

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,51	11	30	0,46	0,06	101
2	0,99	17; 39	17; 39	1,0	1,0	97
3		4; 25	4; 25			
4	0,58	16; 35	16; 35	0,58	0,59	"--"
5		7; 38	7; 38			
6	0,764	15; 32	15; 32	0,761	0,767	102
7	0,542	9	22	0,541	0,543	100
8	0,567	10; 23	10; 23	0,568	0,566	
9	0,533	13; 24	13; 24	0,538	0,528	
10	0,633	27	41	0,61	0,655	93
11	0,549	2; 19	2; 19	0,555	0,545	99,2

5.1.3 Methylparaben

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,1005	11	30	0,1	0,1009	99
2	0,10	17; 39	17; 39	0,11	0,12	89
3	0,104	4	25	0,106	0,101	97.96 (A); 99.82(B)
4	0,11	16; 35	16; 35	0,100	0,110	"--"
5	0,099	7; 38	7; 38	0,099	0,099	99,5
6	0,148	15; 32	15; 32	0,149	0,147	102
7	0,101	9	22	0,101	0,101	100
8	0,098	10; 23	10; 23	0,098	0,098	
9	0,099	13; 24	13; 24	0,099	0,099	
10	0,1	27	41	0,098	0,101	100
11	0,102	2; 19	2; 19	0,107	0,103	98,6

5.1.4 Ethylparaben

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,0242	11	30	0,0246	0,0238	99
2	0,02	17; 39	17; 39	0,022	0,023	93
3	0,025	4	25	0,025	0,025	101.24 (A); 97.73(B)
4	< 0,05	16; 35	16; 35	< 0,05	< 0,05	"--"
5	0,03	7; 38	7; 38	0,024	0,025	95,2
6	0,03	15; 32	15; 32	0,030	0,030	101
7	0,025	9	22	0,025	0,025	100
8	0,02	10; 23	10; 23	0,022	0,021	
9	0,03	13; 24	13; 24	0,025	0,024	
10	0,03	27	41	0,025	0,025	102
11	0,02	2; 19	2; 19	0,025	0,024	99,2

5.1.5 Butylparaben

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,0093	11	30	0,0093	0,0093	105
2	0,018	17; 39	17; 39	0,018	0,019	96
3	0,025	4	25	0,026	0,024	96.84 (A); 101.57 (B)
4	< 0,017	16; 35	16; 35	< 0,017	< 0,017	"--"
5	0,028	7; 38	7; 38	0,027	0,028	86,7
6	0,028	15; 32	15; 32	0,028	0,028	97
7	0,025	9	22	0,025	0,025	100
8	0,011	10; 23	10; 23	0,012	0,01	
9	0,027	13; 24	13; 24	0,026	0,027	
10	0,024	27	41	0,024	0,024	101
11	0,024	2; 19	2; 19	0,025	0,024	99,5

5.1.6 Propylparaben

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,0123	11	30	0,0123	0,0122	99
2	0,0064	17; 39	17; 39	0,0064	0,0067	98
3	0,013	4	25	0,013	0,013	98.10 (A); 101.59 (B)
4	< 0,017	16; 35	16; 35	< 0,017	< 0,017	"--"
5	0,013	7; 38	7; 38	0,013	0,013	95,3
6	0,015	15; 32	15; 32	0,015	0,015	100
7	0,013	9	22	0,013	0,013	100
8	0,009	10; 23	10; 23	0,009	0,008	
9	0,013	13; 24	13; 24	0,013	0,013	
10	0,012	27	41	0,012	0,012	102
11	0,0122	2; 19	2; 19	0,013	0,012	98,2

5.1.7 Isobutylparaben

Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1		11	30			
2	0,0099	17; 39	17; 39	0,011	0,011	92
3	0,013	4	25	0,013	0,013	103.88 (A); 100.94 (B)
4		16; 35	16; 35			
5		7; 38	7; 38			
6		15; 32	15; 32			
7	0,013	9	22	0,013	0,013	100
8		10; 23	10; 23			
9		13; 24	13; 24			
10	0,012	27	41			
11	0,013	2; 19	2; 19	0,014	0,013	99,6

5.1.8 Isopropylparaben

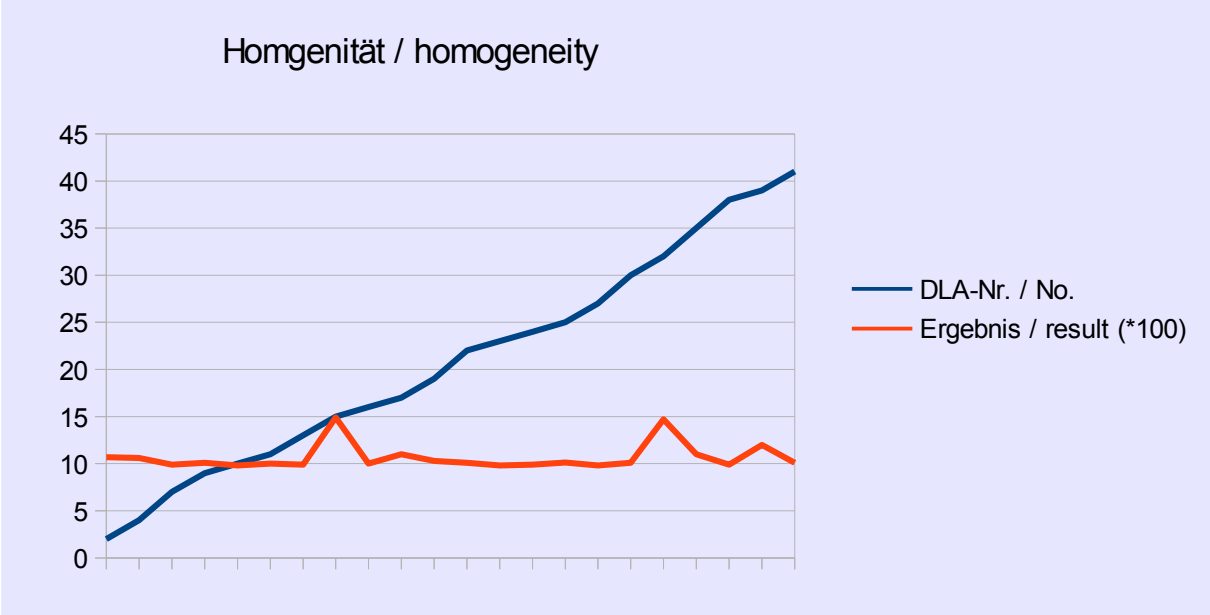
Evaluation number	Result	Sample-No. A	Sample No. B	Result A	Result B	Recovery Rate
	[g/100g]			g/100g	g/100g	%
1	0,0264	11	30	0,03	0,0254	100
2		17; 39	17; 39			
3		4	25			
4	< 0,017	16; 35	16; 35	< 0,017	< 0,017	"--"
5		7; 38	7; 38			
6	<0,010	15; 32	15; 32	<0,010	<0,010	106
7		9	22			
8	<0.0005	10; 23	10; 23	<0.0005	<0.0005	
9		13; 24	13; 24			
10	< 0,0005	27	41	< 0,0005	< 0,0005	103
11		2; 19	2; 19			

5.2 Homogeneity

5.2.1 Repeatability standard deviation of duplicate tests of the participants

The repeatability standard deviation was calculated with the data documented in 5.1.3 for methylparaben. It is 0,0048 g/100g = 4,7 % of X.

5.2.2 Comparison of sample number / test result (Methylparaben)



5.3 Analytical Methods

Details by the participants

5.3.1 Benzylalcohol

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1	30 min. Extraction with ethylacetate at room temperature in ultrasonic bath and GC-MS screeninganalysis	no	yes	
2	GC-MS after extraktion and derivatisattion	no	no	
3				
4	Preservatives by HPLC-DAD	no	no	
5	HPLC-DAD, water-methanol extract		no	
6	2 M H2SO4 is added to the sample, treated with ethanol-water. After filtration and isocratic reversed phase liquid chromatographic separation on a C-18 column, detected by means of a UV detection at 280 nm.	yes	yes	
7	internal method HPLC/DAD	yes	no	
8	HPLC / DAD	yes	yes	
9				
10	Extraction with MTBE, GC-MS	yes	yes	
11	Column: Purospher Star, RP-18e,125*2mm.5 µm, EluentA: Milli-Q, Eluent B: Methanol, Samples in THF pre-dissolved, in MeOH diluted, membrane filtration, 4-point-calibration	yes	yes	

5.3.2 Phenoxyethanol

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1	60 min. Extraction with methanolic acetic acid at 40°C in ultrasonic bath and analysis by LC/MS / GC/MS	no	yes	
2	HPLC-DAD after extraction	no	no	
3				
4	Preservatives HPLC-DAD	no	no	
5				not analysed
6		yes	yes	
7	internal method HPLC/DAD	yes	yes	
8	HPLC / DAD	yes	yes	
9			yes	
10	Extraction with methanol/water, HPLC-DAD	yes	yes	
11	Column: Purospher Star, RP-18e,125*2mm.5 µm, Eluent A: Acetate buffer 5mmol, pH=4,3, Eluent B: Methanol, Samples in THF pre-dissolved, in MeOH diluted, membrane filtration, 4-point-calibration	yes	yes	Isopropylparaben was not detected, but Isobutylparaben was detected

5.2.3 Methyl-, Ethyl-, Butyl- und Propylparaben

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1	60 min. Extraction with methanolic acetic acid at 40°C in ultrasonic bath and analysis by LC/MS / GC/MS	no	yes	
2	HPLC-DAD after extraction	no	no	
3	HPLC			3 decipl as advised ; Isobutylparaben replaced by Isopropylparaben
4	Preservatives HPLC-DAD	no	no	
5	HPLC-DAD, water-methanol extract	yes	yes	
6		yes	yes	
7	internal method HPLC/DAD	yes	yes	
8	HPLC / DAD	yes	yes	Butylparaben showed unusual low recovery
9			yes	
10	Extraction with methanol/water, HPLC-DAD	yes	yes	
11		yes	yes	

5.2.4 Isobutylparaben

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1				
2	GC-MS after extraction and derivatisation	no	no	
3	HPLC			3 deci pl as advised ; Isobutylparaben replaced by Isopropylparaben
4				
5				
6				
7	internal method HPLC/DAD	yes	no	
8				
9				
10				
11	"	yes	yes	

5.2.5 Isopropylparaben

Evaluation number	Method description and further remarks	Recovery with same matrix	Accredited	Remarks
1	60 min. Extraction with methanolic acetic acid at 40°C in ultrasonic bath and analysis by LC/MS / GC/MS	no	yes	
2				
3				
4	Preservatives HPLC-DAD	no	no	
5				not analysed
6		yes	yes	
7				
8	HPLC / DAD	yes	yes	Butylparaben showed unusual low recovery
9				
10	Extraction with methanol/water, HPLC-DAD	yes	yes	Result Isobutylparaben 0,012g/100g
11	"			

6. Index of participant laboratories

Teilnehmer / Participant	Ort / Town	Land / Country
		GERMANY
		ITALY
		GERMANY
		GERMANY
		SINGAPUR
		GERMANY
		GERMANY
		GERMANY
		ESTLAND
		GERMANY
		GERMANY

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

7. Index of references

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. DIN ISO 13528:2009; Statistische Verfahren für Eignungsprüfungen durch Ringversuche / Statistical methods for use in proficiency testing by interlaboratory comparisons
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. Protocol for the design, conduct and interpretation of method performance studies; W. Horwitz; Pure & Applied Chemistry, 67, 331-343 (1995)
12. Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing; M. Thompson; Analyst, 125, 385-386 (2000)
13. ASU § 64 LFGB K 84.00-21 Nachweis und Bestimmung von Benzylalkohol in kosmetischen Mitteln
14. ASU § 64 LFGB K 84.00-23 Nachweis und Bestimmung von Benzoesäure, 4-Hydroxybenzoesäure, Sorbinsäure, Salicylsäure und Propionsäure in kosmetischen Mitteln
15. ASU § 64 LFGB K 84.00-24 Nachweis und Bestimmung von 2-Phenoxyethanol, 1-Phenoxypropan-2-ol, Methyl-, Ethyl-, Propyl-, Butyl- und Benzyl-4-Hydroxybenzoat in kosmetischen Mitteln

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