Evaluation Report
proficiency test

DLA 51/2019

Cosmetic Products I:

Preservatives
Benzylalcohol, Benzoic Acid, Salicylic Acid, Sorbic Acid, 4-Hydroxy-Benzoic Acid

in Body Lotion

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Allgemeine Informationen zur Eignungsprüfung (EP)
General Information on the proficiency test (PT)

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Vertraulichkeit *Confidentiality*	Die Teilnehmerergebnisse sind im EP-Bericht in anonymisierter Form mit Auswertenummern benannt. Daten einzelner Teilnehmer werden ausschließlich nach vorheriger Zustimmung des Teilnehmers an Dritte weitergegeben. Participant result are named anonymously with evaluation numbers in the PT report. Data of individual participants will be passed on to third parties only with prior consent of the participant.

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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, 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 verification and/or validation of the particular testing method [1, 5].
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 / ISO 13528:2015 [2, 3].

2. Realisation

2.1 Test material

The test material is a mixture of common in commerce skin creams and body lotions from European Suppliers with addition of selected preservatives.

The materials were mixed and homogenized. The composition of the PT samples (list of ingredients) is shown in table 1.

Afterwards the samples were portioned to approximately 25 g into 28 ml plastic containers, sealed in metallised PET film bags and chronologically numbered.

Table 1: Composition of DLA-Samples

PT-Samples Skin Cream

Skin cream / Body lotion 1

Ingredients: Aqua, Paraffinum Liquidum, Glycerin, Cocos Nucifera Oil, Prunus Prsica Fruit Extrakt, Yoghurt Powder, Carbomer, Hydrogenated Palm Glycerides, Potassium Cetyl Phosphate, Caprylyl Glycol, p-Anisic Acid, Citric Acid, Sodium Hydroxide, Phenoxyethanol, Potassium Sorbate, Sodium Benzoate, Parfum

Skin cream / Body lotion 2

Ingredients: Aqua, Helianthus Annuus Seed Oil, Glycerin, Cetearyl Alcohol, Butyrospermum Parkii Butter, Orbignya Oleifera Seed Oil, Rosa Canina Fruit Oil, Candelilla Cera, Xanthan Gum, Tocopherol, Ubiquinone, Citric Acid, Sodium Benzoate, Parfum, Linalool, Geraniol, Citronellol, Limonene, Benzyl Salicylate, Benzyl Alcohol, Citral

Skin cream / Body lotion 3

Ingredients: Aqua, Ethylhexyl Stearate, Glycerin, Glyceryl Stearate Se, Hydrogenated Coco-Glycerides, Ceterayl Alcohol, Chamomilla Recutita Flower Extract, Bisabolol, Glucose, Stearic Acid, Palmitic Acid, Lactic Acid, Dimethicone, Propylene Glycol, Carbomer, Parfum, Butylene Glycol, Sodium Hydroxide, Sodium Benzoate, Potassium Sorbate, Phenoxyethanol, Benzyl Alkohol, Caprylyl Glycol, Decylene Glycol, Hexyl Cinnamal, Linalool, Benzyl Salicylate, Limonene, Citronellol, Alpha-Isomethyl Ionone, Citral, Coumarin, Geraniol

Skin cream / Body lotion 4

Ingredients: Aqua, Glyceryl Stearate Se, Isopropyl Palmitate, Glycerin, Simmondsia Chinensis (Jojoba) Seed Oil, Cetearyl Alcohol, Sodium Lactate, Stearic Acid, Palmitic Acid, Salicylic Acid, Salix Alba (Willow) Bark Extract, Helianthus Annuus (Sunflower) Seed Oil, Thuja Occidentalis (Leaf Oil), Pinus Pumilio (Oil), Eucalyptus Globulus (Oil), Citrus Aurantium Dulcis (Oil), Xanthan Gum, Maltodextrin, Tocopherol, Sodium Hydroxide, Citric Acid, Phenoxyethanol, Ethylhexylglycerin, Parfum, Limonene, Linalool, Citronellol, Citral, Hexyl Cinnamal

Skin cream / Body lotion 5

Ingredients:Aqua, Hydrogenated Palm Glycerides, Zea Mays Germ Oil, Paraffinum Liquidum, Cetearyl Alcohol, Ceteareth-100, Glyceryl Stearate, Glycerin, Ethylhexyl Stearate, Lanolin Cera, Propylene Glycol, Panthenol, Camphor, Hamamels Virginiana Leaf Extract, Chamomilla Recutita Flower Extract, Isatis Tinctoria Leaf Extract, Citrus Medica Limonum Fruit Oil, Phenoxyethanol, Methylparaben, Propylparaben, Níacinamide, Salicylic Acid, Parfum, Limonene, Citral

Further ingredients (incl. selected preservatives)

Ingredients: Alcohol, Benzoic Acid, Benzyl Alcohol, 4-Hydroxy Benzoic Acid, Sorbic Acid, CI 16255

Note: *The metrological traceability of temperature, mass and volume during production of the PT samples is ensured by DAkkS calibrated reference materials.*

2.1.1 Homogeneity

The calculation of the **repeatability standard deviations S_r of the participants' double determination** was used as an indicator of homogeneity for this PT. The repeatability standard deviation was in the range of 2,1% - 8,0%) (see Table 2).

The repeatability standard deviations are comparable to the precision data of the respective standardized methods (e.g. ASU K 84.00-21 and -23, s. 3.6.2) [18-19]. The repeatability standard deviations of the participants' results are given in the documentation in the statistic data (see 4.1 to 4.5).

Table 2: Repeatability standard deviation S_r of double determinations of the participants (coefficient of variation CV_r in %)

Parameter	**CV_r**
4-Hydroxy-Benzoic Acid	4,54 %
Benzoic Acid	2,98 %
Benzylalcohol	2,07 %
Salicylic Acid	3,41 %
Sorbic Acid	8,02 %

Furthermore, the homogeneity was graphically characterized for information by the **trend line function of participants' results for chronological bottled single samples** (s. 5.2.1).

In case the criterion for sufficient homogeneity of the test items is not fulfilled the impact on the target standard deviation will be verified. If necessary the evaluation of results will be done considering the standard uncertainty of the assigned value by z'-scores (s. 3.8 and 3.11) [3].

2.1.2 Stability

Experience has shown that unopened preserved skin creams are stable for several years. For the products, the manufacturer gave a shelf life of 12 months after opening. The stability of the sample material was thus ensured during the investigation period under the specified storage conditions.

2.2 Sample shipment and information to the test

Two portions of test material were sent to every participating laboratory in the 6th week of 2019. The testing method was optional. The tests should be finished at 22th March 2019 the latest.

With the cover letter along with the sample shipment the following information was given to participants:

The two portions contain identical samples of a mixture of common in commerce skin creams (bodylotions) with the preservatives benzylalcohol, benzoic acid, salicylic acid, sorbic acid and 4-hydroxy-benzoic acid to be determined.

Note: Please store the samples at 2-10°C on arrival.

Please note the attached information on the proficiency test.
(see documentation, section 5.3 Information on the PT)

2.3 Submission of results

The participants submitted their results in standard forms, which have been handed out with the samples (by email).

The finally calculated concentrations of the parameter as average of duplicate determinations of both numbered samples were used for the statistical evaluation. For the calculation of the repeatability– and reproducibility standard deviation the single values of the double determination were used.

Queried and documented were single results, recovery and the used testing methods. In case participants submitted several results for the same parameter obtained by different methods these results were evaluated with the same evaluation number with a letter as a suffix and indication of the related method.

All 13 participants submitted their results in time.

3. Evaluation

3.1 Consensus value from participants (assigned value)

The robust mean of the submitted results was used as assigned value (X_{pt}) („consensus value from participants") providing a normal distribution. The calculation was done according to algorithm A as described in annex C of ISO 13528 [3]. If there are < 12 quantitative results and an increased difference between robust mean and median, the median may be used as the assigned value (criterion: Δ median - rob. mean > 0,3 σ_{pt}) [3].

The condition is that the majority of the participants' results show a normal distribution or are distributed unimodal and symmetrically. To this end, an examination of the distribution is carried out, inter alia, using the kernel density estimate [3, 12].

In case there are indications for sources of higher variability such as a bimodal distribution of results, a cause analysis is performed. Frequently different analytical methods may cause an anomaly in results' distribution. If this is the case, separate evaluations with own assigned values (X_{pti}) are made whenever possible.

The statistical evaluation is carried out for all the parameters for a minimum of 7 values are present, in justified cases, an evaluation may also be carried out from 5 results onwards.

The actual measurement results will be drafted. Individual results, which are outside the specified measurement range of the participating laboratory (for example with the result > 25 mg/kg or < 2,5 mg/kg) or the indicating "0" will not be considered for the statistic evaluation [3].

3.2 Robust standard deviation

For comparison to the target standard deviation σ_{pt} (standard deviation for proficiency assessment) a robust standard deviation (S^x) was calculated. The calculation was done according to algorithm A as described in annex C of ISO 13528 [3].

3.3 Repeatability standard deviation

The repeatability standard deviation S_r is based on the laboratory´s standard deviation of (outlier free) individual participant results, each under repeatability conditions, that means analyses was performed on the same sample by the same operator using the same equipment in the same laboratory within a short time. It characterizes the mean deviation of the results within the laboratories [3] and is used by DLA as an indication of the homogeneity of the sample material.

In case single results from participants are available the calculation of the repeatability standard deviation S_r, also known as standard deviation within laboratories S_w, is performed by: [3, 4].

The relative repeatability standard deviation as a percentage of the mean value is indicated as coefficient of variation CV_r in the table of statistical characteristics in the results section in case single results

from participants are available.

3.4 Reproducibility standard deviation

The reproducibility standard deviation S_R represents a inter-laboratory estimate of the standard deviation for the determination of each parameter on the bases of (outlier free) individual participant results. It takes into account both the repeatability standard deviation S_r and the within-laboratory standard deviation S_S. Reproducibility standard deviations of PT´s may differ from reproducibility standard deviations of ring trials, because the participating laboratories of a PT generally use different internal conditions and methods for determining the measured values.
In the present evaluation, the specification of the reproducibility standard deviation, therefore, does not refer to a specific method, but characterizes approximately the comparability of results between the laboratories, assumed the effect of homogeneity and stability of the sample are negligible.

In case single results from participants are available the calculation of the reproducibility standard deviation S_R is performed by: [3, 4].

The relative reproducibility standard deviation CV_R in percent of the mean is given as variation coefficient in the statistical data of participant for each parameter. The significance of CV_R is further explained in section 3.9.

3.5 Exclusion of results and outliers

Before statistical evaluation obvious blunders, such as those with incorrect units, decimal point errors, too few significant digits (valid digits) or results for another proficiency test item can be removed from the data set [2]. Even if a result e.g. with a factor >10 deviates significantly from the mean and has an influence on the robust statistics, a result of the statistical evaluation can be excluded [3].

All results should be given at least with 2 significant digits. Specifying 3 significant digits is usually sufficient.

Results obtained by different analytical methods causing an increased variability and/or a bi- or multimodal distribution of results, are treated separately or could be excluded in case of too few numbers of results. For this results are checked by kernel density estimation [3, 12].

Results are tested for outliers by the use of robust statistics (algorithm A): If a value deviates from the robust mean by more than 3 times the robust standard deviation, it can be classified as an outlier (see above) [3]. Due to the use of robust statistics outliers are not excluded, provided that no other reasons are present [3]. Detected outliers are only mentioned in the results section, if they have been excluded from the statistical evaluation.

3.6 Target standard deviation (for proficiency assessment)

The target standard deviation of the assigned value σ_{pt} (= standard deviation for proficiency assessment) can be determined according to the following methods.

If an acceptable quotient S^*/σ_{pt} is present, the target standard deviation of the general model by Horwitz is preferably used for the proficiency assessment. It is usually suitable for evaluation of interlaboratory studies, where different methods are applied by the participants. On the other hand the target standard deviation from the evaluation of precision data of an precision experiment is derived from collaborative studies with specified analytical methods.

For valuation of all parameters in the present PT the target standard deviation according to the general model of Horwitz was applied (see 3.6.1).

Additionally for all parameters the standard uncertainty was considered by evaluation using z'-scores (see 3.6.8).

3.6.1 General model (Horwitz)

Based on statistical characteristics obtained in numerous PTs for different parameters and methods Horwitz has derived a general model for estimating the reproducibility standard deviation σ_R [6]. Later the model was modified by Thompson for certain concentration ranges [10]. The reproducibility standard deviation σ_R can be applied as the relative target standard deviation σ_{pt} in % of the assigned values and calculated according to the following equations [3]. For this the assigned value X_{pt} is used for the concentration c.

Equations	**Range of concentrations**	**corresponds to**
$\sigma_R = 0{,}22c$	$c < 1{,}2 \times 10^{-7}$	< 120 µg/kg
$\sigma_R = 0{,}02c^{0{,}8495}$	$1{,}2 \times 10^{-7} \leq c \leq 0{,}138$	≥ 120 µg/kg
$\sigma_R = 0{,}01c^{0{,}5}$	$c > 0{,}138$	> 13,8 g/100g

with c = mass content of analyte (as relative size, e.g. 1 mg/kg = 1 ppm = 10^{-6} kg/kg)

3.6.2 Value by precision experiment

Using the reproducibility standard deviation σ_R and the repeatability standard deviation σ_r of a precision experiment (collaborative trial or proficiency test) the target standard deviation σ_{pt} can be derived considering the number of replicate measurements m of participants in the present PT [3]:

$$\sigma_{pt} = \sqrt{\sigma_R^2 - \sigma_r^2\left(m - 1/m\right)}$$

The German official ASU §64 method for the determination of benzoic acid, benzyl alcohol and sorbic acid in cosmetic products (K 84.00-21 and -23) gives a maximum deviation of 10% for the repeatability determination [18, 19]. Reproducibility standard deviation and repeatability standard deviation are not reported.

3.6.3 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 [3].

For the present evaluation the target standard deviation according to 3.6.1 was regarded suitable.

Table 3 shows selected statistic data of participants results of present PT compared to PT results of previous years.

3.7 z-Score

To assess the results of the participants the z-score is used. It indicates about which multiple of the target standard deviation (σ_{pt}) the result (x_i) of the participant is deviating from the assigned value (X_{pt}) [3].
Participants' z-scores are derived from:

$$z_i = \frac{\left(x_i - x_{pt}\right)}{\sigma_{pt}}$$

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

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

The valid z-Score for each parameter is indicated as z-Score (σ_{pt}).

3.7.1 Warning and action signals

In accordance with the norm ISO 13528 it is recommended that a result that gives rise to a *z*-score above 3,0 or below −3,0, shall be considered to give an "action signal" [3]. Likewise, a *z*-score above 2,0 or below −2,0 shall be considered to give a "warning signal". A single "action signal", or "warning signal" in two successive PT-rounds, shall be taken as evidence that an anomaly has occurred which requires investigation.

An error or cause analysis can be carried out by checking the analysis process including understanding and implementation of the measurement by the staff, details of the measurement procedure, calibration of equipment and composition of reagents, transmission error or an error in the calculation, in the trueness and precision and use of reference material. If necessary, the problems must be addressed through appropriate corrective action [3].

In the figures of z-scores DLA gives the limits of warning and action signals as yellow and red lines respectively. According to ISO 13528 the signals are valid only in case of a number of ≥ 10 results [3].

Table 3: Characteristics of the present PT (on dark grey) in comparison to previous PTs since 2015 (SD = standard deviation, CV = coefficient of variation)

Parameter	Matrix	robust Mean [mg/kg]	rob. SD (S*) [mg/kg]	rel. SD (VK_{S*}) [%]	Quotient $S^*/\sigma_{pt'}$	DLA-Report
Methyliso-thiazolinone	Liquid Soap	0,000388 g/100g	0,0000154 g/100g	3,97	0,30*	DLA 44/2015
Methyl-chloroiso-thiazolinone	Liquid Soap	0,00121 g/100g	0,000172 g/100g	14,2	1,3*	DLA 44/2015
Benzoic Acid	Liquid Soap	0,296 g/100g	0,0141 g/100g	4,76	1,0*	DLA 44/2015
Benzoic Acid	Body Lotion	0,105 g/100g	0,0165 g/100g	15,8	2,0	DLA 51/2019
Benzylalcohol	Liquid Soap	0,826 g/100g	0,0488 g/100g	5,91	1,4*	DLA 44/2015
Benzylalcohol	Body Lotion	0,613 g/100g	0,0822 g/100g	13,4	1,9	DLA 51/2019
Sorbic Acid	Liquid Soap	0,0506 g/100g	0,00332 g/100g	6,56	1,0*	DLA 44/2015
Sorbic Acid	Body Lotion	0,417 g/100g	0,0425 g/100g	10,2	1,7	DLA 51/2019
4-Hydroxybenzo-ic Acid	Body Lotion	0,307 g/100g**	0,0431 g/100g	13,7	1,8	DLA 51/2019
Salicylic Acid	Body Lotion	0,0327 g/100g	0,0108 g/100g	32,9	2,2	DLA 51/2019

** with target standard deviation σ_{pt}*
*** Median*

3.8 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. 3.11). The z'-score represents the relation of the deviation of the result (x) of the participant from the respective consensus value (X) to the square root of quadrat sum of the target standard deviation (σ_{pt}) and the standard uncertainty (Ux_{pt}) [3].

The calculation is performed by:

$$z'_i = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u_{(x_{pt})}^2}}$$

If carried out an evaluation of the results by means of z 'score, we have defined below the expression in the denominator as a target standard deviation σ_{pt}'.

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

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

For warning and action signals see 3.7.1.

3.9 Reproducibility cofficient of variation (CV_R)

The variation coefficient (CV) of the reproducibility (= *relative reproducibility standard deviation)* is calculated from the standard deviation and the mean as follows [4, 13]:

$$CV_R = \frac{S_R * 100}{X}$$

In contrast to the standard deviation as a measure of the absolute variability the CV gives the relative variability within a data region. While a low CV, e.g. <5-10% can be taken as evidence for a homogeneous set of results, a CV of more than 50% indicates a "strong inhomogeneity of statistical mass", so that the suitability for certain applications such as the assessment of exceeded maximum levels or the performance evaluation of the participating laboratories possibly can not be done [3].

3.10 Quotient S*/σ_{pt}

Following the HorRat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation S* and target standard deviation σ_{pt} 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 [3].

3.11 Standard uncertainty of the assigned value

Every assigned value has a standard uncertainty that depends on the analytical method, differences between the analytical methods used, the test material, the number of participating laboratories (P) and on other factors. The standard uncertainty ($U_{(Xpt)}$) for this PT is calculated as follows [3]:

$$u_{(x_{pt})} = 1{,}25 \times \frac{s^*}{\sqrt{p}}$$

If $U_{(Xpt)} \leq 0{,}3\ \sigma_{pt}$ the standard uncertainty of the assigned value needs not to be included in the interpretation of the results of the PT [3]. Values exceeding 0,3 imply, that the target standard deviation could be too low with respect to the standard uncertainty of the assigned value.

The traceability of the assigned value is ensured on the basis of the consensus value as a robust mean of the participant results.

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 first table the characteristics are listed:

Statistic Data
Number of results
Number of outliers
Mean
Median
Robust mean(X_{pt})
Robust standard deviation (S^*)
Number with m replicate measurements
Repeatability standard deviation (S_r)
Coefficient of Variation (CV_r) in %
Reproducibility standard deviation (S_R)
Coefficient of Variation (CV_R) in %
Target range:
Target standard deviation σ_{pt} or σ_{pt}'
Target standard deviation for information
lower limit of target range ($X_{pt} - 2\sigma_{pt}$) or ($X_{pt} - 2\sigma_{pt}$') *
upper limit of target range ($X_{pt} + 2\sigma_{pt}$) or ($X_{pt} + 2\sigma_{pt}$´) *
Quotient S/σ_{pt} or S*/σ_{pt}'*
Standard uncertainty U(X_{pt})
Number of results in the target range
Percent in the target range

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

In the table below, the results of the participating laboratories are formatted in 3 valid digits**:

Auswerte-nummer Evaluation number	Parameter [Einheit / Unit]	Abweichung Deviation	z-Score σpt	Hinweis Remark

*** In the documentation part, the results are given as they were transmitted by the participants.*

4.1 4-Hydroxy-Benzoic Acid (in g/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	0,308
Robust Mean	0,314
Median (X_{pt})	**0,307**
Robust standard deviation (S*)	**0,0431**
Number with 2 replicates	8
Repeatability SD (S_r)	0,0139
Repeatability (CV_r)	4,54%
Reproducibility SD (S_R)	0,0524
Reproducibility (CV_R)	17,1%
Target range:	
Target standard deviation $\sigma_{pt'}$	**0,0240**
lower limit of target range	**0,258**
upper limit of target range	**0,355**
Quotient S/$\sigma_{pt'}$*	*1,8*
Standard uncertainty $U_{(Xpt)}$	*0,0190*
Results in the target range	*6*
Percent in the target range	*75%*

Comments to the statistic data:

The median was used as the assigned value (see 3.1).

The target standard deviation was calculated according to the general model of Horwitz (s. 3.6.1).

The evaluation of all methods showed an increased variability of results, with a quotient S*/σ_{pt} above 2,0. Therefore the evaluation was done by z'-score considering the standard uncertainty. The quotient S*/$\sigma_{pt'}$ was then below 2,0.
The repeatability and reproducibility standard deviations were in the range of previous PTs (see 3.6.3). The comparability of results is given.

75% of results were in the target range.

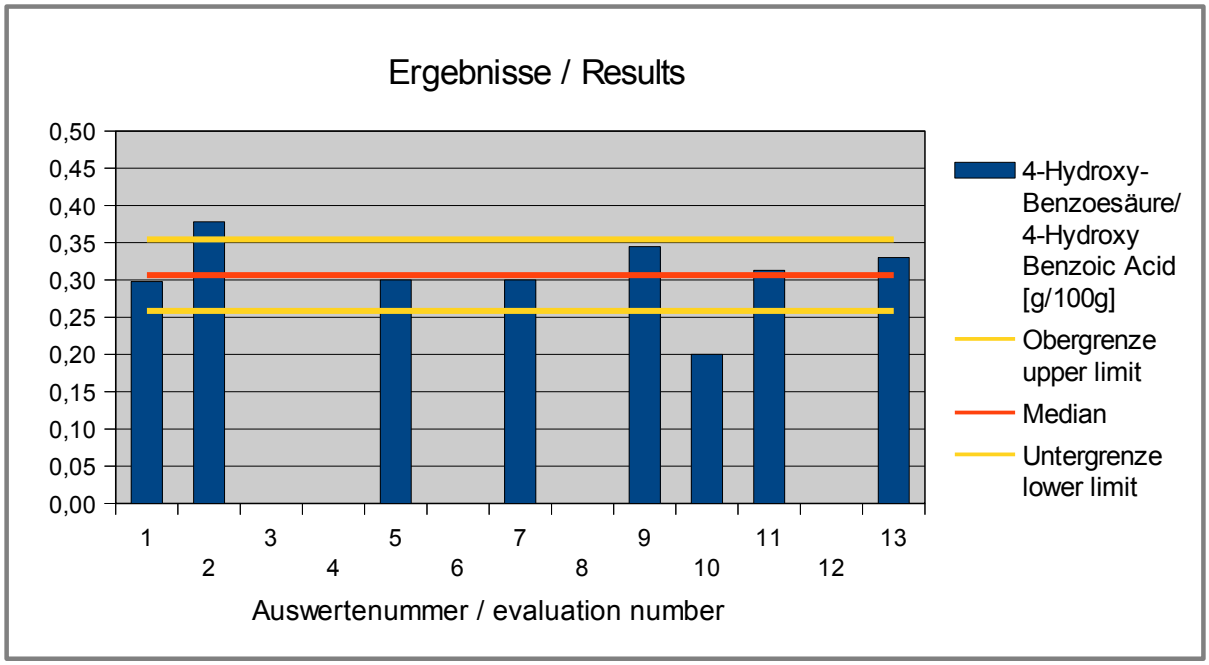


Abb. / Fig. 1: Ergebnisse 4-Hydroxybenzoesäure / Results 4-Hydroxy Benzoic Acid

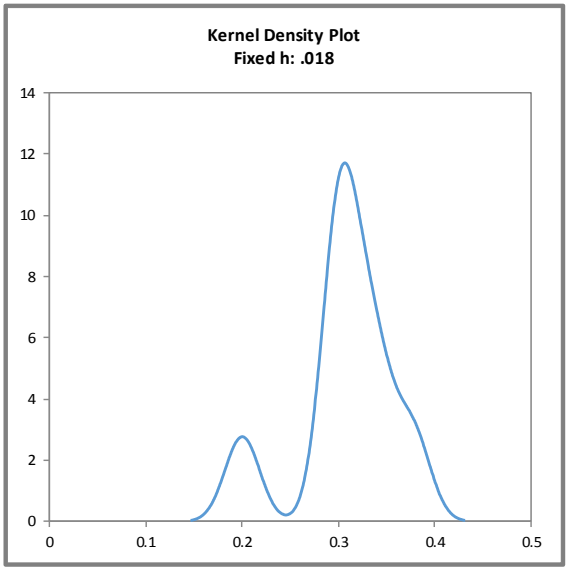


Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x σ_{pt} von X_{pt})

Kernel density plot of results (with h = 0,75 x σ_{pt} of X_{pt})

Comment:
The kernel density plot shows almost a symmetrical distribution of results with a smaller peak at approx. 0,2 g/100g and a shoulder, due to results outside the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	4-Hydroxy-Benzoesäure/ 4-Hydroxy Benzoic Acid [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z'-Score (σ_{pt})	Hinweis Remark
1	0,298	-0,0085	-0,35	
2	0,378	0,0715	3,0	
3				
4				
5	0,300	-0,0065	-0,27	
6				
7	0,300	-0,0065	-0,27	
8				
9	0,345	0,0384	1,6	
10	0,200	-0,1065	-4,4	
11	0,313	0,0065	0,27	
12				
13	0,330	0,0235	1,0	

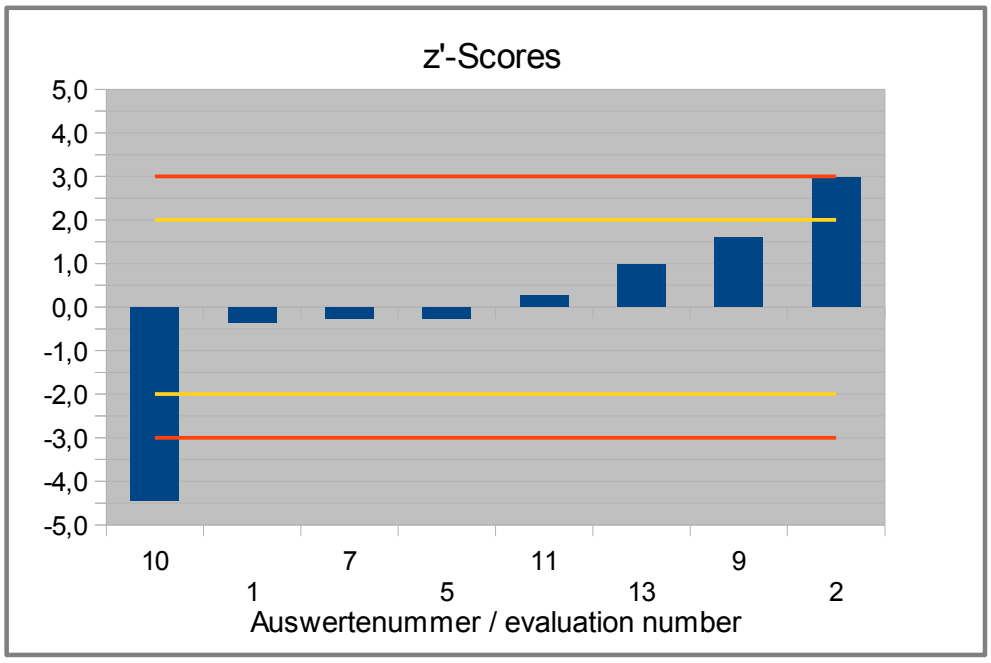


Abb. / Fig. 3: z'-Scores 4-Hydroxybenzoesäure / 4-Hydroxy Benzoic Acid

4.2 Benzoic Acid (in g/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results°	12
Number of outliers	1
Mean	0,105
Median	0,106
Robust Mean (X_{pt})	**0,105**
Robust standard deviation (S*)	**0,0165**
Number with 2 replicates	12
Repeatability SD (S_r)	0,00312
Repeatability (CV_r)	2,98%
Reproducibility SD (S_R)	0,0143
Reproducibility (CV_R)	13,7%
Target range:	
Target standard deviation $\sigma_{pt'}$	**0,00839**
lower limit of target range	**0,0882**
upper limit of target range	**0,122**
Quotient $S^*/\sigma_{pt'}$	*2,0*
Standard uncertainty $U_{(Xpt)}$	*0,00597*
Results in the target range	*9*
Percent in the target range	*75%*

° Results without outlier (No. 7)

Comments to the statistic data:

The target standard deviation was calculated according to the general model of Horwitz (s. 3.6.1).

The evaluation of all methods showed an increased variability of results, with a quotient S^*/σ_{pt} above 2,0. Therefore the evaluation was done by z'-score considering the standard uncertainty. The quotient $S^*/\sigma_{pt'}$ was then below 2,0.
The repeatability and reproducibility standard deviations were in the range of previous PTs (see 3.6.3). The comparability of results is given.

75% of results were in the target range.

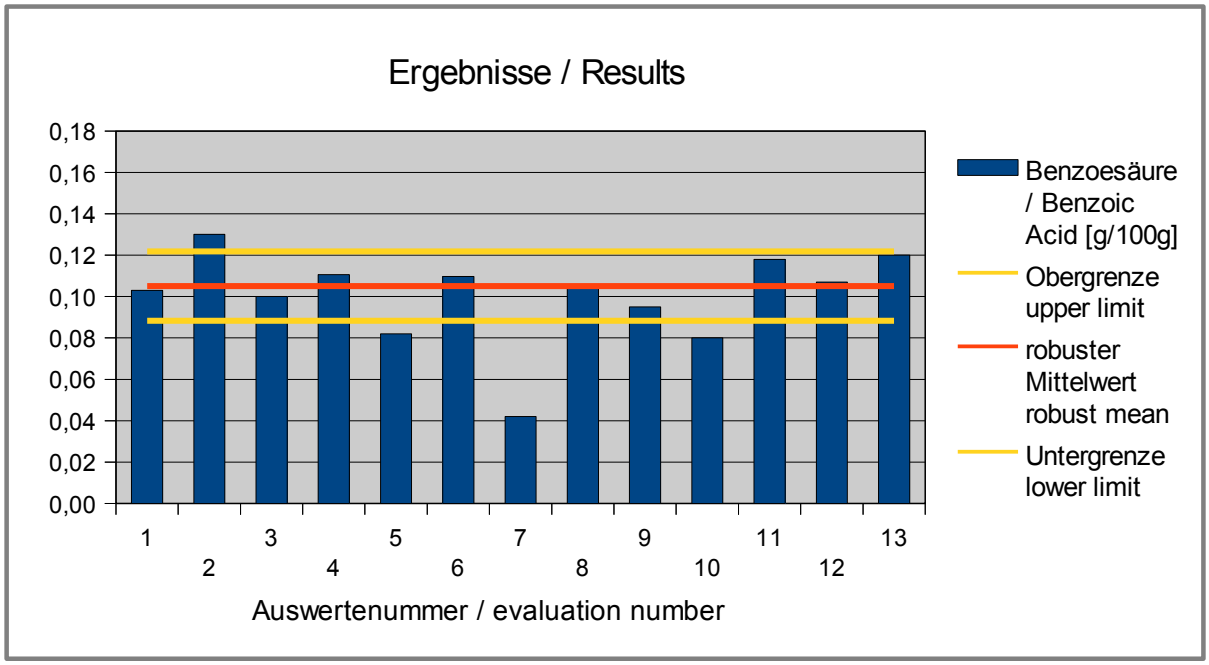


Abb. / Fig. 4: Ergebnisse Benzoesäure / Results Benzoic Acid

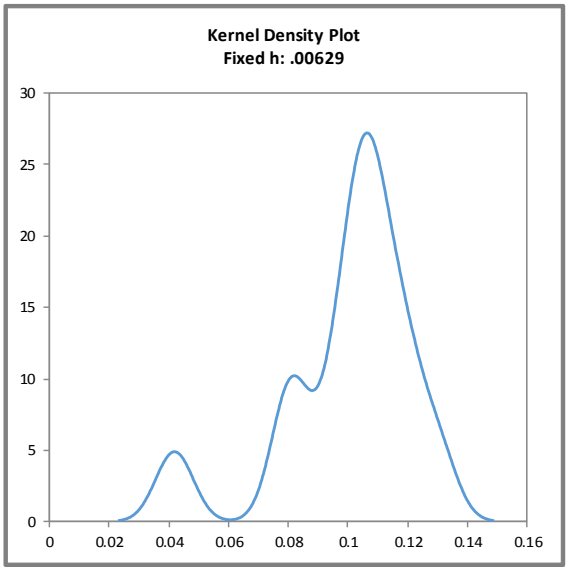


Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x σ_{pt} von X_{pt})

Kernel density plot of results (with h = 0,75 x σ_{pt} of X_{pt})

Comment:
The kernel density plot shows almost a symmetrical distribution of results with two smaller peaks at approx. 0,04 g/100g and approx. 0,08 g/100g, due to results out of the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Benzoesäure / Benzoic Acid [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z'-Score (σ_{pt})	Hinweis Remark
1	0,103	-0,0020	-0,24	
2	0,130	0,0250	3,0	
3	0,100	-0,0050	-0,60	
4	0,111	0,0056	0,66	
5	0,082	-0,0230	-2,7	
6	0,110	0,0047	0,56	
7	0,0420	-0,0607		Ausreißer ausgeschlossen / outlier excluded
8	0,105	0,0000	0,00	
9	0,095	-0,0100	-1,2	
10	0,080	-0,0250	-3,0	
11	0,118	0,0130	1,5	
12	0,107	0,0020	0,23	
13	0,120	0,0150	1,8	

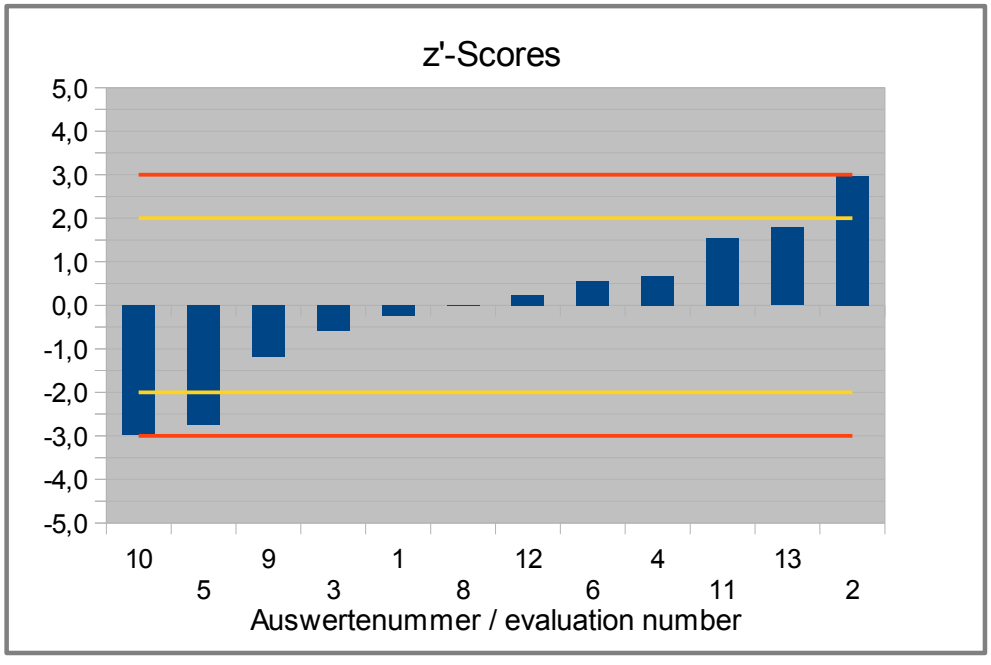


Abb. / Fig. 6: z'-Scores Benzoesäure / Benzoic Acid

4.3 Benzylalcohol (in g/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results°	9
Number of outliers	2
Mean	0,609
Median	0,607
Robust Mean (X_{pt})	**0,613**
Robust standard deviation (S*)	**0,0822**
Number with 2 replicates	9
Repeatability SD (S_r)	0,0126
Repeatability (CV_r)	2,07%
Reproducibility SD (S_R)	0,0898
Reproducibility (CV_R)	14,8%
Target range:	
Target standard deviation $\sigma_{pt'}$	**0,0432**
lower limit of target range	**0,526**
upper limit of target range	**0,699**
Quotient $S^*/\sigma_{pt'}$	*1,9*
Standard uncertainty $U_{(Xpt)}$	*0,0342*
Results in the target range	7
Percent in the target range	*78%*

° Results without outliers (No. 9 and 13)

Comments to the statistic data:

The target standard deviation was calculated according to the general model of Horwitz (s. 3.6.1).

The evaluation of all methods showed an increased variability of results, with a quotient S^*/σ_{pt} above 2,0. Therefore the evaluation was done by z'-score considering the standard uncertainty. The quotient $S^*/\sigma_{pt'}$ was then below 2,0.
The repeatability and reproducibility standard deviations were in the range of previous PTs (see 3.6.3). The comparability of results is given.

78% of results were in the target range.

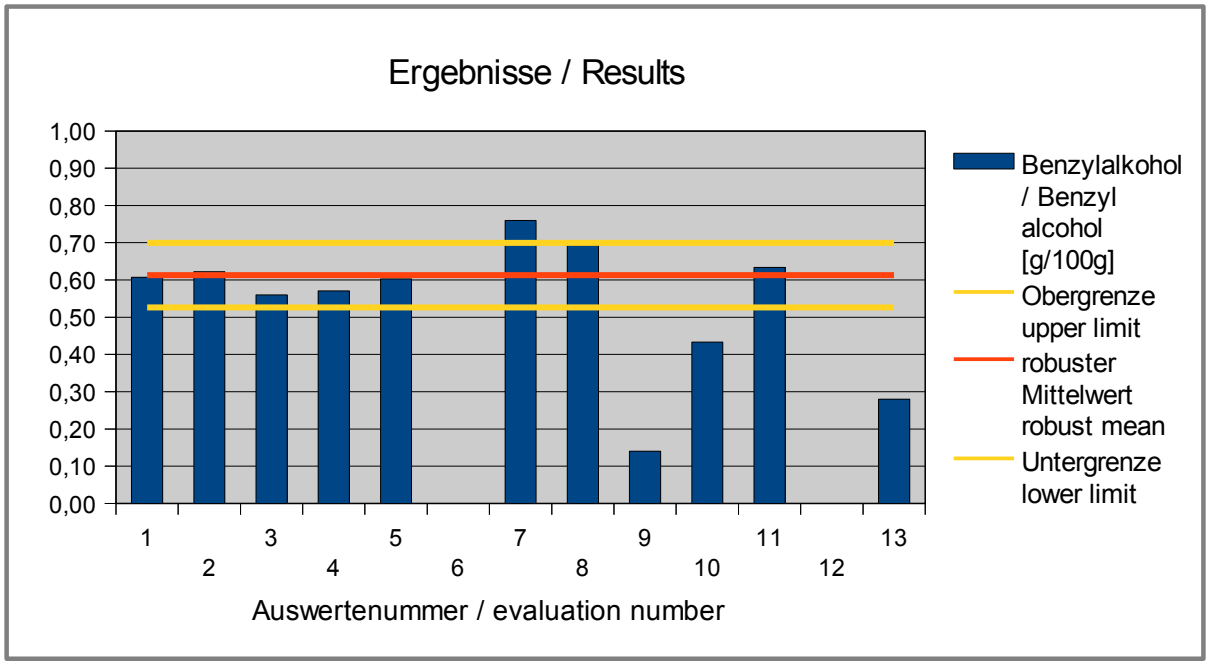


Abb. / Fig. 7: Ergebnisse Benzylalkohol / Results Benzyl alcohol

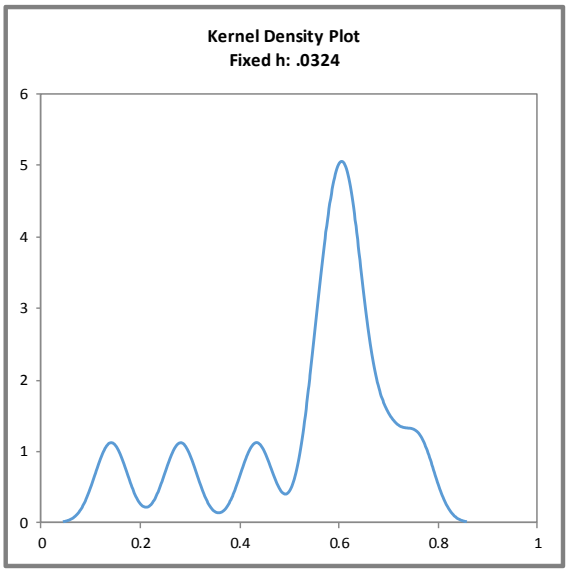


Abb. / Fig. 8:
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

Kernel density plot of results
(with h = 0,75 x σ_{pt} of X_{pt})

Comment:
The kernel density plot shows almost a symmetrical distribution of results with a shoulder at approx. 0,7 g/100g and several smaller peaks <0,5 g/100g, due to single results out of the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Benzylalkohol/ Benzyl alcohol [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z'-Score (σ_{pt})	Hinweis Remark
1	0,607	-0,0058	-0,14	
2	0,622	0,0092	0,21	
3	0,560	-0,0528	-1,2	
4	0,571	-0,0419	-0,97	
5	0,603	-0,0098	-0,23	
6				
7	0,760	0,1472	3,4	
8	0,693	0,0802	1,9	
9	0,140	-0,4129		Ausreißer ausgeschlossen / outlier excluded
10	0,433	-0,1798	-4,2	
11	0,634	0,0212	0,49	
12				
13	0,280	-0,2729		Ausreißer ausgeschlossen / outlier excluded

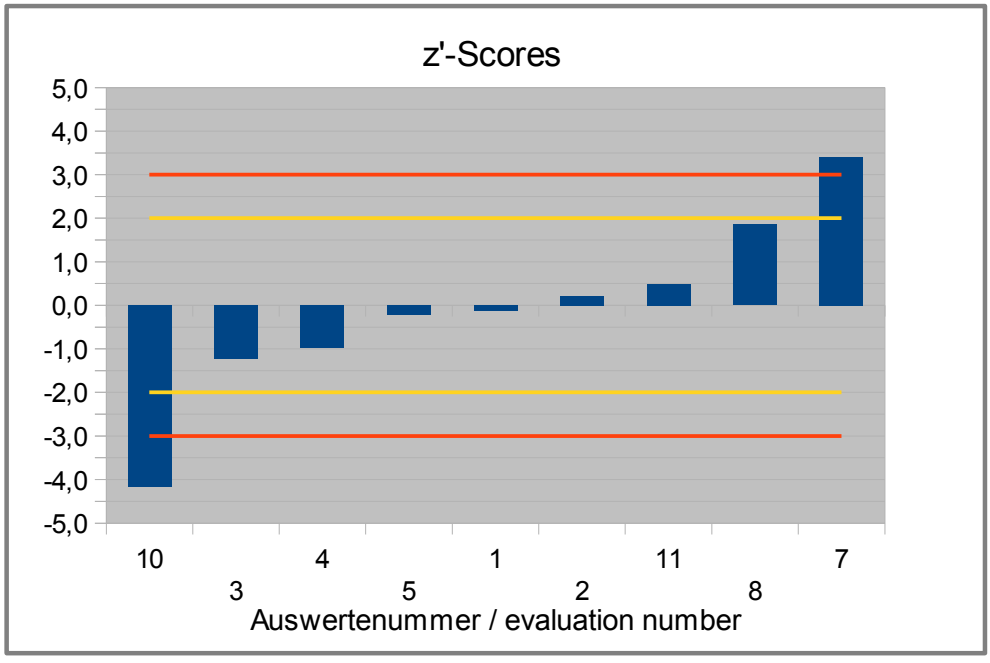


Abb. / Fig. 9: z'-Scores Benzylalkohol / Benzyl alcohol

4.4 Salicylic Acid (in g/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	10
Number of outliers	0
Mean	0,0330
Median	0,0315
Robust Mean (X_{pt})	**0,0327**
Robust standard deviation (S*)	**0,0108**
Number with 2 replicates	10
Repeatability SD (S_r)	0,00112
Repeatability (CV_r)	3,41%
Reproducibility SD (S_R)	0,0112
Reproducibility (CV_R)	34,1%
Target range:	
Target standard deviation σ_{pt}'	**0,00478**
lower limit of target range	**0,0231**
upper limit of target range	**0,0422**
Quotient S^*/σ_{pt}'	*2,2*
Standard uncertainty $U_{(Xpt)}$	*0,00425*
Results in the target range	7
Percent in the target range	*70%*

Comments to the statistic data:

The target standard deviation was calculated according to the general model of Horwitz (s. 3.6.1).

The evaluation of all methods showed an increased variability of results, with a quotient S^*/σ_{pt} above 2,0. Therefore the evaluation was done by z'-score considering the standard uncertainty. The quotient S^*/σ_{pt}' was then 2,2.
The repeatability and reproducibility standard deviations were in the range of previous PTs (see 3.6.3). The comparability of results is given.

70% of results were in the target range.

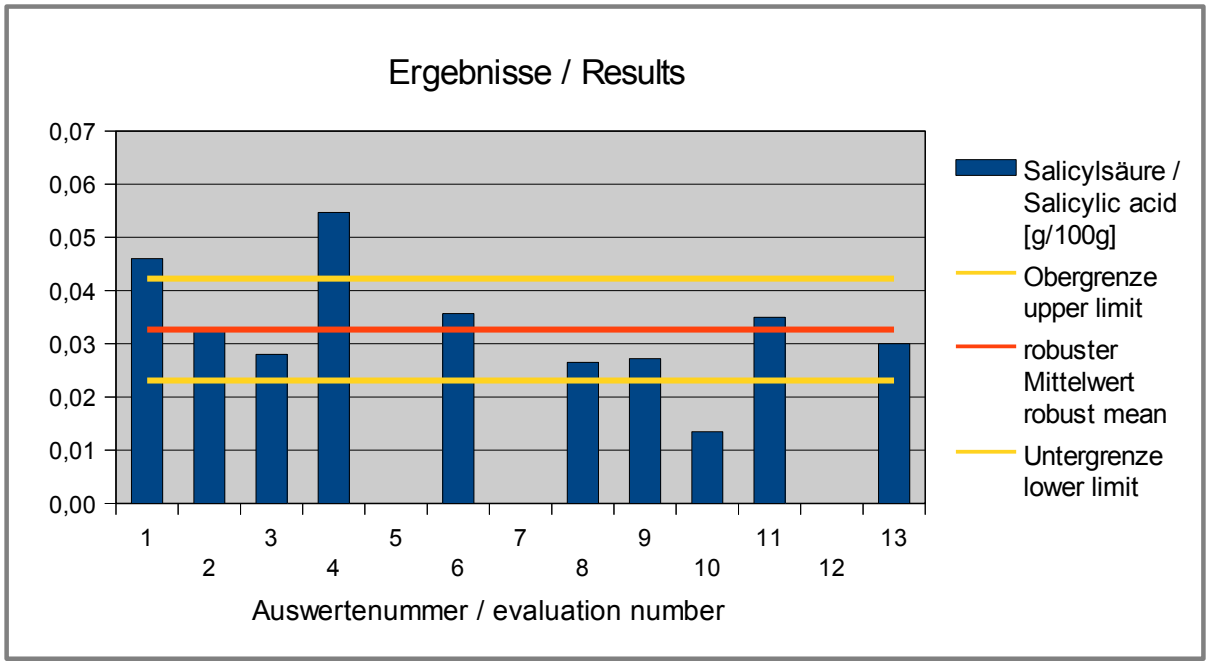


Abb. / Fig. 10: Ergebnisse Salicylsäure / Results Salicylic Acid

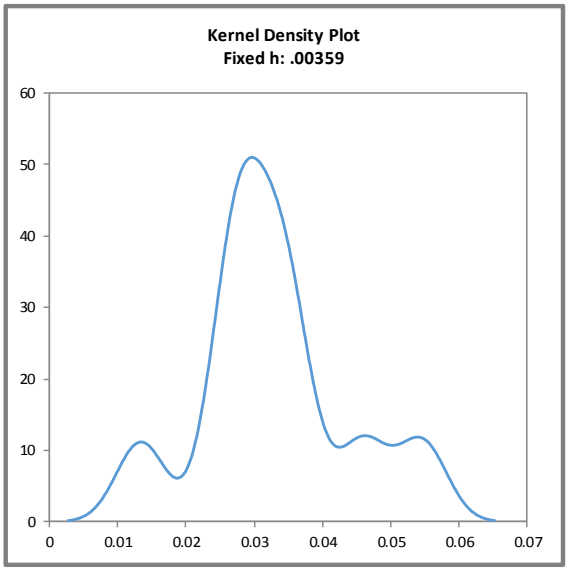


Abb. / Fig. 11:
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

Kernel density plot of results
(with h = 0,75 x σ_{pt} of X_{pt})

Comment:
The kernel density plot shows almost a symmetrical distribution of results with a smaller peak at approx. 0,015 g/100g and another smaller peak with two maxima in the area >0,04 g/100g, due to results out of the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Salicylsäure / Salicylic acid [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z'-Score (σ_{pt})	Hinweis Remark
1	0,0460	0,01333	2,8	
2	0,0330	0,00033	0,07	
3	0,0280	-0,00467	-1,0	
4	0,0547	0,02203	4,6	
5				
6	0,0357	0,00303	0,63	
7				
8	0,0265	-0,00617	-1,3	
9	0,0272	-0,00547	-1,1	
10	0,0135	-0,01917	-4,0	
11	0,0350	0,00233	0,49	
12				
13	0,0300	-0,00267	-0,56	

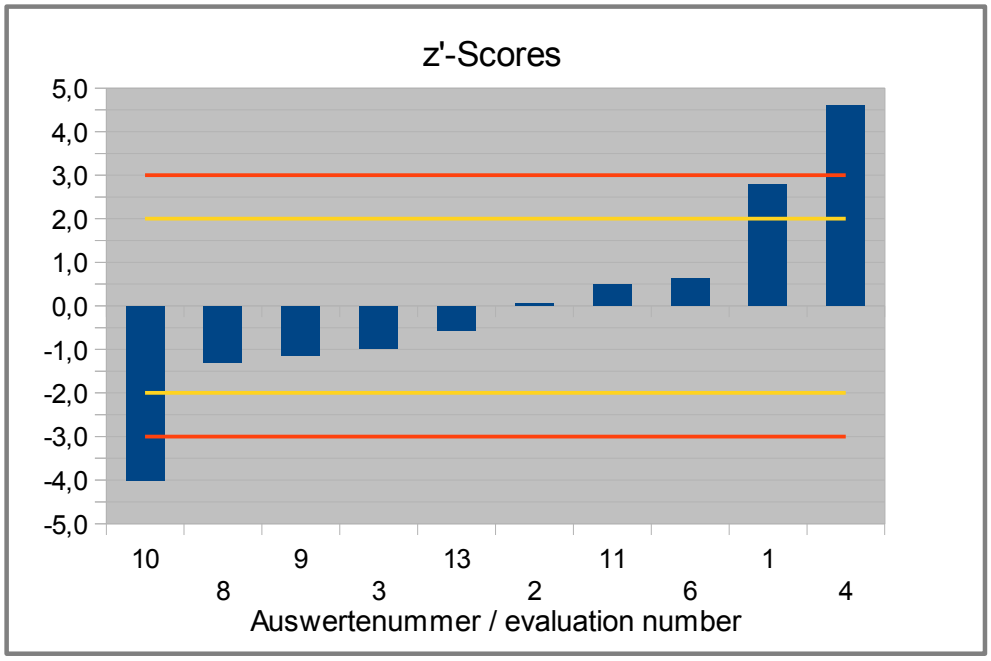


Abb. / Fig. 12: z'-Scores Salicylsäure / Salicylic Acid

4.5 Sorbic Acid (in g/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results°	12
Number of outliers	1
Mean	0,421
Median	0,412
Robust Mean (X_{pt})	**0,417**
Robust standard deviation (S*)	**0,0425**
Number with 2 replicates	11
Repeatability SD (S_r)	0,0326
Repeatability (CV_r)	8,02%
Reproducibility SD (S_R)	0,0481
Reproducibility (CV_R)	11,8%
Target range:	
Target standard deviation σ_{pt}'	**0,0244**
lower limit of target range	**0,368**
upper limit of target range	**0,466**
Quotient S/σ_{pt}'*	*1,7*
Standard uncertainty $U_{(Xpt)}$	*0,0153*
Results in the target range	*10*
Percent in the target range	*83%*

° Results without outlier (No. 13)

Comments to the statistic data:

The target standard deviation was calculated according to the general model of Horwitz (s. 3.6.1).

The evaluation of all methods showed an increased variability of results, with a quotient S*/σ_{pt} above 2,0. Therefore the evaluation was done by z'-score considering the standard uncertainty. The quotient S*/σ_{pt}' was then below 2,0.
The repeatability and reproducibility standard deviations were in the range of previous PTs (see 3.6.3). The comparability of results is given.

83% of results were in the target range.

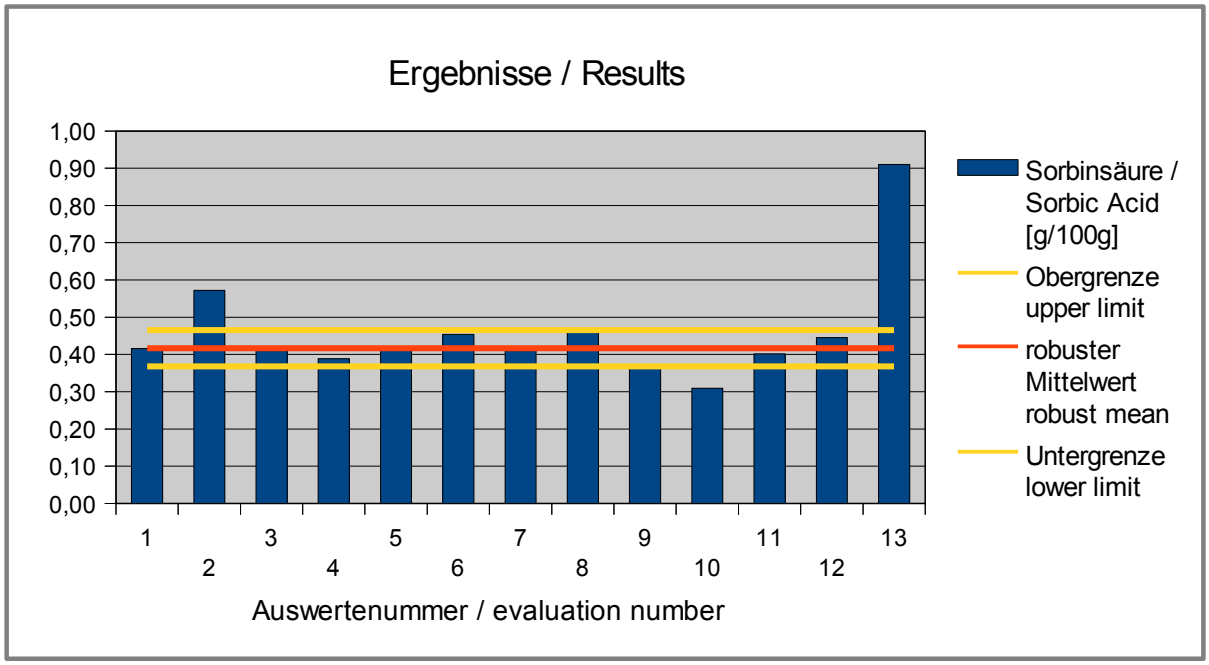


Abb. / Fig. 13: Ergebnisse Sorbinsäure / Results Sorbic Acid

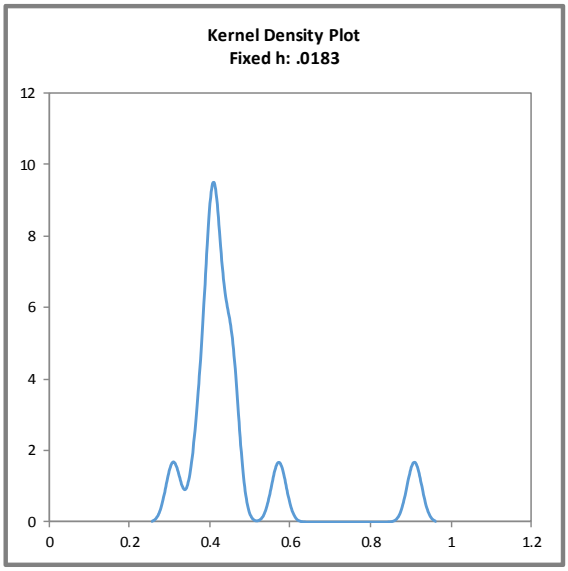


Abb. / Fig. 14:
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x σ_{pt} von X_{pt})

Kernel density plot of results (with h = 0,75 x σ_{pt} of X_{pt})

Comment:
The kernel density plot shows almost a symmetrical distribution of results with smaller peaks at approx. 0,3 g/100g, 0,55 g/100g and 0,9 g/100g, due to results out of the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Sorbinsäure / Sorbic Acid [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z'-Score (σ_{pt})	Hinweis Remark
1	0,416	-0,0008	-0,03	
2	0,572	0,1552	6,4	
3	0,410	-0,0068	-0,28	
4	0,389	-0,0278	-1,1	
5	0,414	-0,0028	-0,11	
6	0,454	0,0372	1,5	
7	0,410	-0,0068	-0,28	
8	0,459	0,0422	1,7	
9	0,369	-0,0477	-2,0	
10	0,309	-0,1078	-4,4	
11	0,402	-0,0148	-0,61	
12	0,445	0,0282	1,2	
13	0,910	0,485		Ausreißer ausgeschlossen / Outlier excluded

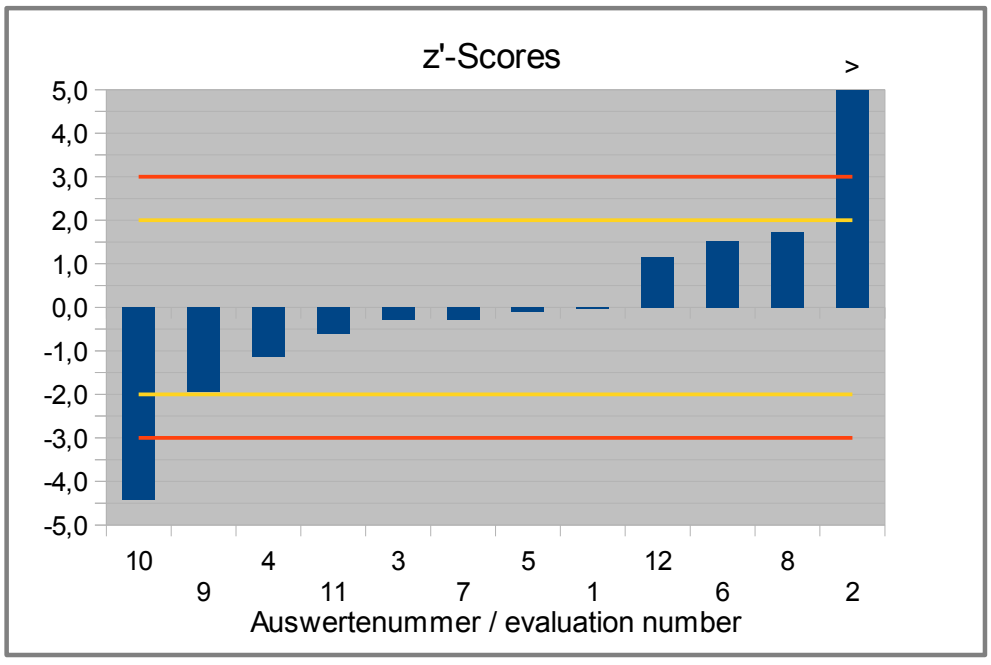


Abb. / Fig. 15: z'-Scores Sorbinsäure / Sorbic Acid

5. Documentation

5.1 Details by the participants

Note: Information given in German were translated by DLA to the best of our knowledge (without guarantee of correctness).

5.1.1 Primary Data

Parameter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quan-tification	Incl. RR	Recovery rate [%]
					Day/Month					yes / no	in %
4-Hydroxy-Benzoesäure/ 4-Hydroxy-Benzoic Acid	1	g/100g	2	78	18.03.19	0,298	0,301	0,295	0,01 g/100g	no	
	2	g/100g	22	58	13./14.03.	0,378	0,377	0,379	0,005	no	
	3	g/100g	-	-	-	-	-	-	-	-	-
	4	g/100g									
	5	g/100g	25	55	13.02.19	0,3	0,32	0,279	0,026	yes	93,2
	6	g/100g	51	29							
	7	g/100g	3	77	01.03.19	0,3	0,3	0,29	0,005	no	no analysis
	8	g/100g									
	9	g/100g	14	66	5.3.-21.3.	0,3449	0,3365	0,3533		no	
	10	g/100g	12	68	21.03.19	0,2	0,195	0,205	not determined	no	not determined
	11	g/100g	30	50	20.03.19	0,313	0,314	0,312	0,02	yes	100
	12	g/100g									
	13	g/100g	33	47	04/03	0,33	0,31	0,34	0,00241	No	

Parameter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quan-tification	Incl. RR	Recovery rate [%]
					Day/Month					yes / no	in %
Benzoesäure/ Benzoic Acid	1	g/100g	2	78	18.03.19	0,103	0,103	0,102	0,02 g/100g	no	109
	2	g/100g	22	58	13./14.03.	0,13	0,128	0,131	0,001	no	
	3	g/100g	27	53	11.03.19	0,1	0,1	0,1	0,001	no	96,8
	4	g/100g	39	40	06.03.19	0,1106	0,1099	0,1113		no	
	5	g/100g	25	55	13.02.19	0,082	0,087	0,077	0,051	yes	99,8
	6	g/100g	51	29	18.02.19	0,1097	0,1102	0,1091	5 mg/kg		
	7	g/100g	3	77	01.03.19	0,042	0,041	0,042	0,005	no	no analysis
	8	g/100g	60	20	05.03.19	0,105	0,104	0,106		no	
	9	g/100g	14	66	5.3.-21.3.	0,095	0,0952	0,0948		no	
	10	g/100g	12	68	21.03.19	0,08	0,078	0,082	not determined	no	not determined
	11	g/100g	30	50	20.03.19	0,118	0,118	0,118	0,02	yes	100
	12	g/100g	8	72	07.02.	0,107	0,107	0,107	0,001g/100g	yes	99
	13	g/100g	33	47	04/03	0,12	0,12	0,11	0,00197	No	

Parameter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quan-tification	Incl. RR	Recovery rate [%]
					Day/Month					yes / no	in %
Benzylalkohol/ Benzylalcohol	1	g/100g	2	78	18.03.19	0,607	0,61	0,604	0,08 g/100g	no	
	2	g/100g	22	58	22.02.	0,622	0,627	0,618	0,014	no	
	3	g/100g	27	53	08.03.19	0,56	0,56	0,56	0,001	no	95
	4	g/100g	39	40	27.02.19	0,5709	0,5737	0,5681		no	
	5	g/100g	25	55	13.02.19	0,603	0,626	0,58	0,026	yes	89,9
	6	g/100g	51	29							
	7	g/100g	3	77	01.03.19	0,76	0,75	0,76	0,005	no	no analysis
	8	g/100g	60	20	20.03.19	0,693	0,692	0,693		no	
	9	g/100g	14	66	5.3.	0,1398	0,1479	0,1316		no	
	10	g/100g	12	68	21.03.19	0,433	0,422	0,444	not determined	no	not determined
	11	g/100g	30	50	21.03.19	0,634	0,634	0,633	0,01	yes	100
	12	g/100g									
	13	g/100g	33	47	04/03	0,28	0,28	0,27	0,00033	No	

Parameter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quan-tification	Incl. RR	Recovery rate [%]
					Day/Month					yes / no	in %
Salicylsäure/ Salicylic Acid	1	g/100g	2	78	18.03.19	0,046	0,046	0,045	0,02 g/100g	no	106
	2	g/100g	22	58	13./14.03.	0,033	0,033	0,033	0,0015	no	
	3	g/100g	27	53	08.03.19	0,028	0,028	0,028	0,002	no	95,7
	4	g/100g	39	40	27.02.19	0,0547	0,0539	0,0555		no	
	5	g/100g	25	55	13.02.19	< BG	< BG	< BG	0,052	no	
	6	g/100g	51	29	18.02.19	0,0357	0,0353	0,0361	5 mg/kg		
	7	g/100g	3	77	01.03.19	no analysis	no analysis	no analysis			
	8	g/100g	60	20	05.03.19	0,0265	0,026	0,027		no	
	9	g/100g	14	66	5.3.-21.3.	0,0272	0,0265	0,0279		no	
	10	g/100g	12	68	21.03.19	0,0135	0,014	0,013	not determined	no	not determined
	11	g/100g	30	50	20.03.19	0,035	0,034	0,035	0,02	yes	100
	12	g/100g									
	13	g/100g	33	47	04/03	0,03	0,032	0,028	0,00137	No	

Parameter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quan-tification	Incl. RR	Recovery rate [%]
					Day/Month					yes / no	in %
Sorbinsäure/ Sorbic Acid	1	g/100g	2	78	18.03.19	0,416	0,419	0,413	0,01 g/100g	no	
	2	g/100g	22	58	13./14.03.	0,572	0,522	0,621	0,0015	no	
	3	g/100g	27	53	11.03.19	0,41	0,41	0,41	0,001	no	102
	4	g/100g	39	40	06.03.19	0,389	0,4	0,378		no	
	5	g/100g	25	55	13.02.19	0,414	0,469	0,359	0,026	yes	96,9
	6	g/100g	51	29	18.02.19	0,454	0,454	0,453	5 mg/kg		
	7	g/100g	3	77	01.03.19	0,41	0,36	0,46	0,005	no	no analysis
	8	g/100g	60	20	13.03.19	0,459	0,467	0,451		no	
	9	g/100g	14	66	5.3.-21.3.	0,3691	0,3583	0,3799		no	
	10	g/100g	12	68	21.03.19	0,309	0,309	0,309	not determined	no	not determined
	11	g/100g	30	50	20.03.19	0,402	0,405	0,399	0,02	yes	100
	12	g/100g	8	72	07.02.	0,445	0,448	0,441	0,001/g/100g	yes	99
	13	g/100g	33	47	04/03	0,91	0,91	0.90	0,00114	No	

Further Parameters	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quan-tification	Incl. RR	Recovery rate [%]
					Day/Month					yes / no	in %
p-Anissäure	11	g/100g	30	50	20.03.19	0,039	0,039	0,038	0,02	yes	100
Phenoxyethanol	11	g/100g	30	50	20.03.19	0,417	0,416	0,417	0,01	yes	100
2-Phenoxyethanol	1	g/100g	2	78	18.03.19	0,384	0,386	0,382	0,1 g/100g	no	109

5.1.2 Analytical Methods

Parameter	Participant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
						yes / no	yes / no	
4-Hydroxy-Benzoesäure/ 4-Hydroxy-Benzoic Acid	1							
	2	ASU K 84.00-23(EG) modified		HPLC-DAD			yes	
	3	-	-	-	-	-	-	-
	4							
	5	in-house method	Extraction (MeOH/H3SO4)	HPLC-DAD	external, certified	yes	no	
	6							
	7	GC-MS after extraction and derivatization			CRM	no analysis	yes	
	8							
	9	in-house method	Liquid extraction	HPLC-DAD			no	
	10	Agilent Application Note 5991-2735EN	solid-supported liquid-liquid extraction (SLE)	HPLC-DAD	4-Hydroxybenzoic acid, ReagentPlus, >99%, Aldrich Art. 240141	not determined	no	
	11	Determination of organic acids in cosmetic products, HPLC-DAD	Extraction with 90Vol% ethanol (acidified with 20ml 2M H2SO4/L)	HPLC-DAD		yes	yes	
	12							
	13	Phenomenex TN-1095				No	No	

Parameter	Participant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
						yes / no	yes / no	
Benzoesäure/ Benzoic Acid	1							
	2	ASU K 84.00-23(EG) modified		HPLC-DAD			yes	
	3	HPLC/DAD	-	-	-	yes	yes	-
	4	in-house method	in water	HPLC-DAD			no	
	5	in-house method	Extraction (MeOH/H3SO4)	HPLC-DAD	external, certified	yes	no	
	6	ASU L 00.00-9 mod., HPLC					yes	
	7	GC-MS after extraction and derivatiziation			CRM	no analysis	yes	
	8	HPLC-UV internal method				no	no	
	9	in-house method	Liquid extraction	HPLC-DAD			yes	
	10	Agilent Application Note 5991-2735EN	solid-supported liquid-liquid extraction (SLE)	HPLC-DAD	Benzoic Acid, ACS Reagent, >99.5%, Sigma Aldrich Art. 242381	not determined	no	
	11	Determination of organic acids in cosmetic products, HPLC-DAD	Extraction with 90Vol% ethanol (acidified with 20ml 2M H2SO4/L)	HPLC-DAD		yes	yes	
	12	ASU L 00.00-9 modified	Weigh 0,5g + ISTD + 10mL Methanol + 14,5mL ammonium acetate buffer; vortex, ultrasonic bath, centrifuge, filter extract, inject clear solution	LC-DAD-Detector	External calibration; Internal standard	yes	yes	
	13	Phenomenex TN-1095				No	No	

Parameter	Participant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
						yes / no	yes / no	
Benzylalkohol/ Benzylalcohol	1	PM228-013.01	Extraction in Methanol	HPLC-DAD		yes	yes	
	2	ASU K 84.00-21(EG) modified		HPLC-DAD			yes	
	3	GC/MS	-	-	-	yes	no	-
	4	in-house method	in ACN	HPLC-DAD			no	
	5	in-house method	Extraction (MeOH/H3SO4)	HPLC-DAD	external, certified	yes	yes	
	6							
	7	GC-MS after extraction and derivatization			CRM	no analysis	yes	
	8	HPLC-UV internal method				no	no	
	9	in-house method	Liquid extraction	GC-MS			yes	
	10	Agilent Application Note 5991-2735EN	solid-supported liquid-liquid extraction (SLE)	HPLC-DAD	Benzyl alcohol, Honeywell Art. 402834	not determined	no	
	11	Determination of parabens (p-hydroxybenzoic acid esters) and phenoxyethanol in cosmetic products, HPLC-DAD	Extraction with Methanol (acidified with 1Vol% formic acid)	HPLC-DAD		yes	yes	
	12							
	13	Phenomenex TN-1095				No	No	

Parameter	Participant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
						yes / no	yes / no	
Salicylsäure/ Salicylic Acid	1							
	2	ASU K 84.00-23(EG) modified		HPLC-DAD			yes	
	3	HPLC/DAD	-	-	-	yes	no	-
	4	in-house method	in water	HPLC-DAD			no	
	5	in-house method	Extraction (MeOH/H3SO4)	HPLC-DAD	external, certified	yes	no	
	6	ASU L 00.00-9 mod., HPLC					yes	
	7							
	8	HPLC-UV internal method				no	no	
	9	in-house method	Liquid extraction	HPLC-DAD			no	
	10	Agilent Application Note 5991-2735EN	solid-supported liquid-liquid extraction (SLE)	HPLC-DAD	Salicylic Acid ACS Reagent, >99.0%, Sigma Aldrich Art. 247588, Lot. MKCG0197	not determined	no	
	11	Determination of organic acids in cosmetic products, HPLC-DAD	Extraction with 90Vol% ethanol (acidified with 20ml 2M H2SO4/L)	HPLC-DAD		yes	yes	
	12							
	13	Phenomenex TN-1095				No	No	

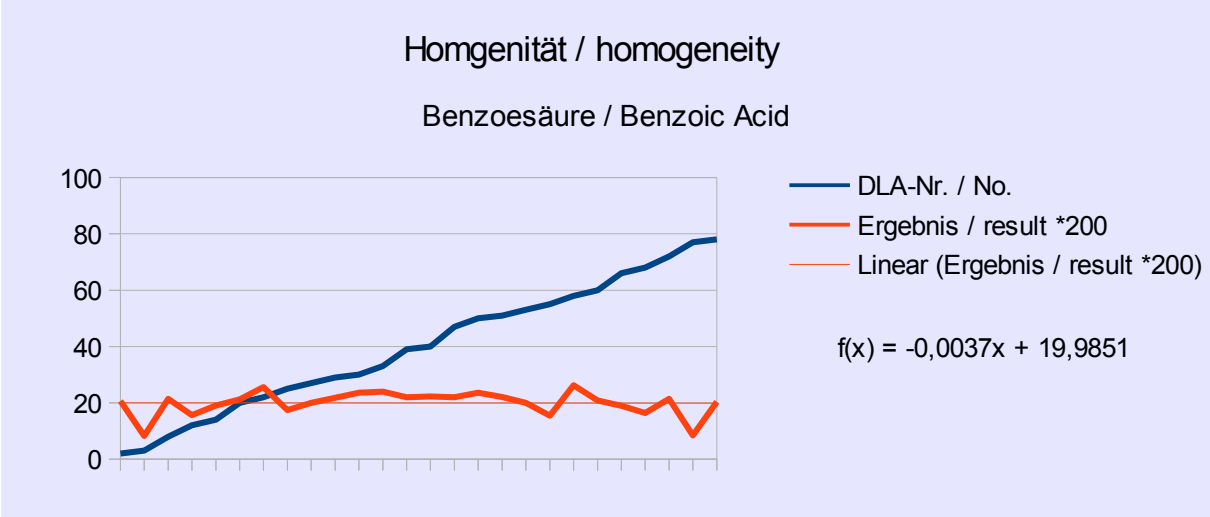
Parameter	Participant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
						yes / no	yes / no	
Sorbinsäure/ Sorbic Acid	1							
	2	ASU K 84.00-23(EG) modified		HPLC-DAD			yes	
	3	HPLC/DAD	-	-	-	yes	yes	-
	4	in-house method	in water	HPLC-DAD			no	
	5	in-house method	Extraction (MeOH/H3SO4)	HPLC-DAD	external, certified	yes	no	
	6	ASU L 00.00-9 mod., HPLC					yes	
	7	GC-MS after extraction and derivatization			CRM	no analysis	yes	
	8	HPLC-UV internal method				no	no	
	9	in-house method	Liquid extraction	HPLC-DAD			yes	
	10	Agilent Application Note 5991-2735EN	solid-supported liquid-liquid extraction (SLE)	HPLC-DAD	Sorbic Acid, >99.5%, Sigma Aldrich Art. S1626	not determined	no	
	11	Determination of organic acids in cosmetic products, HPLC-DAD	Extraction with 90Vol% ethanol (acidified with 20ml 2M H2SO4/L)	HPLC-DAD		yes	yes	
	12	ASU L 00.00-9 modified	Weigh 0,5g + ISTD + 10mL Methanol + 14,5mL ammonium acetate buffer; vortex, ultrasonic bath, centrifuge, filter extract, inject clear solution	LC-DAD-Detector	External calibration; Internal standard	yes	yes	
	13	Phenomenex TN-1095				No	No	

Further Parameters	Participant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
						yes / no	yes / no	
P-Anisic acid	11	Determination of organic acids in cosmetic products, HPLC-DAD	Extraction with 90Vol% ethanol (acidified with 20ml 2M H2SO4/L)	HPLC-DAD		yes	yes	Dehydroacetic acid in traces detectable (<LOQ)
Phenoxyethanol	11	Determination of parabens (p-hydroxybenzoic acid esters) and phenoxyethanol in cosmetic products, HPLC-DAD	Extraction with Methanol (acidified with 1Vol% formic acid)	HPLC-DAD		yes	yes	
2-Phenoxyethanol	1							

5.2 Homogeneity

5.2.1 Trend line function of the participants results

By comparison of the increasing sample numbers and the measurement results of participants, the homogeneity of the chronological bottled PT items can be shown by the trend line for information:



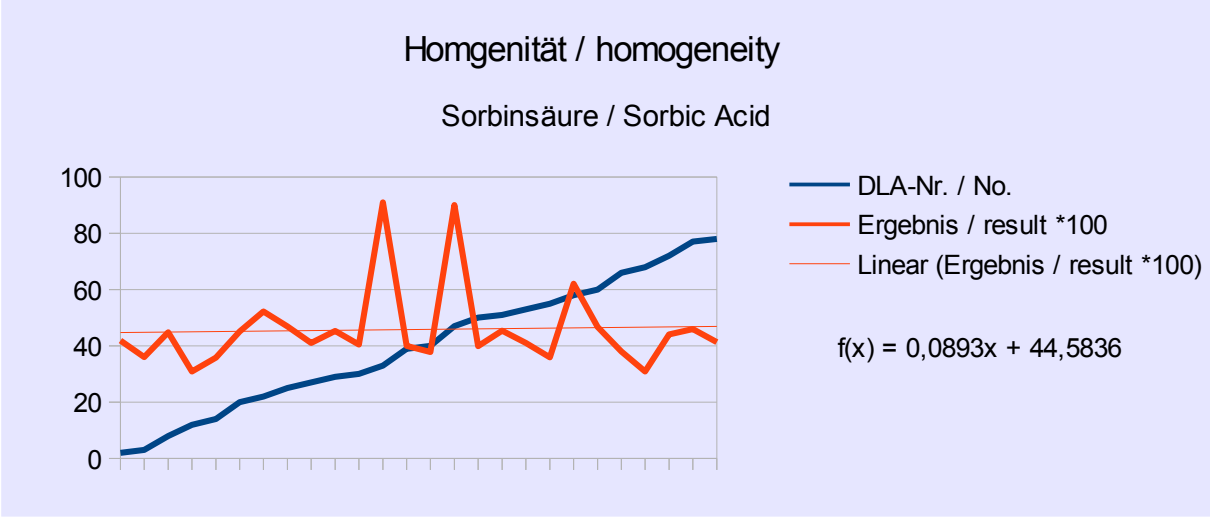


Abb./Fig. 16:
Trendfunktion Probennummern vs. Ergebnisse: Benzoesäure und Sorbinsäure (200-fach und 100-fach dargestellt)
trend line function sample number vs. results: Benzoic Acid and Sorbic Acid (200-fold and 100-fold shown)

5.3 Information on the Proficiency Test (PT)

Before the PT the participants received the following information in the sample cover letter:

PT number	***DLA 51-2019***
PT name	*Cosmetic Products I: Preservatives (Benzylalcohol, Benzoic Acid, Salicylic Acid, Sorbic Acid, 4-Hydroxy-Benzoic Acid) in Body Lotion*
*Sample matrix**	*Samples I + II: Skin Cream/Bodylotion common in commerce ingredients*
Number of samples and sample amount	*2 identical samples I + II, 20 g each.*
Storage	*Samples I + II: cooled 2 - 10°C (dark and dry)*
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative: Benzylalcohol, Benzoic Acid, Salicylic Acid, Sorbic Acid and 4-Hydroxy-Benzoic Acid*
Methods of analysis	*Analytical methods are optional*
Notes to analysis	*The analysis of PT samples should be performed like a routine laboratory analysis.* *In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights.*
Result sheet	*The results for sample I and II as well as the final results calculated as mean of the double determination (samples I and II) should be filled in the result submission file. The recovery rates, if carried out, has to be included in the calculation.*
Units	*g/100g*
Number of significant digits	*at least 2*
Further information	*For information please specify:* – *Date of analysis* – *DLA-sample-numbers (for sample I and II)* – *Limit of detection* – *Assignment incl. Recovery* – *Recovery with the same matrix* – *Method is accredited*
Result submission	*The result submission file should be sent by e-mail to:* ***pt@dla-lvu.de***
Deadline	***the latest 22nd March 2019***
Evaluation report	*The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.*
Coordinator and contact person of PT	*Matthias Besler-Scharf PhD*

* Control of mixture homogeneity and qualitative testings are carried out by DLA. Any testing of the content, homogeneity and stability of PT parameters is subcontracted by DLA.

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		USA
		AUSTRIA
		Germany
		Germany
		FRANCE
		Germany
		Germany
		SWITZERLAND
		Germany
		Germany
		Germany
		Germany
		Germany

[Die Adressdaten der Teilnehmer wurden für die allgemeine Veröffentlichung des Auswerte-Berichts nicht angegeben.]

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

7. Index of references

1. 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
2. DIN EN ISO/IEC 17043:2010; Konformitätsbewertung – Allgemeine Anforderungen an Eignungsprüfungen / Conformity assessment – General requirements for proficiency testing
3. ISO 13528:2015 & DIN ISO 13528:2009; Statistische Verfahren für Eignungsprüfungen durch Ringversuche / Statistical methods for use in proficiency testing by interlaboratory comparisons
4. ASU §64 LFGB: Planung und statistische Auswertung von Ringversuchen zur Methodenvalidierung / DIN ISO 5725 series part 1, 2 and 6 Accuracy (trueness and precision) of measurement methods and results
5. Verordnung / Regulation 882/2004/EU; Verordnung über über amtliche Kontrollen zur Überprüfung der Einhaltung des Lebensmittel- und Futtermittelrechts sowie der Bestimmungen über Tiergesundheit und Tierschutz / Regulation on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules
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15. MTSE SOP No. 010.01 (2014): Quantitative measurement of mixing uniformity and carry-over in powder mixtures with the rotary detector technique, MTSE Micro Tracers Services Europe GmbH
16. Homogeneity and stability of reference materials; Linsinger et al.; Accred Qual Assur, 6, 20-25 (2001)
17. AOAC Official Methods of Analysis: Guidelines for Standard Method Performance Requirements, Appendix F, p. 2, AOAC Int (2016)
18. ASU § 64 LFGB K 84.00-21 Nachweis und Bestimmung von Benzylalkohol in kosmetischen Mitteln [Detection and determination of benzylalcohol in cosmetic products]
19. ASU § 64 LFGB K 84.00-23 Nachweis und Bestimmung von Benzoesäure, 4-Hydroxybenzoesäure, Sorbinsäure, Salicylsäure und Propionsäure in kosmetischen Mitteln [Detection and determination of benzoic acid, 4-hydroxy benzoic acid, sorbic acid, salicylic acid and propionic acid in cosmetic products]