Proficiency Tests

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Evaluation Report
proficiency test

DLA 72/2016

Contact Material IV:

Volatile Matter and Extractable Matter of Silicone Food Contact Material

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

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EP-Nummer *PT-Number*	DLA 72/2016
EP-Koordinator *PT-Coordinator*	Dr. Matthias Besler
Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report (8 May 2017) Gültig ist die jeweils letzte Version/Korrektur des Berichts. Sie ersetzt alle vorangegangenen Versionen. Only the latest version/correction of the report is valid. It replaces all preceding versions.
EP-Bericht Freigabe *PT-Report Authorization*	Dr. Matthias Besler (Technischer Leiter / Technical Manager) *- gezeichnet / signed M. Besler* Dr. Gerhard Wichmann (QM-Beauftragter / Quality Manager) *- gezeichnet / signed G. Wichmann* Datum / Date: 8 May 2017
Unteraufträge *Subcontractors*	Die Prüfung der Gehalte, Homogenität und Stabilität von EP-Parametern wird von DLA im Unterauftrag vergeben. The analysis of the content, homogeneity and stability of PT-parameters are subcontracted by DLA.
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.

Inhalt / 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 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 common food contact material made of silicone (backing moulds) coloured in mint-green (origin: China). The material was purchased in the trade by DLA as specimen from one production unit. As described by the manufacturer the material is suitable for temperatures up to 230 °C. The silicone material was sliced into approx. 1 - 2 cm^2 pieces.
The scope of determination was given on the basis of the BfR Recommendations on Food Contact Materials for commodities in the sense of § 2, Para. 6, No. 1 of the German Food and Feed Code [17].
Due to preliminary investigations it was ensured that the content of volatile and extractable matter (10% ethanol v/v) were in the measuring range of common laboratory methods.

After slicing and mixing, the samples were portioned to approximately 80 g into metallised PET film bags.

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 suitability of the test material was proofed by determination of volatile matter with 0,30% and extractable matter with 0,034% (extraction solvent 10% etahnol v/v) according to the guidelines of the BfR Recommendations on Food Contact Materials for commodities in the sense of the German Food and Feed Code [17].

The calculation of the **repeatability standard deviation S_r of the participants** was used as an indicator of homogeneity. The results for volatile matter were 4,9% and for the extractable matter 30% and 18% respectively using extraction solvent I (3% acetic acid w/v) and II (10% ethanol v/v). The repeatability standard deviation of volatile matter can be regarded common for the used method, whereas the repeatability standard deviation for both extractable matters were higher due to the small content of migrates. The repeatability standard deviation of participants are given in the statistic data (see 4.1 to 4.3).

If the criteria for sufficient homogeneity of the test material are not fulfilled on a particular parameter, the impact on the target standard deviation is checked and optionally the evaluation of the results of the participants will be done using the z'-score considering the standard uncertainty of the assigned value (see 3.8 and 3.11) [3].

2.1.2 Stability

Solid test items made of silicone are usually known to be stable at room temperature and dry storage. The stability of the material can be considered given for the examination period of the PT.

2.2 Sample shipment and information to the test

Two samples (sample 1 and 2) of test material were sent to every participating laboratory in the 48th week of 2016. The testing method was given by DLA. The tests should be finished at 13th January 2017 the latest.

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

The identical test samples 1 and 2 are cut baking moulds made of siliconee. The determination of the volatile matter and the extractable matter with two different extraction solvents should be performed. The following examination conditions are given in accordance with the notices for analysis of consumer goods made of siliconee elastomers from the German Federal Insitute for Risk Assessment (BfR) (notifications for analysis of plastics according to German food law – LFGB):

Volatile matter:	***Extractable matter:***
1. Sample size to be prepared: 10 g *2. Time and temperature: 4 h, 200°C* *3. Result in weight percent.*	***1.*** *Sample size to be prepared: 10 g* *2. Extraction solvent* *i) 3% acetic acid (w/v)* *ii) 10% ethanol (v/v),* *3. Time and temperature:* *5 h, reflux,* *4. Result in weight percent.*

2.3 Submission of results

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

The concentrations of the parameters given in the column "final results" were used for the statistical evaluation. For the calculation of the repeatability- and reproducibility standard deviation the single values were used.

Queried and documented were single results, and basic informations (bullet points) about 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 16 participants submitted at least one result. In agreement with DLA one participant submitted the results delayed.

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].

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 which a minimum of 7 values are present.

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 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. Its meaning is explained in more detail in 3.9.

3.5 Exclusion of results and outliers

Before statistical evaluation obvious blunders, such as those with incorrect units, decimal point errors, and results for a another proficiency test item can be removed from the data set [2]. 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 identified as outliers by the use of robust statistics. If a value deviates from the robust mean by more than 3 times the robust standard deviation, it is classified as an outlier [3]. Detected outliers are stated for information only, when z-score are < -2 or > 2. Due to the use of robust statistics outliers are not excluded, provided that no other reasons are present [3].

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 respectively Horwitz/Thompson (concentration < 120 ppb) is preferably used for the proficiency assessment. It is usually suitable for for evaluation of interlaboratory studies, where different analytical 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.

In cases where both above-mentioned models are not suitable, the target standard deviation is determined based on values by perception, see under 3.6.3.

For information the z-scores of both models are given in the evaluation, if available.

The evaluation was performed according to section 3.6.3 with respect to the performance of used methods considering the height of obtained analysis results in this PT in comparison to existing maximum value requirements ("fitness for purpose").

3.6.1 General model of Horwitz/Thompson

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 BfR Recommendations on Food Contact Materials for commodities give no experimental precision data [17]. Further we have no knowledge of other experimental data of ring trials using standardized methods. For information the relevant repeatability standard deviation (RSD_r) and reproducibility standard deviation (RSD_R) of a ring trial for determination of total migration of food contact materials made of plastic material is given in Table 3. It should be considered that differing extraction conditions and matrices were used in this trial.

Table 1: Relative target standard deviations σ_{pt} of selected evaluations of precision experiments [16].

Method	**Contact Material**	**Mean** [mg/dm³]	**RSD_r** [mg/dm³]	**RSD_R** [mg/dm³]	**σ_{pt}**	**Literature** [16]
Simulation solvent B (3% acetic acid), 24h / 40°C, gravimetric	Polyamide	10,7	1,1	2,3	2,2%	B 80.30-12
Simulation solvent C (10% ethanol), 24h / 40°C, gravimetric	Polyamide	11,9	1,1	2,9	2,8%	B 80.30-12

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].

As the general model of Horwitz (see 3.6.1) was not suitable for evaluation of present results and a target standard deviation can not derived using the data from precision experiments (see 3.6.2), the following evaluation basis was chosen.

According to the BfR Recommendation XV. Silicone on Food Contact Materials for commodities in the sense of § 2, Para. 6, No. 1 of the German Food and Feed Code the allowed maximum values for silicone elastomers are 0,5% volatile matter and 0,5% extractable matter [17]. The corresponding methods are described in the 61st Communication on testing of plastics. Precision data are not given in this communication [18].

Considering the performance of used methods as well as the height of obtained results in the present PT compared to the allowed maximum values the half of the robust standard deviation S* of participant's results was regarded as a suitable target standard deviation σ_{pt} for evaluation of the results for all parameters in the present PT.

Table 2 shows selected characteristics of participants results of the present PT in comparison to the previous year.

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 z-score valid for the PT evaluation is designated z-score (σ_{pt}), while the value of z-score (Info) is for information only. The two z-scores are calculated using the different target standard deviations according to 3.6.

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. For example a fault isolation or a root cause analysis through the examination of transmission error or an error in the calculation, in the trueness and precision must be performed and if necessary appropriate corrective measures should be applied [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 2: Characteristics of the present PT (on dark gray) in comparison to previous PTs since 2011 (SD = standard deviation, CV = coefficient of variation)

Parameter	**Matrix**	**rob. Mean**	**rob. SD (S*)**	**rel. SD (VK_{S*}) [%]**	**Quotient S^*/σ_{pt}**	**DLA-Report**
Volatile Matter	Silicone-coaster	0,279 g/100g	0,144 g/100g	51,6%	-	DLA 40/2011
Volatile Matter	Silicone-baking mould	0,454 g/100g	0,149 g/100g	32,8%	2,0	DLA 72/2016
Extractable Matter (different extraction solvents)	Silicone-coaster	0,046 g/100g	0,045 g/100g	97,8%	-	DLA 40/2011
Overall Migration (3% acetic acid)	Drinking cup (Polyethylene)	10,6 mg/L	8,67 mg/L	81,8%	2,2	DLA 50/2015
Extractable Matter (3% acetic acid)	Silicone-baking mould	0,0349 g/100g	0,0120 g/100g	34,4%	2,0	DLA 72/2016
Overall Migration (10% ethanol)	Drinking cup (Polyethylene)	18,4 mg/L	18,1 mg/L	98,4%	2,3	DLA 50/2015
Extractable Matter(10% ethanol)	Silicone-baking mould	0,0269 g/100g	0,0146 g/100g	54,3%	2,0	DLA 72/2016

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 ($\hat{\sigma}$) 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 coefficient of variation (CV_R)

The coefficient of variation (CV_R) 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_K gives the relative variability within a data region. While a low CV_R, e.g. < 5-10% can be taken as evidence for a homogeneous set of results, a CV_R 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 values or the performance evaluation of the participants 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

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

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

If $U(X_{pt}) \leq 0{,}3\ \sigma_{pt}$ the standard uncertainty of the consensus value needs not to be included in the interpretation of the results of the PT [3]. A clear exceeded the value of 0,3 is an indication that the target standard deviation was possibly set too low for the standard uncertainty of the assigned value.

The quotient $U(X_{pt})/\sigma_{pt}$ 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.

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 ($X_{pt} - 2\sigma_{pt}$)*
upper limit of target range ($X_{pt} + 2\sigma_{pt}$)*
Variation coefficient V_K in %
Quotient S/σ_{pt} or S*/σ_{pt}'*
Standard uncertainty $U(X_{pt})$
Quotient $U(X_{pt})/\sigma_{pt}$ or $U(X_{pt})/\sigma_{pt}$'
Number of results in the target range
Percent in the target range

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

In the second table the individual results of the participating laboratories are listed formatted to 3 digits**:

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

** In the documentation the results are given as submitted by the participants.

4.1 Volatile Matter in g/100g

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	15
Number of outliers	0
Mean	0,454
Median	0,490
Robust Mean (X)	**0,456**
Robust standard deviation (S*)	**0,149**
Number with 2 replicates	15
Repeatability SD (S_r)	0,0224
Repeatability (CV_r)	4,90%
Reproducibility SD (S_R)	0,137
Reproducibility (CV_R)	29,9%
Target range:	
Target standard deviation σ_{pt}	**0,0743**
lower limit of target range	**0,308**
upper limit of target range	**0,605**
Quotient S/σ_{pt}*	*2,0*
Standard uncertainty $U_{(Xpt)}$	*0,0479*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,65*
Results in the target range	*11*
Percent in the target range	*73%*

Comments to the statistic data:

According to 3.6.3 values by perception the target standard deviation was set to the half of the robust standard deviation S* of participant's results.

The distribution of results shows a normal variability. The quotient S*/σ_{pt} is 2,0. The robust standard deviation is comparable to those of prior PTs (see 3.6.3). The repeatability and reproducibility standard deviation are in the range which can usually be expected for the applied methods. Thus the comparability of results is given.

With 0,65 the quotient $U_{(Xpt)}/\sigma_{pt}$ is higher than 0,3 and acceptable due to the small number of results and the expectable precision of the method.

73% of results were in the target range. Approx. half of the results were above and below the maximum allowed value of 0,5 % (g/100 g).

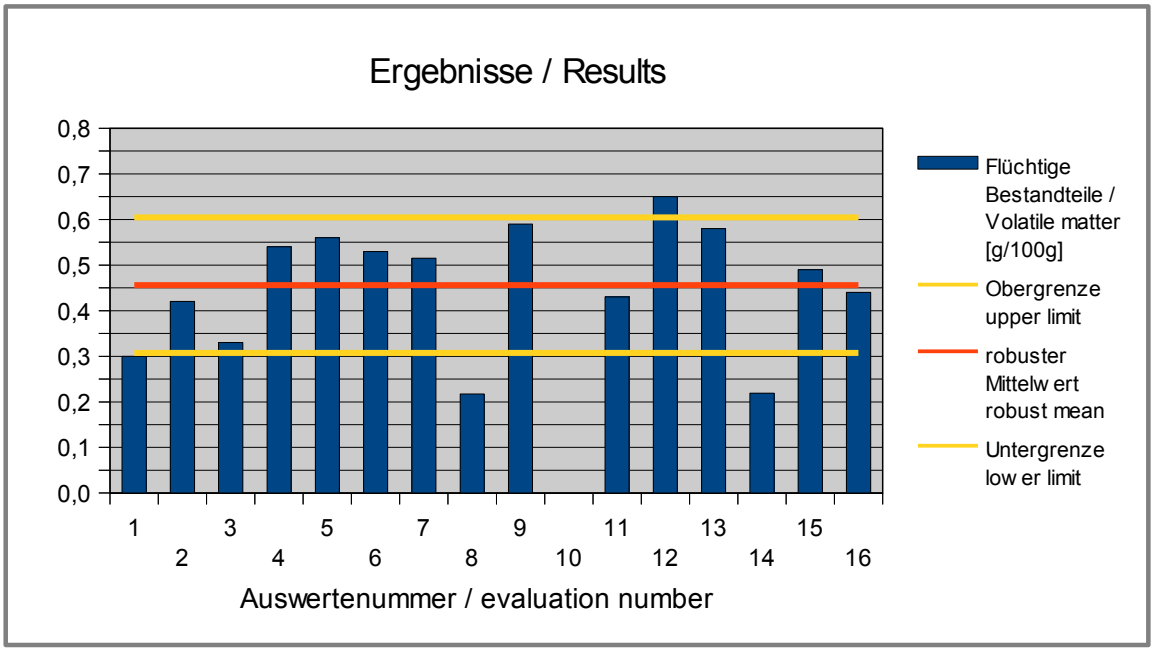

Abb. / Fig. 1: Ergebnisse flüchtige Bestandteile / Results volatile matter

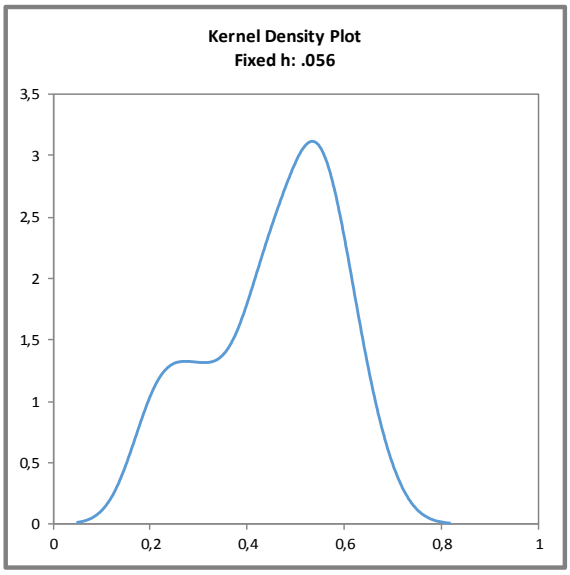

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

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

Comment:
The kernel density shows nearly a normal distribution of results with a shoulder at approx. 0,2 g/100 g, due to two results below the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Flüchtige Bestandteile / Volatile matter [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z-Score (σ_{pt})	Hinweis Remark
1	0,300	-0,156	-2,1	
2	0,420	-0,036	-0,5	
3	0,330	-0,126	-1,7	
4	0,540	0,0839	1,1	
5	0,560	0,104	1,4	
6	0,530	0,0739	1,0	
7	0,515	0,0587	0,8	
8	0,217	-0,239	-3,2	
9	0,590	0,134	1,8	
10				
11	0,430	-0,026	-0,4	
12	0,650	0,194	2,6	
13	0,580	0,124	1,7	
14	0,219	-0,237	-3,2	
15	0,490	0,0339	0,5	
16	0,440	-0,0161	-0,2	

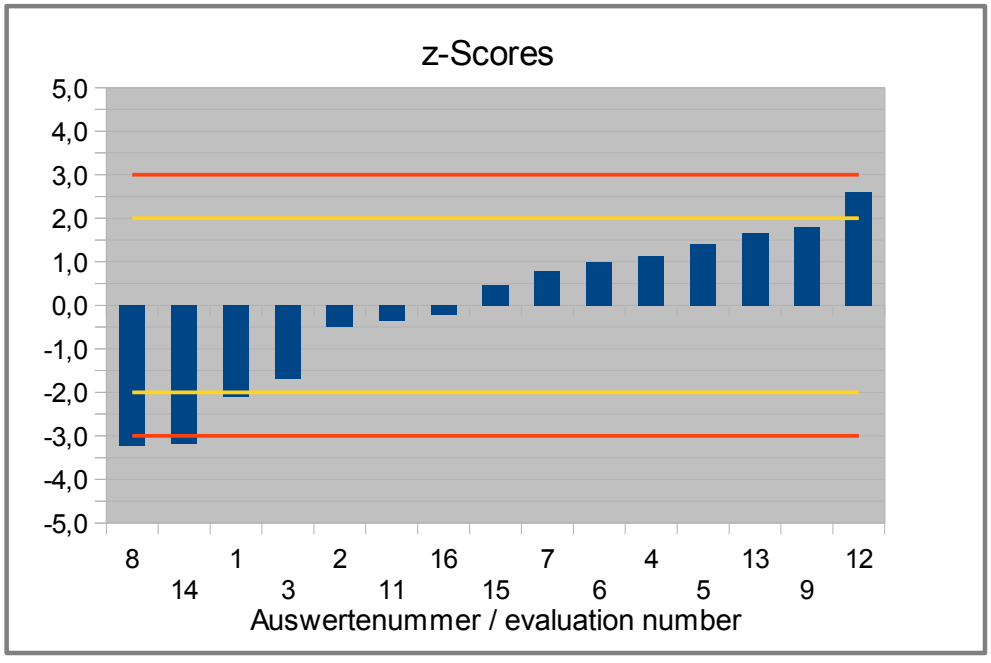

Abb. / Fig. 3: z-Scores flüchtige Bestandteile / volatile matter

4.2 Extractable Matter (3% Acetic Acid) in g/100g

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	10
Number of outliers	1
Mean	0,0634
Median	0,0390
Robust Mean (X)	**0,0349**
Robust standard deviation (S*)	**0,0120**
Number with 2 replicates	10
Repeatability SD (S_r)	0,0190
Repeatability (CV_r)	30,0%
Reproducibility SD (S_R)	0,102
Reproducibility (CV_R)	162%
Target range:	
Target standard deviation σ_{pt}	**0,00599**
lower limit of target range	**0,0229**
upper limit of target range	**0,0469**
Quotient S/σ_{pt}*	*2,0*
Standard uncertainty $U_{(Xpt)}$	*0,00473*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,79*
Results in the target range	7
Percent in the target range	70%

Comments to the statistic data:

According to 3.6.3 values by perception the target standard deviation was set to the half of the robust standard deviation S* of participant's results.

The distribution of results shows a normal variability. The quotient S^*/σ_{pt} is 2,0. The robust standard deviation is comparable to those of prior PTs (see 3.6.3). The repeatability and reproducibility standard deviation are in the range which can usually be expected for the applied methods. Thus the comparability of results is given.

With 0,79 the quotient $U_{(Xpt)}/\sigma_{pt}$ is higher than 0,3 and acceptable due to the small number of results and the expectable precision of the method.

70% of results were in the target range. All of the results were located below the maximum allowed value of 0,5 % (g/100 g), in which an uniform evaluation of the PT material were obtained. Thus all participants results were in qualitative agreement.

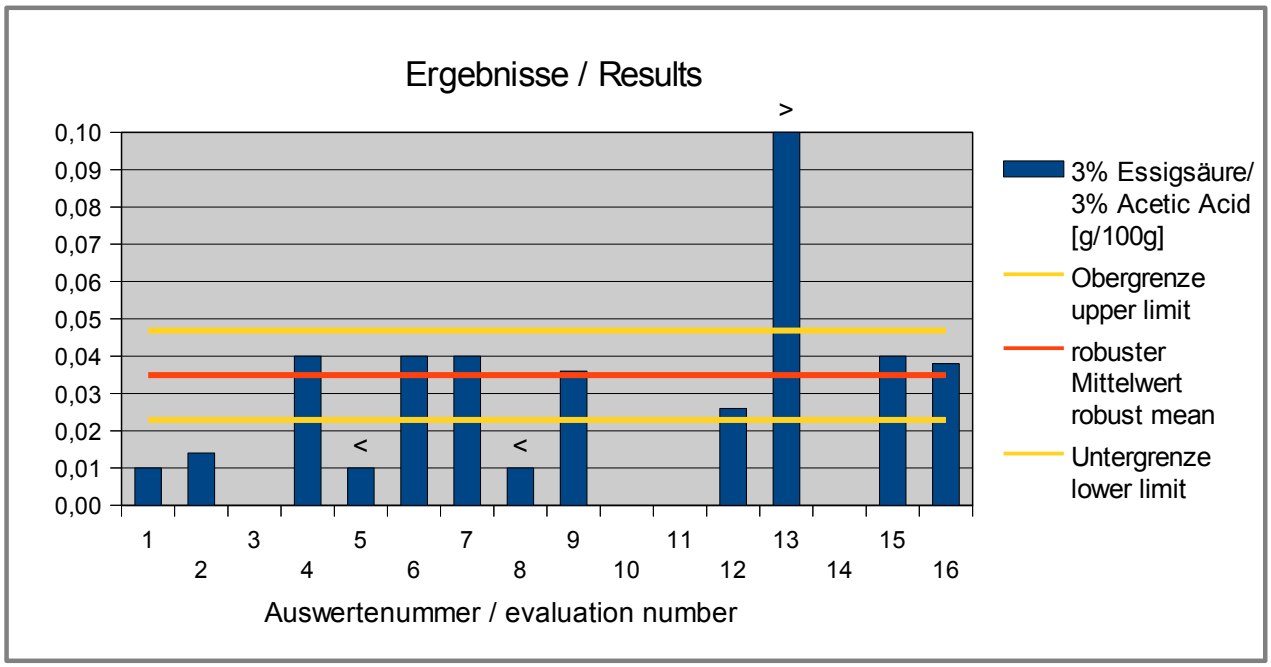

Abb. / Fig. 4: Ergebnisse 3% Essigsäure / Results 3% Acetic Acid

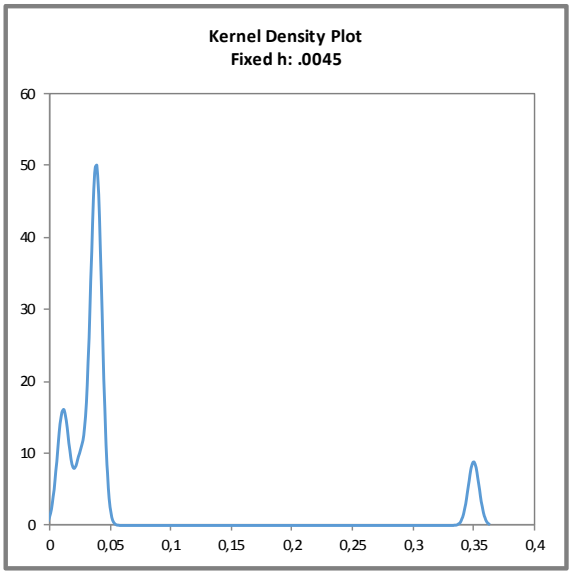

Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse

(mit h = 0,75 x σ_{pt} von Xpt)

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

Comment:
For the results within the target range the kernel density shows nearly a normal distribution. The two side-peaks are due to two results below and an outlier above the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	3% Essigsäure/ 3% Acetic Acid [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z-Score (σ_{pt})	Hinweis Remark
1	0,0100	-0,0249	-4,2	
2	0,0140	-0,0209	-3,5	
3	-			
4	0,0400	0,00511	0,9	
5	< 0,0100			
6	0,0400	0,00511	0,9	
7	0,0400	0,00511	0,9	
8	< 0,0100			
9	0,0360	0,00111	0,2	
10				
11				
12	0,0260	-0,00889	-1,5	
13	0,350	0,315	52,6	Ausreisser / Outlier
14				
15	0,0400	0,00511	0,9	
16	0,0380	0,00311	0,5	

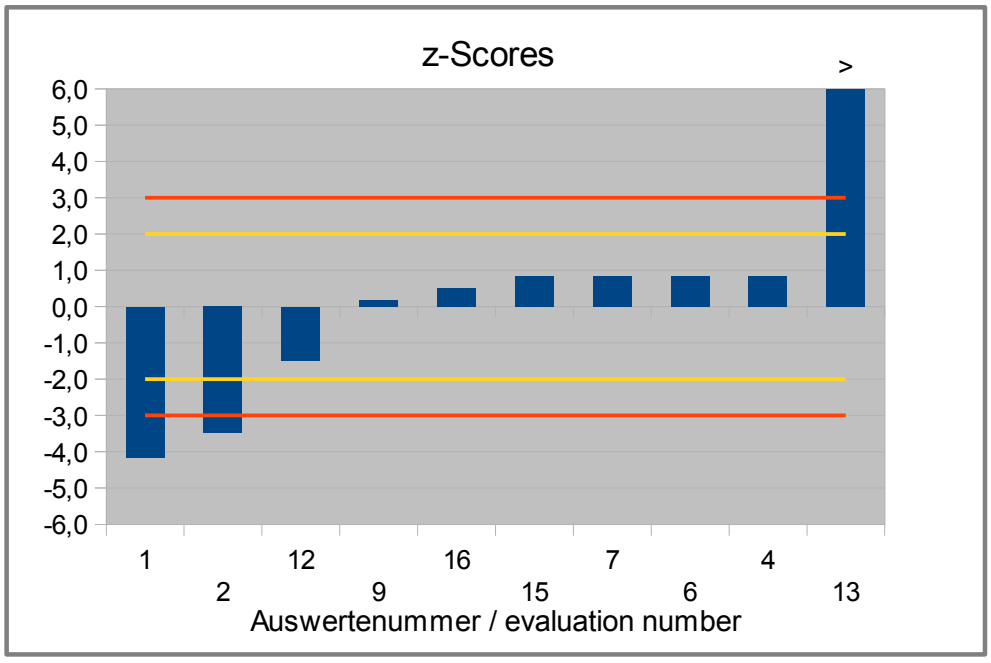

Abb. / Fig. 6: z-Scores 3% Essigsäure / 3% Acetic Acid

4.3 Extractable Matter (10% Ethanol) in g/100g

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	9
Number of outliers	0
Mean	0,0269
Median	0,0280
Robust Mean (X)	**0,0269**
Robust standard deviation (S*)	**0,0146**
Number with 2 replicates	9
Repeatability SD (S_r)	0,00485
Repeatability (CV_r)	18,1%
Reproducibility SD (S_R)	0,0135
Reproducibility (CV_R)	50,4%
Target range:	
Target standard deviation σ_{pt}	**0,00732**
lower limit of target range	**0,0122**
upper limit of target range	**0,0415**
Quotient S/σ_{pt}*	*2,0*
Standard uncertainty $U_{(Xpt)}$	*0,00610*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,83*
Results in the target range	*6*
Percent in the target range	*67%*

Comments to the statistic data:

According to 3.6.3 values by perception the target standard deviation was set to the half of the robust standard deviation S* of participant's results.

The distribution of results shows a normal variability. The quotient S*/σ_{pt} is 2,0. The robust standard deviation is comparable to those of prior PTs (see 3.6.3). The repeatability and reproducibility standard deviation are in the range which can usually be expected for the applied methods. Thus the comparability of results is given.

With 0,83 the quotient $U_{(Xpt)}/\sigma_{pt}$ is higher than 0,3 and acceptable due to the small number of results and the expectable precision of the method.

67% of results were in the target range. All of the results were located below the maximum allowed value of 0,5 % (g/100 g), in which an uniform evaluation of the PT material were obtained. Thus all participants results were in qualitative agreement.

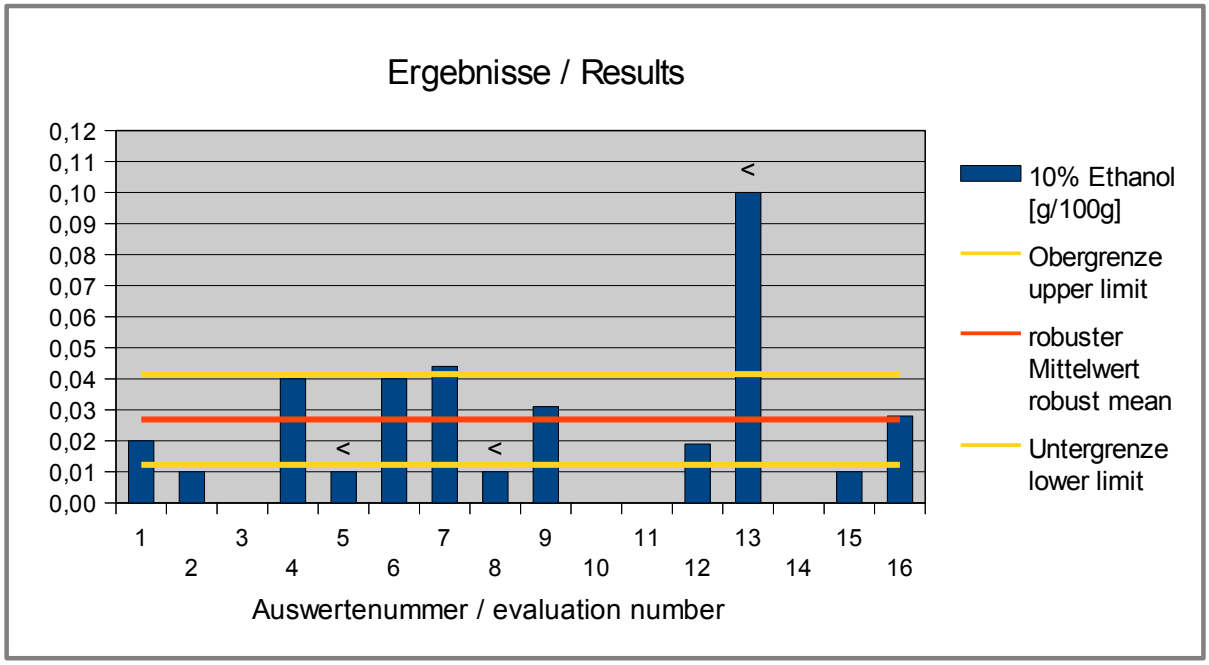

Abb. / Fig. 7: Ergebnisse 10% Ethanol / Results 10% Ethanol

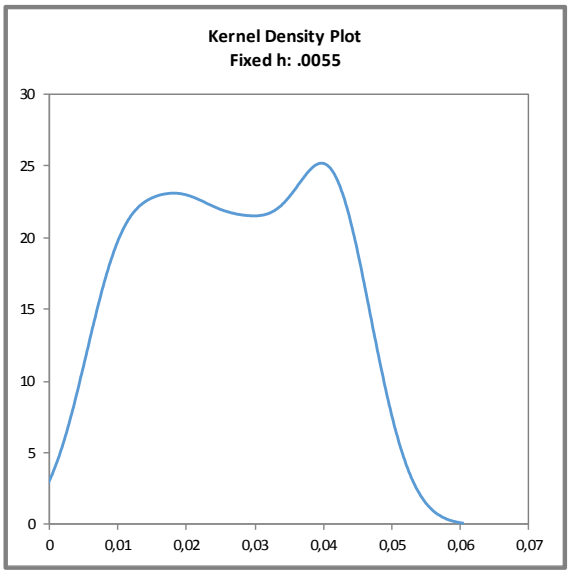

Abb. / Fig. 8:
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x σ_{pt} von X_{pt})

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

Comment:
The kernel density shows a broad distribution of results, which is caused by the small number of results and the low content of volatile matter.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	10% Ethanol [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z-Score (σ_{pt})	Hinweis Remark
1	0,0200	-0,007	-0,9	
2	0,0100	-0,017	-2,3	
3				
4	0,0400	0,0131	1,8	
5	< 0,0100			
6	0,0400	0,0131	1,8	
7	0,0440	0,0171	2,3	
8	< 0,0100			
9	0,0310	0,004	0,6	
10				
11				
12	0,0190	-0,008	-1,1	
13	< 0,100			
14				
15	0,0100	-0,0169	-2,3	
16	0,0280	0,0011	0,2	

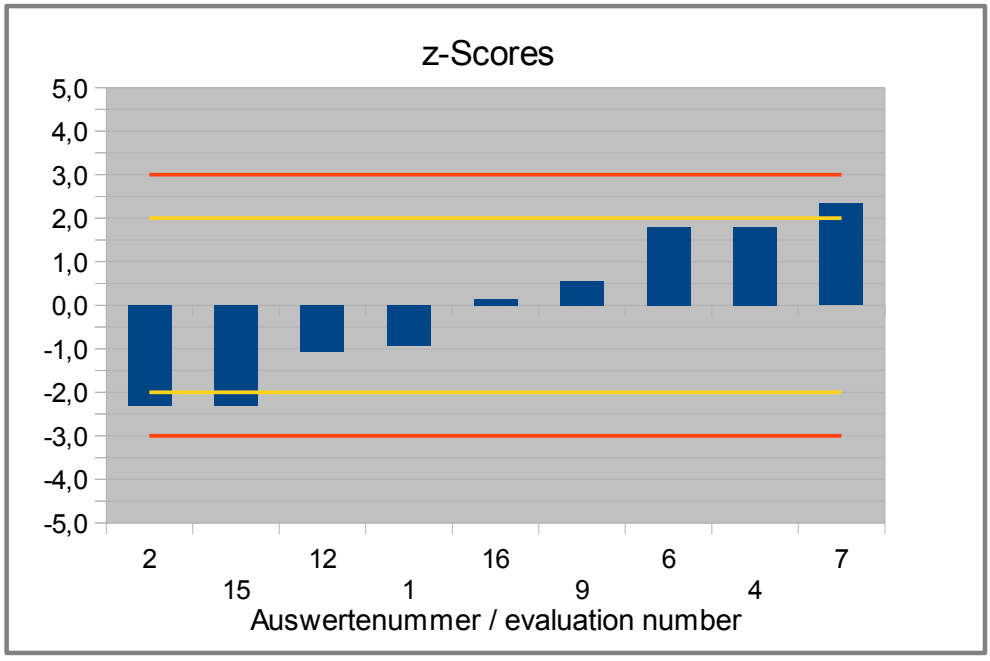

Abb. / Fig. 9: z-Scores 10% Ethanol

5. Documentation

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

5.1 Details by the participants

5.1.1 Primary Data and Analytical Methods

Parameter: Volatile Matter

Analyte	Partici-pant	Unit	Date of Analy-sis	Final Result	Result Sam-ple 1	Result Sam-ple 2	Description of the methods like in a report ana-lysis	Precondition of sample material
Volatile Matter	1	g/100g	08.12.	0,3	0,28	0,32	Bgesundheitsblatt 46 (2003) 362	48h in desiccator
Volatile Matter	2	g/100g	30.12.16	0,42	0,39	0,44		48h in desiccator
Volatile Matter	3	g/100g	06.01.-12.01.2017	0,33	0,36	0,3	CH 067 A	yes
Volatile Matter	4	g/100g	10.01.17	0,54	0,54	0,54	the 61th Communication on testing of plastics, Bundesgesundheitsbl. 46 (2003) 362	Put the sample into the desiccator, for 48hours at RT
Volatile Matter	5	g/100g	29.12.16	0,56	0,56	0,56	volatile organic matter	conditioning
Volatile Matter	6	g/100g	05.01.17	0,53	0,52	0,53	Platics in food transport (Book 2, Part B II, XV, P15)	48h
Volatile Matter	7	g/100g	23.12.16	0,5148	0,5289	0,5007	61th Communication on testing of plastics, Bundesgesundheitsbl. 46 (2003) 362	48 hrs
Volatile Matter	8	g/100g	04.01.17	0,217	0,216	0,218	Determination was perfomed according to 61th Communication of the BfR on testing of plastics, Bundesgesundheitsbl. 46 (2003) 362	Storage for 48 h above calcium chloride
Volatile Matter	9	g/100g	16.12.16	0,59	0,61	0,57	Bundesgesundheitsbl 46(2003) 362	desiccator, 48h
Volatile Matter	10	g/100g	08.12.16		0,48	0,505	Gravimetric	Conditioning for 48h above CaCl2
Volatile Matter	11	g/100g	10.01.17	0,43			Recommendation of BfR – XV Silicone	Dried above Calcium chloride
Volatile Matter	12	g/100g	04.01.	0,65	0,66	0,65	BfR-Recommendation, A XV 5*	Conditioning: 48h
Volatile Matter	13	g/100g	19.12.	0,58	0,56	0,61	according to BfR-Recommendation XV. Silicone	Conditioning
Volatile Matter	14	g/100g	28./30.12.16	0,219	0,206	0,232	Volatile matter out of silicone gravimetric (10 g sample, 200°C, 4 h)	Conditioning: 10 g sample were cutted into 1 x 2 cm pieces and stored for 48 h at RT above Calicumchloride in the desiccator. Conditioned pieces were weight out with a precision of ±0,1 mg and 4 h in oven at 200°C. After cooling in desiccator weighting again and calculation of volatile matter by gravimetric difference.
Volatile Matter	15	g/100g	08.12.16	0,49	0,49	0,48	61. Communication Bundesgesundheitsblatt 46 (2003) 362	Conditioning for 48 h above Silica
Volatile Matter	16	g/100g	08.02.17	0,44	0,45	0,42	French	-

continued Parameter: volatile Matter

Participant	Time and Temperature 4h at 200°C	Remarks to analysis	Method accredited	Further Remarks
	yes / no		yes / no	
1	yes		yes	
2	yes		yes	
3	yes	-	yes	-
4	yes		no	
5	yes		yes	
6	-		-	
7	-		-	
8	-		-	
9	yes		-	
10	yes		yes	
11	yes		yes	
12	yes	Given results were each mean values from two measurements	no	Were sample 1 +2 identical?
13	yes		yes	
14	yes	see Method description	yes	
15	yes		yes	
16	yes	-	no	-

Parameter: Extractable Matter: 3% Acetic Acid

Analyte	Partici-pant	Unit	Date of Analy-sis	Final Result	Result Sam-ple 1	Result Sam-ple 2	Description of the methods like in a report analysis	Precondition of sample material
i) 3% Acetic Acid (w/v)	1	g/100g	13.12.	0,01	0,01	0,01	Bgesundheitsblatt 4(12) 189	24h in desiccator
i) 3% Acetic Acid (w/v)	2	g/100g	04.01.17	0,014	0,014	0,013		
i) 3% Acetic Acid (w/v)	3	g/100g	-	-	-	-	-	-
i) 3% Acetic Acid (w/v)	4	g/100g	10.01.17	0,04	0,04	0,04	13th Communication on testing of plastics, Bundesgesundheitsbl. 12 (1969) 324	Put the sample into the desiccator, for 48hours at RT
i) 3% Acetic Acid (w/v)	5	g/100g	29.12.16	<0,01	<0,01	<0,01	extractable matter	
i) 3% Acetic Acid (w/v)	6	g/100g	04.01.17	0,04	0,04	0,04	Platics in food transport (Book 2, Part B II, XV, P15)	48h
i) 3% Acetic Acid (w/v)	7	g/100g	05.01.17	0,04	0,0427	0,038	13th Communication on testing of plastics, Bundesgesundheitsbl. 12 (1969) 324	48 hrs
i) 3% Acetic Acid (w/v)	8	g/100g	10.01.17	<0,01	<0,01	<0,01	Determinationwof extractable matter s performed according to the simulation solvents given in the first Commentation above „Analysis of plastics in contact material, which are used als contact material in the sense of German Food and Feed Code	no
i) 3% Acetic Acid (w/v)	9	g/100g	12.12.16	0,036	0,045	0,026	Bundesgesundheitsbl 4 (1961) 189	desiccator 24h
i) 3% Acetic Acid (w/v)	10	g/100g						
i) 3% Acetic Acid (w/v)	11	g/100g	not tested					
i) 3% Acetic Acid (w/v)	12	g/100g	04.01.	0,026	0,025	0,027	BfR-Recommendation, A XV 5*	24h conditioning
i) 3% Acetic Acid (w/v)	13	g/100g	27.12.16	0,35	0,39	0,31	according to BfR-Recommendation XV. Silicone	conditioning
i) 3% Acetic Acid (w/v)	14	g/100g						
i) 3% Acetic Acid (w/v)	15	g/100g	09.12.16	0,04	0,03	0,05	DIN EN 1186	Conditioning for 48 h above Silica
i) 3% Acetic Acid (w/v)	16	g/100g	08.02.17	0,038	0,037	0,038	EN 1186	-

continued Parameter: ***3% Acetic Acid***

Participant	Extraction solvent (i) (3% Acetic Acid w/v)	Extraction solvent volume	Time and temperature: 5 h by reflux	Remarks to analysis	Method accredited	Further Remarks
	yes / no	ml	yes / no		yes / no	
1	yes		yes		yes	
2	yes	250	yes		yes	
3	-		-	-	-	-
4	yes	100	yes		no	
5	yes	200	yes		yes	
6	-	100	-		-	
7	-	100	-		-	
8	-	200	-		-	
9	yes	250 ml	yes	Extracts were filtered warm	no	
10	-		-		-	
11	-		-		-	
12	yes		yes	Given results were mean values from two measurements each	no	Were sample 1 +2 identical?
13	yes	50	yes		yes	
14	-		-		-	
15	yes	200	yes		yes	
16	yes	100	yes	-	no	-

Parameter: Extractable Matter: 10% Ethanol

Analyte	Partici-pant	Unit	Date of Analy-sis	Final Result	Result Sam-ple 1	Result Sam-ple 2	Description of the methods like in a report analysis	Precondition of sample material
ii) 10% Ethanol (v/v)	1	g/100g	07.12.	0,02	0,02	0,02	Bgesundheitsblatt 4(12) 189	24h in desiccator
ii) 10% Ethanol (v/v)	2	g/100g	04.01.17	0,01	0,007	0,012		
ii) 10% Ethanol (v/v)	3	g/100g	-	-	-	-	-	-
ii) 10% Ethanol (v/v)	4	g/100g	10.01.17	0,04	0,04	0,04	13th Communication on testing of plastics, Bundesgesundheitsbl. 12 (1969) 324	Put the sample into the desiccator, for 48hours at RT
ii) 10% Ethanol (v/v)	5	g/100g	29.12.16	<0,01	<0,01	<0,01	extractable matter	
ii) 10% Ethanol (v/v)	6	g/100g	04.01.17	0,04	0,04	0,04	Platics in food transport (Book 2, Part B II, XV, P15)	48h
ii) 10% Ethanol (v/v)	7	g/100g	05.01.17	0,044	0,041	0,047	13th Communication on testing of plastics, Bundesgesundheitsbl. 12 (1969) 324	48 hrs
ii) 10% Ethanol (v/v)	8	g/100g	10.01.17	<0,01	<0,01	<0,01	Determinationwof extractable matter s performed according to the simulation solvents given in the first Commentation above „Analysis of plastics in contact material, which are used als contact material in the sense of German Food and Feed Code	no
ii) 10% Ethanol (v/v)	9	g/100g	12.12.16	0,031	0,04	0,021	Bundesgesundheitsbl 4 (1961) 189	desiccator 24h
ii) 10% Ethanol (v/v)	10	g/100g						
ii) 10% Ethanol (v/v)	11	g/100g	not tested					
ii) 10% Ethanol (v/v)	12	g/100g	04.01.	0,019	0,018	0,019	BfR-Recommendation, A XV 5*	24h conditioning
ii) 10% Ethanol (v/v)	13	g/100g	06.01.17	<0,1	<0,1	<0,1	according to BfR-Recommendation XV. Silicone	conditioning
ii) 10% Ethanol (v/v)	14	g/100g						
ii) 10% Ethanol (v/v)	15	g/100g	09.12.16	0,01	0,01	0,01	DIN EN 1186	Conditioning for 48 h above Silica
ii) 10% Ethanol (v/v)	16	g/100g	08.02.17	0,028	0,028	0,028	EN 1186	-

continued Parameter: 10% Ethanol

Participant	Extraction solvent (i) (10% Ethanol w/v)	Extraction solvent volume	Time and temperature: 5 h by reflux	Remarks to analysis	Method accredited	Further Remarks
	yes / no	ml	yes / no		yes / no	
1	yes		yes		yes	
2	yes	250	yes		yes	
3	-		-	-	-	-
4	yes	100	yes		no	
5	yes	200	yes		yes	
6	-	100	-		-	
7	-	100	-		-	
8	-	200	-		-	
9	yes	250 ml	yes	Extracts were filtered warm	no	
10	-		-		-	
11	-		-		-	
12	yes	250	yes	Given results were mean values from two measurements each	no	Were sample 1 +2 identical?
13	yes	50	yes		yes	
14	-		-		-	
15	yes	200	yes		yes	
16	yes	100	yes	-	no	-

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		SWITZERLAND
		Germany
		THAILAND
		Germany
		P.R. CHINA
		Germany
		Germany
		P.R. CHINA
		P.R. CHINA
		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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7. The International Harmonised Protocol for the Proficiency Testing of Ananlytical Laboratories ; J.AOAC Int., 76(4), 926 – 940 (1993)
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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. ASU § 64 LFGB B 80.30-12 Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Kunststoffe - Teil 9: Prüfverfahren für die Gesamtmigration in wässrige Prüflebensmittel durch Füllen des Gegenstandes / EN 1186-9:2002 Materials and articles in contact with foodstuffs. Plastics. Test methods for overall migration into aqueous food simulants by article filling
17. XV. Silicone, BfR-Empfehlung für Kunststoffe für Bedarfsgegenstände im Sinne des LFGB §2 Abs. 6 Nr. 1 / XV. Silicones, BfR Recommendations on Food Contact Materials for commodities in the sense of § 2, Para. 6, No. 1 of the German Food and Feed Code
18. 61. Mitteilung über die Untersuchung von Kunststoffen / 61st Communication on testing of plastics, Bundesgesundheitsblatt, Gesundheitsforschung, Gesundheitsschutz 46 (2003) 362