*Proficiency Tests*

**DLA**

food
cosmetics
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**Evaluation Report**
proficiency test

**DLA 52/2018**

# Cosmetic Products II:

# UV-Filter

## in Sunscreen Product

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

| | |
|---|---|
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| *EP-Nummer*<br>*PT-Number* | DLA 52/2018 |
| *EP-Koordinator*<br>*PT-Coordinator* | Dr. Matthias Besler-Scharf |
| *Status des EP-Bericht*<br>*Status of PT-Report* | Abschlussbericht / Final report (26 June 2018)<br><br>Gültig ist die jeweils letzte Version/Korrektur des Berichts. Sie ersetzt alle vorangegangenen Versionen.<br>Only the latest version/correction of the report is valid. It replaces all preceding versions. |
| *EP-Bericht Freigabe*<br>*PT-Report Authorization* | Dr. Matthias Besler-Scharf (Technischer Leiter / Technical Manager)<br>*- gezeichnet / signed M. Besler-Scharf*<br>Dr. Gerhard Wichmann (QM-Beauftragter / Quality Manager)<br>*- gezeichnet / signed G. Wichmann*<br>Datum / Date: 26 June 2018 |
| *Unteraufträge*<br>*Subcontractors* | Falls im Rahmen der Eignungsprüfung eine Prüfung der Gehalte, Homogenität und Stabilität von EP-Parametern durchgeführt wurde, hat DLA diese im Unterauftrag vergeben.<br>In case the analysis of the content, homogeneity and stability of PT-parameters was part of the proficiency test, the determinations were subcontracted by DLA. |
| *Vertraulichkeit*<br>*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.<br>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 mixture of two common in commerce sunscreen lotions (SPF 50) from European Suppliers with the allowed UV filters Octocrylene, Butyl Methoxydibenzoylmethane, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine and Titanium Dioxide as well as Ethylhexyl Salicylate. 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-Sample Sunscreen Product (SPF 50)** |
|---|
| **Sunscreen lotion (SPF 50)**<br>Ingredients: Aqua, Octocrylene, Alcohol Denat, Glycerin, C12-15 Alkyl Benzoate, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Titanium Dioxide (nano), Dicaprylyl Ether, Tocopheryl Acetate, VP/Hexadecene Copolymer, Silica, Panthenol, Triacontanyl PVP, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Parfum, Caprylyl Glycol, Ethylhexylglycerin,Sodium Hydroxide, Carbomer, Xanthan Gum, Dimethicone, Disodium EDTA, Linalool, Limonene, Caprylhydroxamic Acid, Alpha-Isomethyl Ionone, Benzyl Alcohol, Benzyl Benzoate, Hexyl Cinnamal, Citronellol, Geraniol, Tocopherol |
| **Sunscreen lotion for children (SPF 50)**<br>Ingredients: Aqua, Octocrylene, Alcohol Denat, Glycerin, C12-15 Alkyl Benzoate, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Titanium Dioxide (nano), Dicaprylyl Ether, Tocopheryl Acetate, VP/Hexadecene Copolymer, Silica, Panthenol, Triacontanyl PVP, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Caprylyl Glycol, Ethylhexylglycerin, Carbomer, Sodium Hydroxide, Xanthan Gum, Dimethicone, Disodium EDTA, Aloe Barbadensis Leaf Juice Powder, Citric Acid, Tocopherol |

***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 deviation $S_r$ of the dublicate determination of the participants** was also used as an indicator of homogeneity. It is for the analytes OC, BMDM and BEMT in the range of 0,9% - 5,1%. Therefore the repeatability standard deviations are similar to the precision data of the standardized method (ASU K 84.00-28 or DIN EN 16344, s. 3.6.2) (see Tab. 3) [18]. The repeatability standard deviation of the participants' results is given in the table of statistic data (see 4.1 to 4.3).

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).

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*

Experience has shown that unopened sunscreens 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 10th week of 2018. The testing method was optional. The tests should be finished at 20th April 2018 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 sun protection milks with a sun protection factor 50 with the UV filters Octocrylene, Butyl Methoxydibenzoylmethane, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine and Titanium Dioxide.*

*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 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 $\sigma_{pt}$) [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 $\sigma_{pt}$ (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, 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 $\sigma_{pt}$ (= standard deviation for proficiency assessment) can be determined according to the following methods.

If an acceptable quotient $S^*/\sigma_{pt}$ is present, the target standard deviation of the general model by Horwitz is preferably used for the proficiency assessment. It is usually suitable for 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.

***For the valuation of Octocrylene (OC), Butyl Methoxydibenzoylmethane (BMDM) and Bis-Ethylhexyloxyphenol Methoxy-phenyl Triazine (BEMT) the target standard deviation of a precision experiment (see 3.6.2) was applied in the present PT (German official method ASU §64 Methode K 84.00-28 corresponding to DIN EN 16344).***
***Additionally, the target standard deviation of the general model of Horwitz was given for information (see 3.6.1).***

***Due to the number of < 7 the results for Titanium Dioxide and Ethylhexyl Salicylate (EHS) were not evaluated with z-scores.***

### *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 $\sigma_R$ [6]. Later the model was modified by Thompson for certain concentration ranges [10]. The reproducibility standard deviation $\sigma_R$ can be applied as the relative target standard deviation $\sigma_{pt}$ 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 $\sigma_R$ and the repeatability standard deviation $\sigma_r$ of a precision experiment (collaborative trial or proficiency test) the target standard deviation $\sigma_{pt}$ 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 values of relative repeatability standard deviation ($RSD_r$) and relative reproducibility standard deviation ($RSD_R$) given in Table 3 were determined in collaborative trials using the specified methods. The in the table indicated resulting target standard deviation $\sigma_{pt}$ was applied for the evaluation of the present PT results.

Table 3: Relative repeatability standard deviations ($RSD_r$) and relative reproducibility standard deviations ($RSD_R$) from precision experiments and resulting target standard deviations $\sigma_{pt}$ [18]

| **Parameter** Abbr.[2] | **Matrix** | **Mittel-werte [g/100g]** | **$RSD_r$** | **$RSD_R$** | **$\sigma_{pt}$** | **Method / Li-terature** |
|---|---|---|---|---|---|---|
| OC | Sunscreen milk SPF 40 (Sample 1) | 6,16 | 1,9% | 5,4% | 5,23%[1] | Aceton/Metha-nol-Extraction / HPLC [18] |
| BMDM | Sunscreen milk SPF 40 (Sample 1) | 4,95 | 1,8% | 4,9% | 4,73%[1] | Aceton/Metha-nol-Extraction / HPLC [18] |
| DEBT | Sunscreen milk SPF 40 (Sample 1) | 1,36 | 2,0% | 7,2% | 7,06% | Aceton/Metha-nol-Extraction / HPLC [18] |
| BEMT | Sunscreen milk SPF 40 (Sample 1) | 0,84 | 1,6% | 8,7% | 8,63%[1] | Aceton/Metha-nol-Extraction / HPLC [18] |

[1] *used for evaluation (s. chapter 4)*

[2] *Abbr.: Octocrylene (OC), Diethylhexyl Butamido Triazon (DEBT), Butyl Methoxydibenzoylmethane (BMDM) and Bis-Ethylhexyloxyphenol Methoxy-phenyl Triazine (BEMT)*

*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 3.6.2 were regarded suitable.

## 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 ($\sigma_{pt}$) 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 ($\sigma_{pt}$), 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. 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 process, calibration of equipment and composition of reagents, transmission or calculation errors, accuracy and precision and use of reference material. 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].

## 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 $\sigma_{pt}$'.

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 $S^*/\sigma_{pt}$

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 $\sigma_{pt}$ 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 and traceability

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 ($U_{(Xpt)}$) 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 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 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 $\sigma_{pt}$ or $\sigma_{pt}$' |
| 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*/$\sigma_{pt}$ or S*/$\sigma_{pt}$'* |
| *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 second table the individual results of the participating laboratories are listed formatted to 3 digits**:

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

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

## 4.1 Octocrylene OC (as Ester in g/100 g)

**Vergleichsuntersuchung / Proficiency Test**

| **Statistic Data** | |
|---|---|
| *Number of results* | 13 |
| *Number of outliers* | - |
| Mean | 9,71 |
| Median | 10,0 |
| **Robust Mean (X)** | **10,0** |
| **Robust standard deviation (S*)** | **0,320** |
| *Number with 2 replicates* | 10 |
| Repeatability SD ($S_r$) | 0,0937 |
| Repeatability ($CV_r$) | 0,93% |
| Reproducibility SD ($S_R$) | 0,177 |
| Reproducibility ($CV_R$) | 1,75% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,525** |
| Target standard deviation (for Information) | 0,284 |
| **lower limit of target range** | **8,98** |
| **upper limit of target range** | **11,1** |
| *Quotient S*/$\sigma_{pt}$* | *0,61* |
| *Standard uncertainty $U_{(Xpt)}$* | *0,111* |
| *Results in the target range* | *10* |
| *Percent in the target range* | *77%* |

*Comments to the statistic data:*

The target standard deviation was calculated according to 3.6.2 precision experiments (ASU K 84.00-28 / DIN EN 16344). The target standard deviation for information was calculated according to the general model of Horwitz (s. 3.6.1).

The results showed a normal to low variability with almost a symmetrical distribution (see kernel density estimation next page).

The quotient S*/$\sigma_{pt}$ was well below 2,0. The repeatability and reproducibility standard deviations were in the range of established values for the applied methods (see 3.6.2). The comparability of results is given.

77% of results were in the target range.

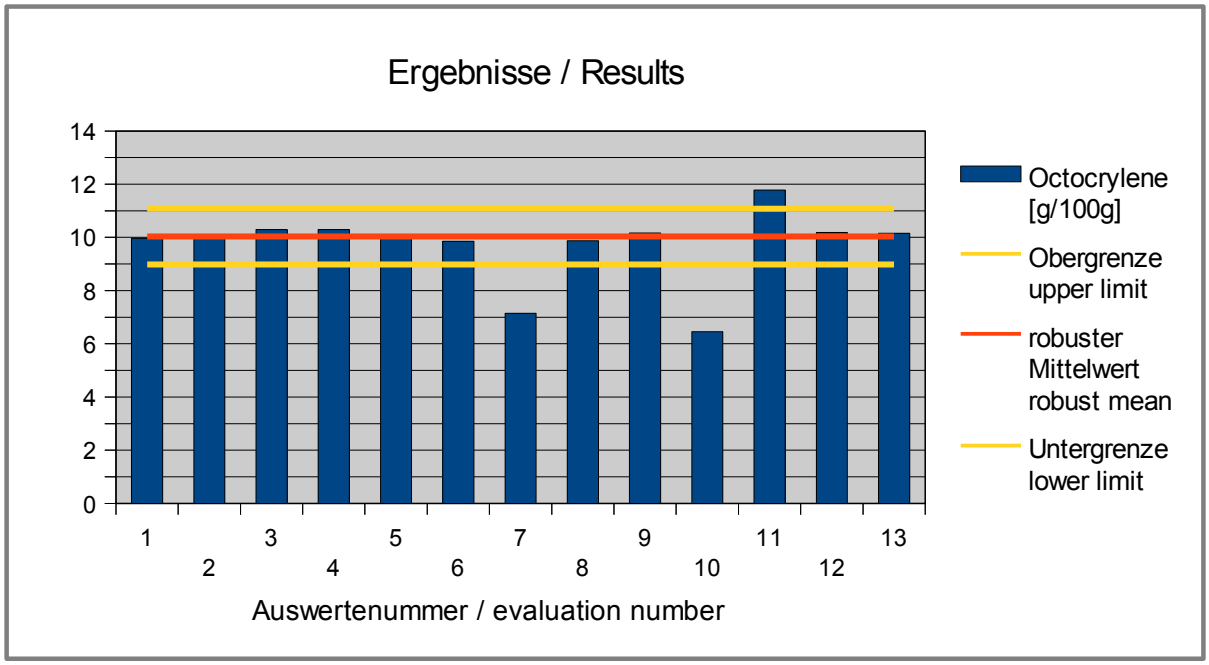


**Abb. / Fig. 1:** Ergebnisse / Results Octocrylene (OC)

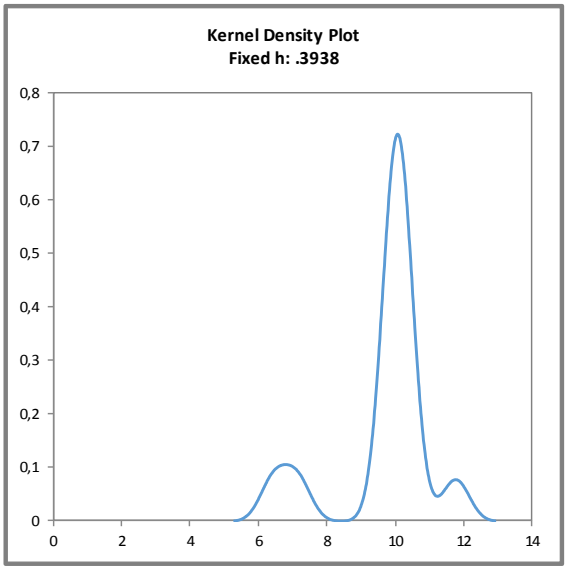


**Abb. / Fig. 2:**
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

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

*Comment:*
The kernel density plot shows almost a symmetrical distribution of results with two side peaks, which are due to three results outside the target range.

**Ergebnisse der Teilnehmer:**
**Results of Participants:**

| Auswerte-nummer<br>Evaluation number | Octocrylene [g/100g] | Abweichung [g/100g]<br>Deviation [g100g] | z-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis<br>Remark |
|---|---|---|---|---|---|
| 1 | 9,97 | -0,062 | -0,12 | -0,22 | |
| 2 | 10,0 | -0,032 | -0,06 | -0,11 | |
| 3 | 10,3 | 0,259 | 0,49 | 0,91 | |
| 4 | 10,3 | 0,268 | 0,51 | 0,94 | |
| 5 | 10,0 * | -0,032 | -0,06 | -0,11 | |
| 6 | 9,85 | -0,182 | -0,35 | -0,64 | |
| 7 | 7,15 | -2,88 | -5,5 | -10 | indicated as acid? |
| 8 | 9,87 | -0,162 | -0,31 | -0,57 | |
| 9 | 10,2 | 0,138 | 0,26 | 0,49 | |
| 10 | 6,46 | -3,57 | -6,8 | -13 | indicated as acid? |
| 11 | 11,8 | 1,75 | 3,3 | 6,2 | |
| 12 | 10,2 | 0,158 | 0,30 | 0,56 | |
| 13 | 10,2 * | 0,128 | 0,24 | 0,45 | |

* Mean calculated by DLA

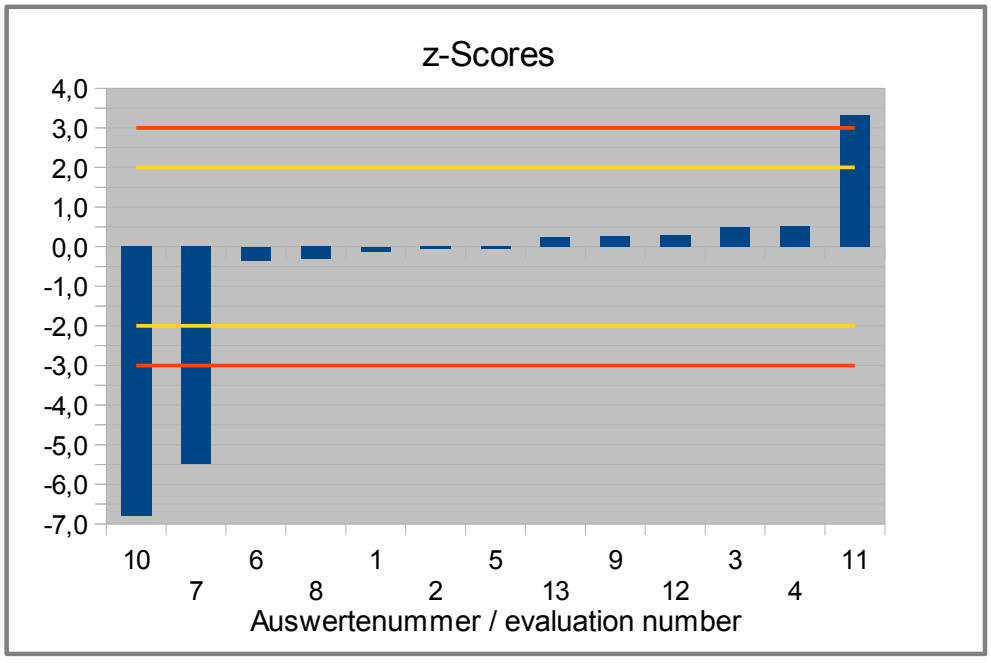


Abb. / Fig. 3: Z-Scores Octocrylene (OC)

## 4.2 Butyl Methoxydibenzoylmethane BMDM (in g/100 g)

**Vergleichsuntersuchung / Proficiency Test**

| **Statistic Data** | |
|---|---|
| *Number of results* | 12 |
| *Number of outliers* | 0 |
| Mean | 5,02 |
| Median | 5,09 |
| **Robust Mean (X)** | **5,03** |
| **Robust standard deviation (S*)** | **0,301** |
| *Number with 2 replicates* | 12 |
| Repeatability SD ($S_r$) | 0,0442 |
| Repeatability ($CV_r$) | 0,88% |
| Reproducibility SD ($S_R$) | 0,294 |
| Reproducibility ($CV_R$) | 5,86% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,238** |
| Target standard deviation (for Information) | 0,158 |
| **lower limit of target range** | **4,56** |
| **upper limit of target range** | **5,51** |
| *Quotient S*/$\sigma_{pt}$* | *1,26* |
| *Standard uncertainty $U_{(Xpt)}$* | *0,109* |
| *Results in the target range* | *9* |
| *Percent in the target range* | *75%* |

*Comments to the statistic data:*

The target standard deviation was calculated according to 3.6.2 precision experiments (ASU K 84.00-28 / DIN EN 16344). The target standard deviation for information was calculated according to the general model of Horwitz (s. 3.6.1).

The results showed a normal to low variability with almost a symmetrical distribution (see kernel density estimation next page).

The quotient S*/$\sigma_{pt}$ was well below 2,0. The repeatability and reproducibility standard deviations were in the range of established values for the applied methods (see 3.6.2). The comparability of results is given.

75% of results were in the target range.

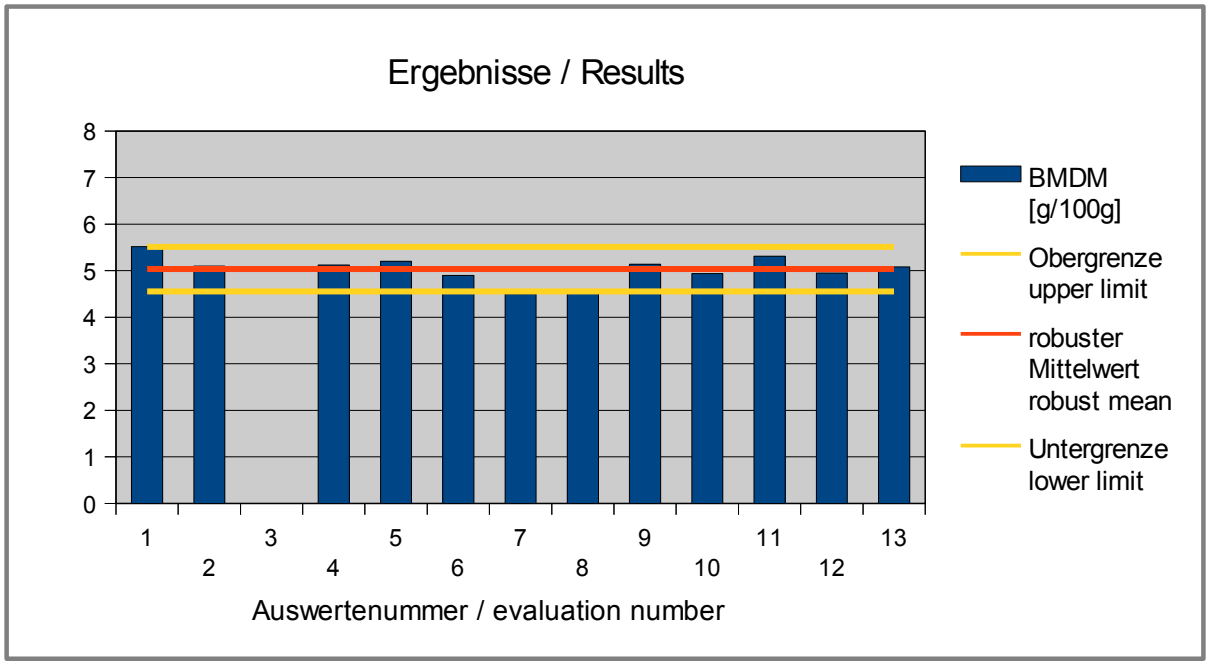


**Abb. / Fig. 4:** Ergebnisse / Results Butyl Methoxydibenzoylmethane (BMDM)

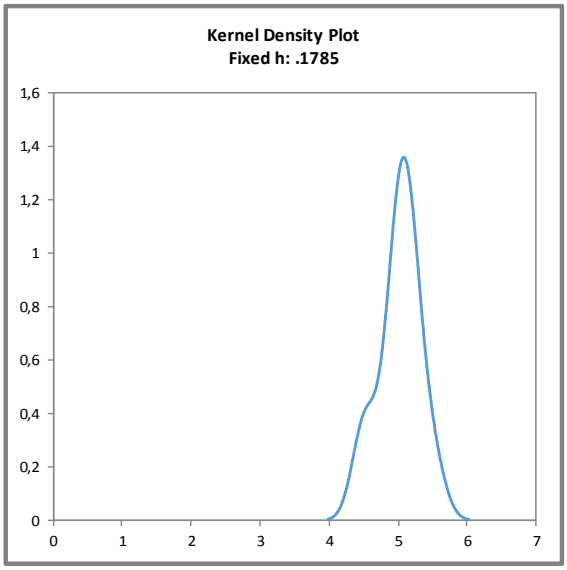


**Abb. / Fig. 5:**
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

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

*Comment:*
The kernel density plot shows almost a symmetrical distribution of results with a slight shoulder.

**Ergebnisse der Teilnehmer:**
**Results of Participants:**

| Auswerte-nummer<br>Evaluation number | BMDM [g/100g] | Abweichung [g/100g]<br>Deviation [g100g] | z-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis<br>Remark |
|---|---|---|---|---|---|
| 1 | 5,52 | 0,488 | 2,0 | 3,1 | |
| 2 | 5,10 | 0,068 | 0,28 | 0,43 | |
| 3 | | | | | |
| 4 | 5,12 | 0,088 | 0,37 | 0,56 | |
| 5 | 5,20 * | 0,168 | 0,70 | 1,1 | |
| 6 | 4,90 | -0,132 | -0,56 | -0,84 | |
| 7 | 4,50 | -0,532 | -2,2 | -3,4 | |
| 8 | 4,53 | -0,502 | -2,1 | -3,2 | |
| 9 | 5,14 | 0,108 | 0,45 | 0,68 | |
| 10 | 4,94 | -0,092 | -0,39 | -0,58 | |
| 11 | 5,31 | 0,278 | 1,2 | 1,8 | |
| 12 | 4,95 | -0,082 | -0,35 | -0,52 | |
| 13 | 5,08 * | 0,048 | 0,20 | 0,30 | |

* Mean calculated by DLA

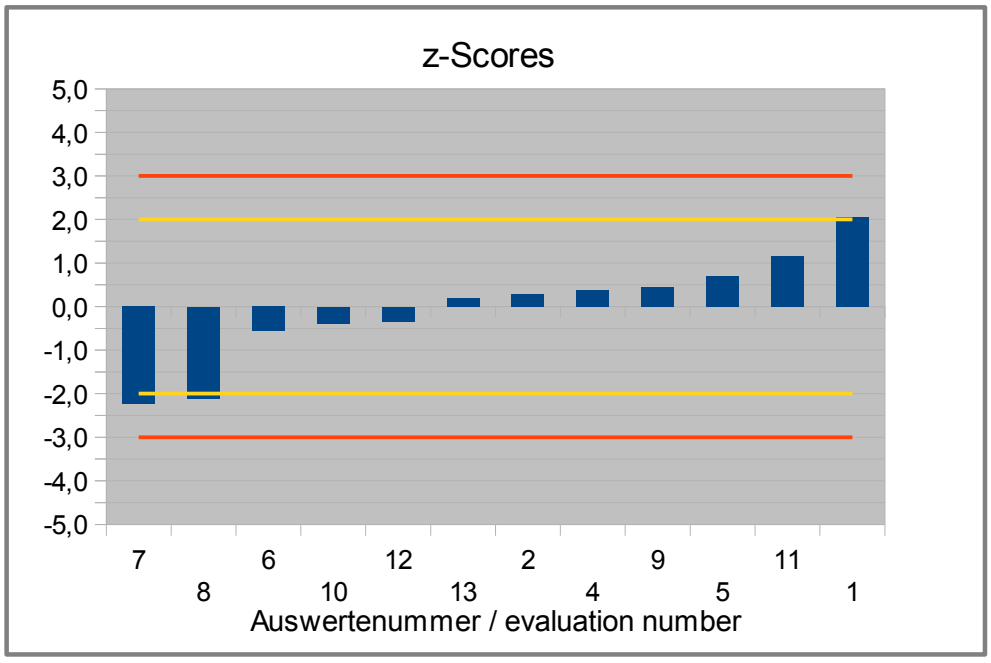


Abb. / Fig. 6: Z-Scores Butyl Methoxydibenzoylmethane (BMDM)

## 4.3 Bis-Ethylhexylphenol Methoxyphenyl Triazine BEMT (in g/100 g)

**Vergleichsuntersuchung / Proficiency Test**

| **Statistic Data** | |
|---|---|
| *Number of results* | 12 |
| *Number of outliers* | 0 |
| Mean | 0,408 |
| Median | 0,405 |
| **Robust Mean (X)** | **0,408** |
| **Robust standard deviation (S*)** | **0,0377** |
| *Number with 2 replicates* | 12 |
| Repeatability SD ($S_r$) | 0,0206 |
| Repeatability ($CV_r$) | 5,06% |
| Reproducibility SD ($S_R$) | 0,0436 |
| Reproducibility ($CV_R$) | 10,7% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,0193** |
| Target standard deviation (for Information) | 0,0187 |
| **lower limit of target range** | **0,369** |
| **upper limit of target range** | **0,446** |
| *Quotient S*/$\sigma_{pt}$* | *2,0* |
| *Standard uncertainty $U_{(Xpt)}$* | *0,0136* |
| *Results in the target range* | *9* |
| *Percent in the target range* | *75%* |

*Comments to the statistic data:*

The target standard deviation was calculated according to 3.6.2 precision experiments (ASU K 84.00-28 / DIN EN 16344). The target standard deviation for information was calculated according to the general model of Horwitz (s. 3.6.1).

The results showed a normal to low variability with almost a symmetrical distribution (see kernel density estimation next page).

The quotient S*/$\sigma_{pt}$ was 2,0. The repeatability and reproducibility standard deviations were in the range of established values for the applied methods (see 3.6.2). The comparability of results is given.

75% of results were in the target range.

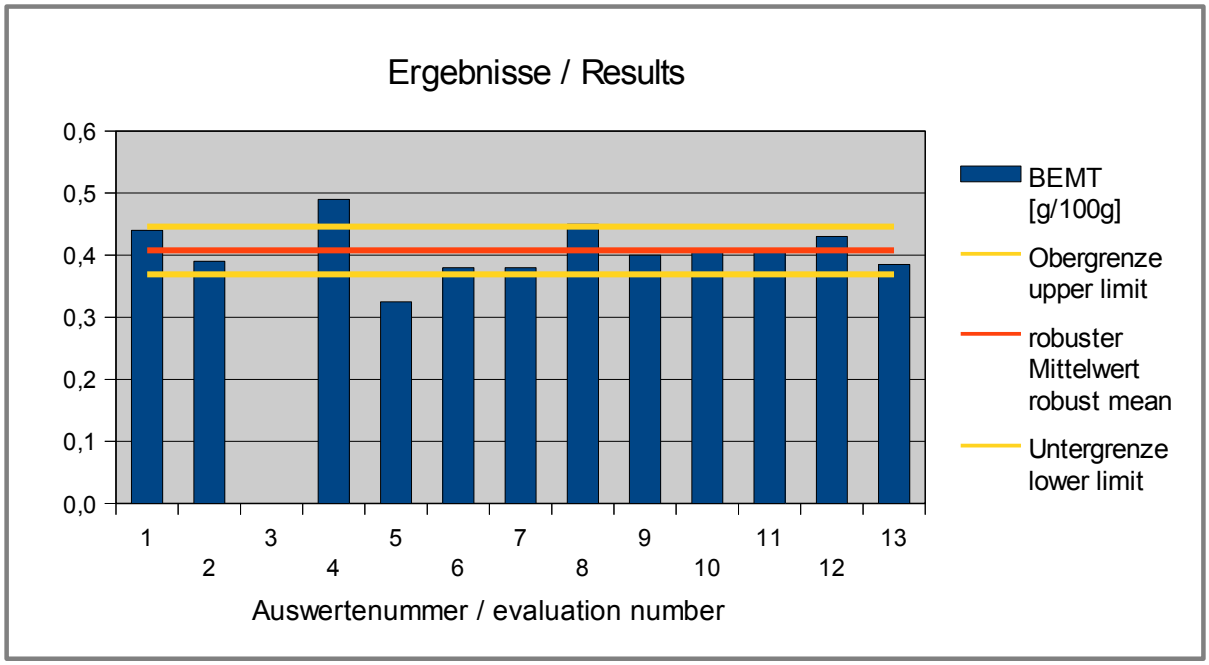


**Abb. / Fig. 7:** Ergebnisse / Results Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT)

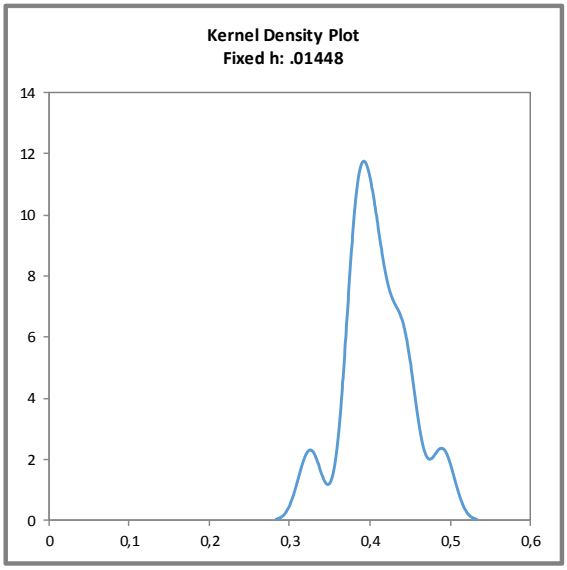


**Abb. / Fig. 8:**
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

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

*Comment:*
The kernel density plot shows almost a symmetrical distribution of results with a slight shoulder and two smaller side peaks, which are due to two results outside the target range.

**Ergebnisse der Teilnehmer:**
**Results of Participants:**

| Auswerte-nummer<br>Evaluation number | BEMT [g/100g] | Abweichung [g/100g]<br>Deviation [g100g] | z-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis<br>Remark |
|---|---|---|---|---|---|
| 1 | 0,440 | 0,0325 | 1,7 | 1,7 | |
| 2 | 0,390 | -0,0175 | -0,91 | -0,94 | |
| 3 | | | | | |
| 4 | 0,490 | 0,0825 | 4,3 | 4,4 | |
| 5 | 0,325 * | -0,0825 | -4,3 | -4,4 | |
| 6 | 0,380 | -0,0275 | -1,4 | -1,5 | |
| 7 | 0,380 | -0,0275 | -1,4 | -1,5 | |
| 8 | 0,450 | 0,0425 | 2,2 | 2,3 | |
| 9 | 0,400 | -0,0075 | -0,39 | -0,40 | |
| 10 | 0,410 | 0,0025 | 0,13 | 0,13 | |
| 11 | 0,410 | 0,0025 | 0,13 | 0,13 | |
| 12 | 0,430 | 0,0225 | 1,2 | 1,2 | |
| 13 | 0,385 * | -0,0225 | -1,2 | -1,2 | |

* Mean calculated by DLA

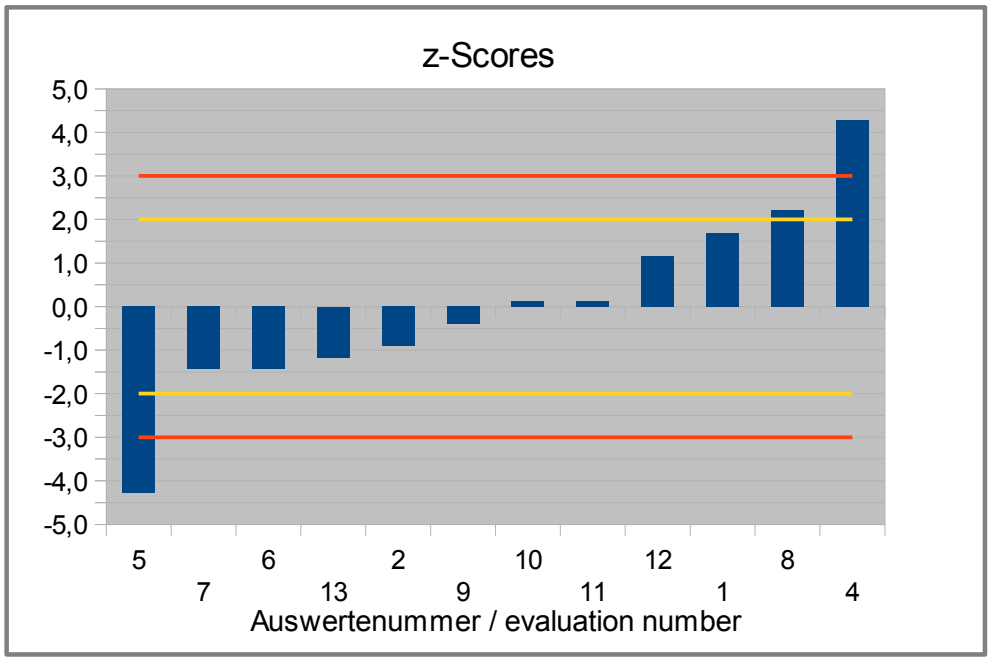


Abb. / Fig. 9: Z-Scores Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT)

## 4.4 Titanium Dioxide (in g/100 g)

### Vergleichsuntersuchung / Proficiency Test

| **Statistic Data** | |
|---|---|
| *Number of results* | 4 |
| *Number of outliers* | 0 |
| Mean | 4,83 |
| Median | 4,80 |
| **Robust Mean (X)** | **4,83** |
| **Robust standard deviation (S*)** | **0,147** |
| *Number with 2 replicates* | 4 |
| Repeatability SD ($S_r$) | 0,109 |
| Repeatability ($CV_r$) | 2,26% |
| Reproducibility SD ($S_R$) | 0,151 |
| Reproducibility ($CV_R$) | 3,13% |

Due to the low number of results < 7 no statistical evaluation was done.

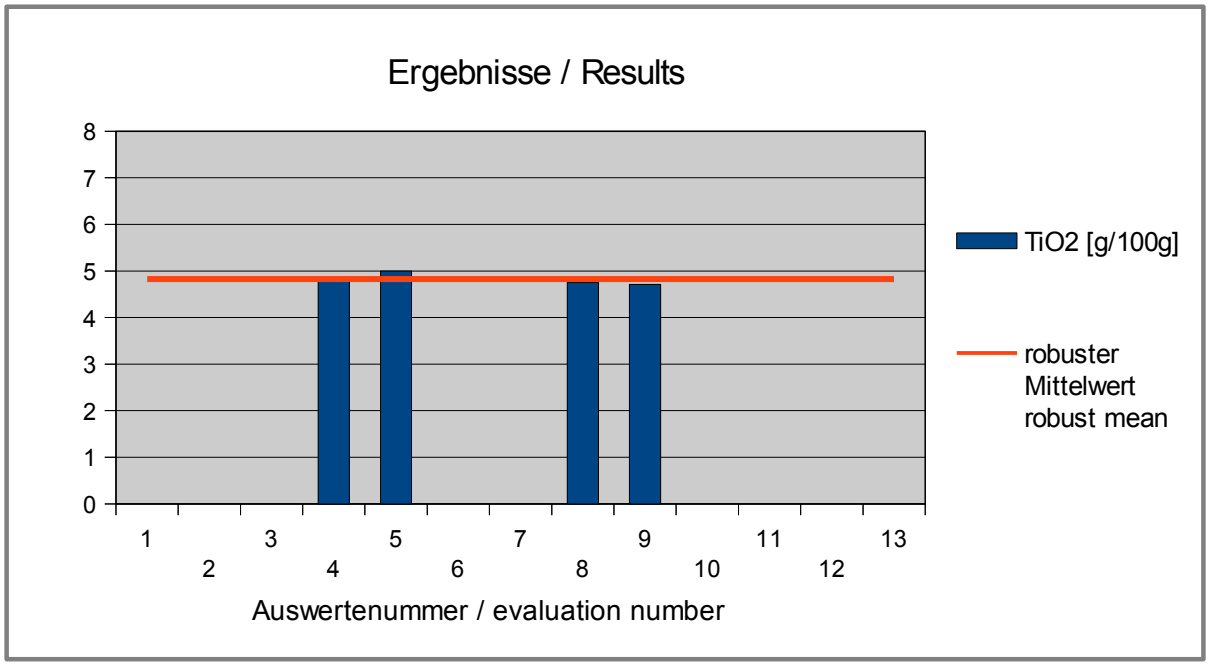


**Abb. / Fig. 10:** Ergebnisse / Results Titanium Dioxide ($TiO_2$)

**Ergebnisse der Teilnehmer:**
**Results of Participants:**

| Auswerte-nummer<br>Evaluation number | TiO2 [g/100g] | Abweichung [g/100g]<br>Deviation [g100g] | z-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis<br>Remark |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | 4,85 | 0,022 | | | |
| 5 | 5,00 * | 0,172 | | | |
| 6 | | | | | |
| 7 | | | | | |
| 8 | 4,75 | -0,078 | | | |
| 9 | 4,71 | -0,118 | | | |
| 10 | | | | | |
| 11 | | | | | |
| 12 | | | | | |
| 13 | | | | | |

* Mean calculated by DLA

## 4.5 Ethylhexyl Salicylate EHS (in g/100 g)

### Vergleichsuntersuchung / Proficiency Test

| **Statistic Data** | |
|---|---|
| *Number of results* | 4 |
| *Number of outliers* | 0 |
| Mean | 5,13 |
| Median | 4,98 |
| **Robust Mean (X)** | **5,13** |
| **Robust standard deviation (S*)** | **0,531** |
| *Number with 2 replicates* | 4 |
| Repeatability SD ($S_r$) | 0,0547 |
| Repeatability ($CV_r$) | 1,07% |
| Reproducibility SD ($S_R$) | 0,467 |
| Reproducibility ($CV_R$) | 9,11% |

Due to the low number of results < 7 no statistical evaluation was done.

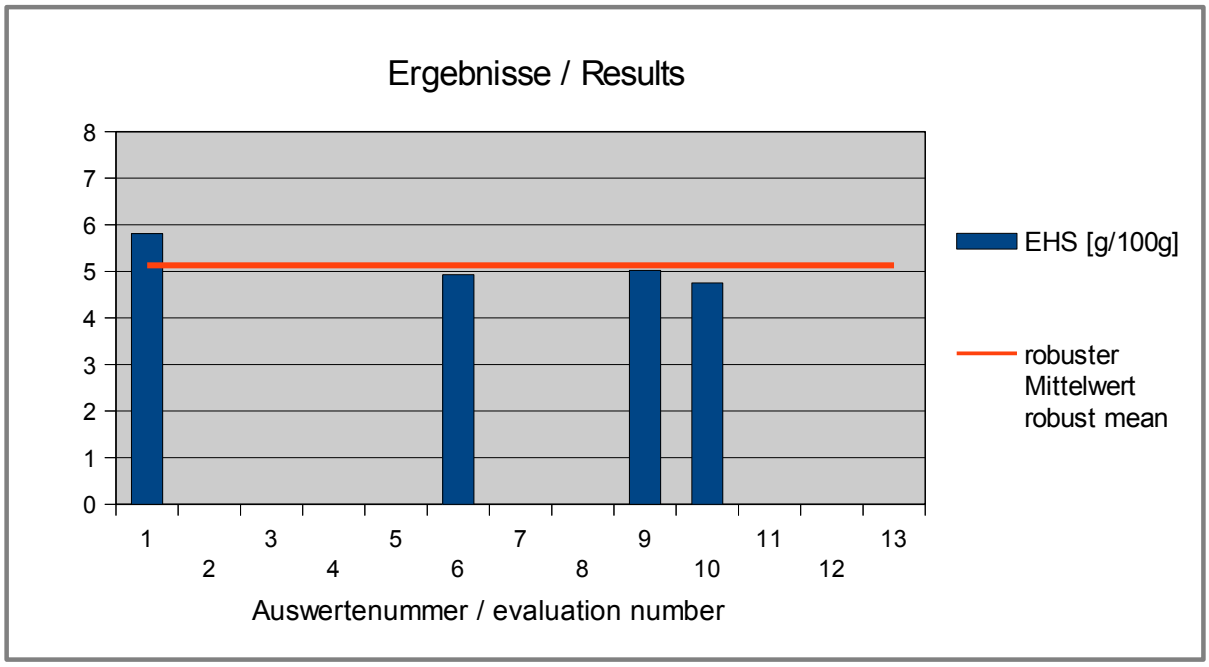


**Abb. / Fig. 11:** Ergebnisse / Results Ethylhexyl Salicylate (EHS)

**Ergebnisse der Teilnehmer:**
**Results of Participants:**

| Auswerte-nummer<br>Evaluation number | EHS [g/100g] | Abweichung [g/100g]<br>Deviation [g/100g] | z-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis<br>Remark |
|---|---|---|---|---|---|
| 1 | 5,81 | 0,683 | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |
| 6 | 4,93 | -0,198 | | | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | 5,02 | -0,108 | | | |
| 10 | 4,75 | -0,377 | | | |
| 11 | | | | | |
| 12 | | | | | |
| 13 | | | | | |

## 4.6 Other (in g/100 g)

### Vergleichsuntersuchung / Proficiency Test

There were to additional results reported for parameters designated by participants as "octylsalicylate" and "octysalicylate", respectively. This may also be ethylhexyl salicylate, for which "octisalate" is a synonymous name.

**Ergebnisse der Teilnehmer:**
**Results of Participants:**

| Auswerte-nummer<br>Evaluation number | Andere / Other [g/100g] | Abweichung [mg/kg]<br>Deviation [mg/kg] | z-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis<br>Remark |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | 4,89 | | | | Octyl Salicylate° |
| 5 | | | | | |
| 6 | | | | | |
| 7 | 5,20 | | | | Octysalicylate° |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |
| 11 | | | | | |
| 12 | | | | | |
| 13 | | | | | |

° indicated by participant

# 5. Documentation

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

## 5.1 Details by participants

### 5.1.1 Primary data

| Analyte | Participant | Unit | Sample No. A | Sample No. B | Date of analysis | Result (Mean) | Result A | Result B | Limit of quantificati-on | Incl. RR | Recovery rate [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Octocrylene (OC) als /as Ester | 1 | g/100g | 18 | 36 | 17.04.18 | 9,97 | 9,95 | 9,98 | 0,18 | no | 112-115 |
| | 2 | g/100g | 19 | 35 | 06.04.18 | 10 | 10 | 10 | 0,1 | no | |
| | 3 | g/100g | 1 | 53 | 28.03.18 | 10,29 | 10,46 | 10,12 | | | |
| | 4 | g/100g | 13 | 41 | 20.04.18 | 10,3 | 10,31 | 10,29 | 0,25 | yes | 87-118 |
| | 5 | g/100g | 4 | 50 | 06.04.18 | | 10 | 10 | / | no | / |
| | 6 | g/100g | 3 | 51 | 18.04. | 9,85 | 9,85 | 9,85 | 0,1 | no | |
| | 7 | g/100g | 14 | 40 | 12.04.18 | 7,15 | 7,1 | 7,2 | 0,02g/l | no | - |
| | 8 | g/100g | 17 | 37 | 16.04.18 | 9,87 | 9,87 | 9,87 | | | |
| | 9 | g/100g | 32 | 21 | 26.03.18 | 10,17 | 10,05 | 10,28 | 0,2 | no | |
| | 10 | g/100g | 11 | 43 | 12./13.04. 18 | 6,46 | 6,59 | 6,33 | 0,12 | no | |
| | 11 | g/100g | 24 | 30 | 12.04.18 | 11,78 | 12,04 | 11,52 | 0,25 | no | |
| | 12 | g/100g | 5 | 49 | 20.03.18 | 10,19 | 10,17 | 10,21 | 0,02 | | |
| | 13 | g/100g | 16 | 38 | 04.04.18 | | 10,15 | 10,17 | | no | |

| Analyte | Participant | Unit | Sample No. A | Sample No. B | Date of analysis | Result (Mean) | Result A | Result B | Limit of quantification | Incl. RR | Recovery rate [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Butyl Methoxydibenzoylmethane (BMDM) | 1 | g/100g | 18 | 36 | 17.04.18 | 5,52 | 5,51 | 5,53 | 0,1 | no | 90-97 |
| | 2 | g/100g | 19 | 35 | 06.04.18 | 5,1 | 5,1 | 5,1 | 0,1 | no | |
| | 3 | g/100g | 1 | 53 | | | | | | | |
| | 4 | g/100g | 13 | 41 | 20.04.18 | 5,12 | 5,14 | 5,09 | 0,25 | yes | 87-118 |
| | 5 | g/100g | 4 | 50 | 06.04.18 | | 5,2 | 5,2 | / | no | / |
| | 6 | g/100g | 3 | 51 | 18.04. | 4,9 | 4,91 | 4,88 | 0,1 | no | |
| | 7 | g/100g | 14 | 40 | 12.04.18 | 4,5 | 4,45 | 4,55 | 0,02 g/l | no | - |
| | 8 | g/100g | 17 | 37 | 16.04.18 | 4,53 | 4,59 | 4,46 | | | |
| | 9 | g/100g | 32 | 21 | 27.03.18 | 5,14 | 5,08 | 5,19 | 0,2 | no | |
| | 10 | g/100g | 11 | 43 | 12./13.04.18 | 4,94 | 4,94 | 4,94 | 0,21 | no | |
| | 11 | g/100g | 24 | 30 | 12.04.18 | 5,31 | 5,31 | 5,31 | 0,25 | no | |
| | 12 | g/100g | 5 | 49 | 20.03.18 | 4,95 | 4,94 | 4,96 | 0,01 | | |
| | 13 | g/100g | 16 | 38 | 04.04.18 | | 5,05 | 5,11 | | no | |

| Analyte | Participant | Unit | Sample No. A | Sample No. B | Date of analysis | Result (Mean) | Result A | Result B | Limit of quantification | Incl. RR | Recovery rate [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) | 1 | g/100g | 18 | 36 | 17.04.18 | 0,44 | 0,44 | 0,44 | 0,21 | no | 105-118 |
| | 2 | g/100g | 19 | 35 | 06.04.18 | 0,39 | 0,39 | 0,39 | 0,02 | no | |
| | 3 | g/100g | 1 | 53 | | | | | | | |
| | 4 | g/100g | 13 | 41 | 20.04.18 | 0,49 | 0,48 | 0,49 | 0,25 | yes | 87-118 |
| | 5 | g/100g | 4 | 50 | 06.04.18 | | 0,34 | 0,31 | / | no | / |
| | 6 | g/100g | 3 | 51 | 18.04. | 0,38 | 0,38 | 0,38 | 0,1 | no | |
| | 7 | g/100g | 14 | 40 | 12.04.18 | 0,38 | 0,35 | 0,4 | 0,4g/l | no | - |
| | 8 | g/100g | 17 | 37 | 16.04.18 | 0,45 | 0,45 | 0,45 | | | |
| | 9 | g/100g | 32 | 21 | 28.03.18 | 0,4 | 0,4 | 0,41 | 0,2 | no | |
| | 10 | g/100g | 11 | 43 | 12./13.04.18 | 0,41 | 0,43 | 0,39 | 0,16 | no | |
| | 11 | g/100g | 24 | 30 | 12.04.18 | 0,41 | 0,41 | 0,41 | 0,25 | no | |
| | 12 | g/100g | 5 | 49 | 27.03.18 | 0,43 | 0,46 | 0,39 | 0,01 | | |
| | 13 | g/100g | 16 | 38 | 04.04.18 | | 0,38 | 0,39 | | no | |

| Analyte | Participant | Unit | Sample No. A | Sample No. B | Date of analysis | Result (Mean) | Result A | Result B | Limit of quantificati-on | Incl. RR | Recovery rate [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Titanium Dioxide | 1 | g/100g | 18 | 36 | | | | | | | |
| | 2 | g/100g | 19 | 35 | | | | | | | |
| | 3 | g/100g | 1 | 53 | | | | | | | |
| | 4 | g/100g | 13 | 41 | 11.04.18 | 4,85 | 5 | 4,7 | 0,5 | yes | 100 |
| | 5 | g/100g | 4 | 50 | 09.04.18 | 43201 | 5,0 | 5,0 | / | no | / |
| | 6 | g/100g | 3 | 51 | | | | | | | |
| | 7 | g/100g | 14 | 40 | | keine Methode | | | | | |
| | 8 | g/100g | 17 | 37 | 04.04.18 | 4,75 | 4,71 | 4,78 | | | |
| | 9 | g/100g | 32 | 21 | 11.04.18 | 4,71 | 4,71 | 4,71 | 0,4 | no | |
| | 10 | g/100g | 11 | 43 | | | | | | | |
| | 11 | g/100g | 24 | 30 | | | | | | | |
| | 12 | g/100g | 5 | 49 | | | | | | | |
| | 13 | g/100g | 16 | 38 | | | | | | | |

| Analyte | Participant | Unit | Sample No. A | Sample No. B | Date of analysis | Result (Mean) | Result A | Result B | Limit of quantificati-on | Incl. RR | Recovery rate [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethylhexyl salicylate (EHS CAS-Nr.: 118-60-5) | 1 | g/100g | 18 | 36 | 17.04.18 | 5,81 | 5,79 | 5,82 | 0,09 | no | 95-103 |
| Ethylhexylsalicylat | 6 | g/100g | 19 | 35 | 18.04. | 4,93 | 4,94 | 4,91 | 0,1 | no | |
| ETHYLHEXYL SALICYLATE | 9 | g/100g | 1 | 53 | 28.03.18 | 5,02 | 4,97 | 5,07 | 0,2 | no | |
| Ethylhexyl Salicylate (EHS) | 10 | g/100g | 13 | 41 | 12./13.04. 18 | 4,75 | 4,81 | 4,7 | 0,18 | no | |
| | | | | | | | | | | | |
| Octyl Salicylate | 4 | g/100g | 3 | 51 | 20.04.18 | 4,89 | 4,91 | 4,86 | 0,25 | yes | 87-118 |
| Octysalicylate | 7 | g/100g | 14 | 40 | 12.04.18 | 5,2 | 5,2 | 5,2 | 0,02g/l | no | - |

## 5.1.2 Analytical methods

| Analyte | Participant | Method description | Sample preparation | Analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| Octocrylene (OC) als /as Ester | 1 | ASU §64 LFBG 84.00-28 February 2014 | | HPLC - DAD | according to ASU §64 | | | |
| | 2 | internal method | | HPLC-DAD | external | no | no | |
| | 3 | CU-3.P.K.004 (HPLC-DAD) | | | | | yes | |
| | 4 | Determination of selected UV filter in cosmetic products, HPLC-DAD Ext.Norm: EN 16344 , Dok.Code: 4839 | Extraction (Aceton/Methanol) | HPLC-DAD | PT sample | no | yes | |
| | 5 | in house method (22X09008.01) | sample weighing and fill up | UPLC - PDA Detector | external - Merck | / | no | / |
| | 6 | ASU 84.00 - 28 | | HPLC-DAD | | | yes | |
| | 7 | Literature | solved in Aceton/Methanol | HPLC/DAD (300nm) | | - | yes | |
| | 8 | LC-UV , internal method | | | | | yes | |
| | 9 | DIN EN 16344:2013-11 modified | Extraction (Aceton/Methanol) | HPLC-DAD | | | yes | |
| | 10 | M 12.4101.03/ ASU K 84.00-28 (2014-02)= DIN EN 16344 (2013-11) | | HPLC-DAD | | | yes | |
| | 11 | §64 LFGB ASU K84.00-28 | | | | | yes | |
| | 12 | HPLC-UV | | | | | no | |
| | 13 | HPLC-DAD | with ACN in ultrasonic bath | | external calibration | | no | |

| Analyte | Participant | Method description | Sample preparation | Analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| Butyl Methoxydibenzoylmethane (BMDM) | 1 | ASU §64 LFBG 84.00-28 February 2014 | | HPLC - DAD | according to ASU §64 | | | |
| | 2 | internal method | | HPLC-DAD | external | no | no | |
| | 3 | | | | | | | |
| | 4 | Determination of selected UV filter in cosmetic products, HPLC-DAD Ext.Norm: EN 16344 , Dok.Code: 4839 | Extraction (Aceton/Methanol) | HPLC-DAD | PT sample | no | yes | |
| | 5 | in house method (22X09008.01) | sample weighing and fill up | UPLC - PDA Detector | external - Merck | / | no | / |
| | 6 | ASU 84.00 - 28 | | HPLC-DAD | | | yes | |
| | 7 | Literature | solved in Aceton/Methanol | HPLC/DAD (300nm) | | - | yes | |
| | 8 | LC-UV , internal method | | | | | yes | |
| | 9 | DIN EN 16344:2013-11 modified | Extraction (Aceton/Methanol) | HPLC-DAD | | | yes | |
| | 10 | M 12.4101.03/ ASU K 84.00-28 (2014-02)= DIN EN 16344 (2013-11) | | HPLC-DAD | | | yes | |
| | 11 | §64 LFGB ASU K84.00-28 | | | | | yes | |
| | 12 | HPLC-UV | | | | | no | |
| | 13 | HPLC-DAD | with ACN in ultrasonic bath | | external calibration | | no | |

| Analyte | Participant | Method description | Sample preparation | Analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) | 1 | ASU §64 LFBG 84.00-28 February 2014 | | HPLC - DAD | according to ASU §64 | | | |
| | 2 | internal method | | HPLC-DAD | external | no | no | |
| | 3 | | | | | | | |
| | 4 | Determination of selected UV filter in cosmetic products, HPLC-DAD Ext.Norm: EN 16344 , Dok.Code: 4839 | Extraction (Aceton/Methanol) | HPLC-DAD | PT sample | no | yes | |
| | 5 | in house method (22X09008.01) | sample weighing and fill up | UPLC - PDA Detector | external - Merck | / | no | / |
| | 6 | ASU 84.00 - 28 | | HPLC-DAD | | | yes | |
| | 7 | Literature | solved in Aceton/Methanol | HPLC/DAD (300nm) | | - | yes | |
| | 8 | LC-UV , internal method | | | | | yes | |
| | 9 | DIN EN 16344:2013-11 modified | Extraction (Aceton/Methanol) | HPLC-DAD | | | yes | |
| | 10 | M 12.4101.03/ ASU K 84.00-28 (2014-02)= DIN EN 16344 (2013-11) | | HPLC-DAD | | | yes | |
| | 11 | §64 LFGB ASU K84.00-28 | | | | | yes | |
| | 12 | HPLC-UV | | | | | no | |
| | 13 | HPLC-DAD | with ACN in ultrasonic bath | | external calibration | | no | |

| Analyte | Participant | Method description | Sample preparation | Analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| Titanium Dioxide | 1 | | | | | | | |
| | 2 | | | | | | | |
| | 3 | | | | | | | |
| | 4 | Determination of titanium dioxide in cosmetic products, photometry Dok.Code: 4837 | incinerated, solved in H2SO4, diluted with water, colled, filtered, H2O2 added | Photometer (409 nm) | PT sample | no | yes | |
| | 5 | according to in house method 42X12001.01 | melting digestion with Li2B4O7 | WD-XRF; Detector: Flow Counter | extern - diverse | / | yes | / |
| | 6 | | | | | | | no method |
| | 7 | | | | | | | |
| | 8 | flame AAS, internal method | | | | | yes | |
| | 9 | Photometric determination | incineration, melting with poatassium disulfate, complexing with H2O2 in diluted H2SO4 | Photometry | | | yes | |
| | 10 | | | | | | | |
| | 11 | | | | | | | |
| | 12 | | | | | | | |
| | 13 | | | | | | | |

| Analyte | Participant | Method description | Sample preparation | Analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| 2-Ethylhexyl salicylate (EHS CAS-Nr.: 118-60-5) | 1 | ASU §64 LFBG 84.00-28 February 2014 | | HPLC - DAD | according to ASU §64 | | | |
| Ethylhexylsalicylat | 6 | ASU 84.00 - 28 | | HPLC-DAD | | | yes | |
| ETHYLHEXYL SALICYLATE | 9 | DIN EN 16344:2013-11 modified | Extraction (Aceton/Methanol) | HPLC-DAD | | | yes | |
| Ethylhexyl Salicylate (EHS) | 10 | M 12.4101.03/ ASU K 84.00-28 (2014-02)= DIN EN 16344 (2013-11) | | HPLC-DAD | | | yes | |
| | | | | | | | | |
| Octyl Salicylate | 4 | Determination of selected UV filter in cosmetic products, HPLC-DAD Ext.Norm: EN 16344 , Dok.Code: 4839 | Extraction (Aceton/Methanol) | HPLC-DAD | PT sample | no | yes | |
| Octysalicylate | 7 | Literature | solved in Aceton/Methanol | HPLC/DAD (300nm) | | - | yes | |

## 5.2 Homogeneity

### 5.2.1 Comparison of sample numbers / test results and trend line

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:

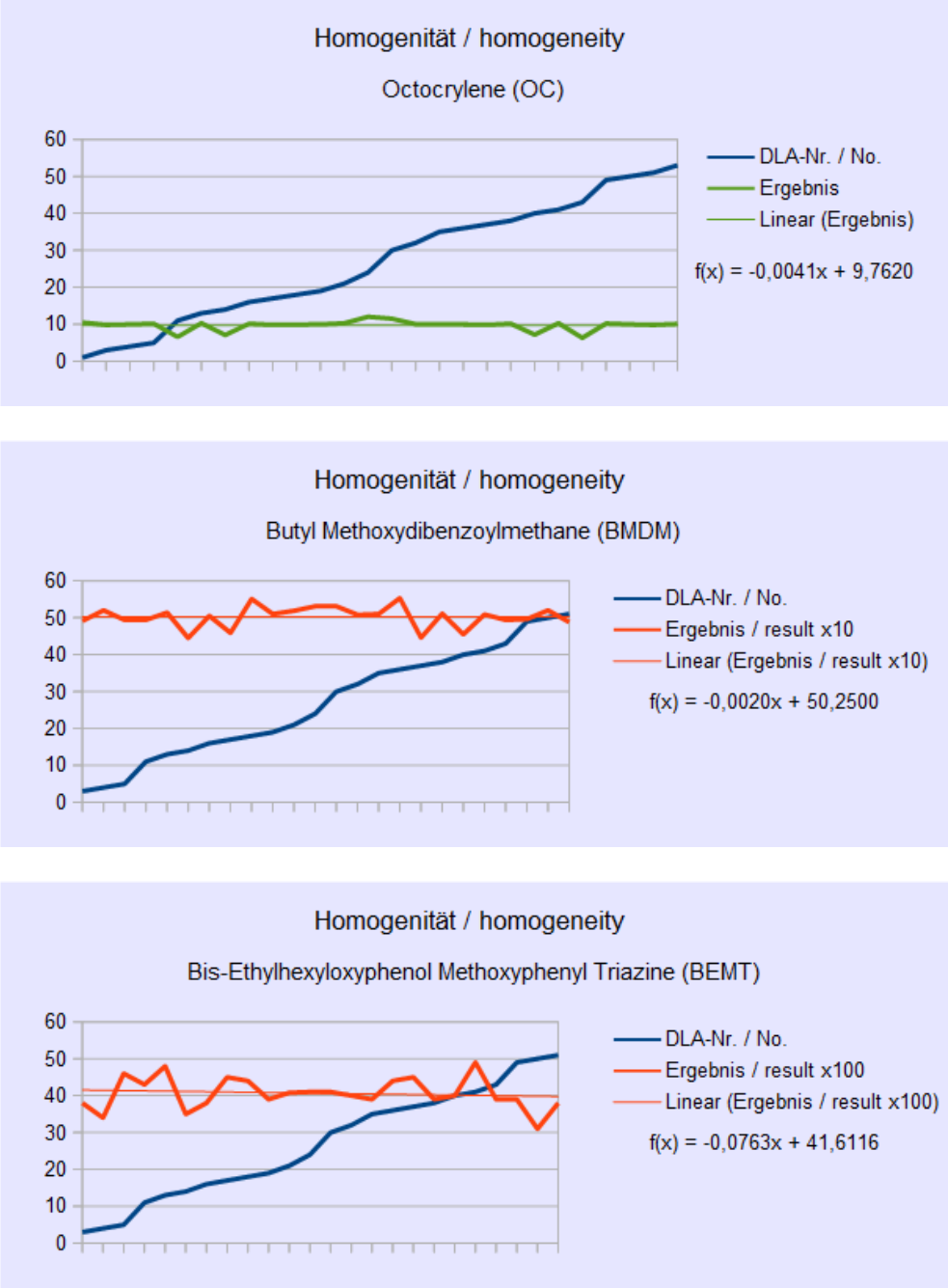


**Abb./Fig. 12:**
Trendlinie Probennummern vs. Ergebnisse
Trend line sample number vs. results

## 5.3 Information on the Proficiency Test (PT)

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

### Information on the Proficiency Test (PT)

| | |
|---|---|
| *PT number* | ***DLA 52-2018*** |
| *PT name* | ***Cosmetic Products II: UV-Filter in Sun Protection Product*** |
| *Sample matrix** | ***Sun Protection Milk (SPF 50), common in commerce ingredients*** |
| *Number of samples and sample amount* | *2 identical samples A + B, 25 g each.* |
| *Storage* | *Samples A + B: cooled 2 - 10°C (dark and dry)* |
| *Intentional use* | *Laboratory use only (quality control samples)* |
| *Parameter* | *quantitative:*<br>***Octocrylene, Butyl Methoxydibenzoylmethane, Bis-Ethylhexyl-oxyphenol Methoxyphenyl Triazine and Titanium Dioxide*** |
| *Methods of analysis* | *Analytical methods are optional* |
| *Notes to analysis* | *The analysis of PT samples should be performed like a routine laboratory analysis.*<br>*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:*<br>– *Date of analysis*<br>– *DLA-sample-numbers (for sample A and B)*<br>– *Limit of detection*<br>– *Assignment incl. Recovery*<br>– *Recovery with the same matrix*<br>– *Method is accredited* |
| *Result submission* | *The result submission file should be sent by e-mail to:*<br>***pt@dla-lvu.de*** |
| *Deadline* | ***the latest 20th April 2018*** |
| *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* | *Dr. Matthias Besler-Scharf* |

* Control of mixture homogeneity and qualitative testings are carried out by DLA. 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 |
|---|---|---|
| | | AUSTRIA |
| | | ITALY |
| | | Germany |
| | | Germany |
| | | FRANCE |
| | | Germany |
| | | Germany |
| | | Germany |
| | | 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
6. Evaluation of analytical methods used for regulation of food and drugs; W. Horwitz; Analytical Chemistry, 54, 67-76 (1982)
7. The International Harmonised Protocol for the Proficiency Testing of Anan-lytical Laboratories ; J.AOAC Int., 76(4), 926 – 940 (1993)
8. A Horwitz-like funktion describes precision in proficiency test; M. Thompson, P.J. Lowthian; Analyst, 120, 271-272 (1995)
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10. Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing; M. Thompson; Analyst, 125, 385-386 (2000)
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13. EURACHEM/CITAC Leitfaden, Ermittlung der Messunsicherheit bei analytischen Messungen (2003); Quantifying Uncertainty in Analytical Measurement (1999)
14. GMP+ Feed Certification scheme, Module: Feed Safety Assurance, chapter 5.7 Checking procedure for the process accuracy of compound feed with micro tracers in GMP+ BA2 Control of residues, Version: 1st of January 2015 GMP+ International B.V.
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 K 84.00-28 Untersuchung von kosmetischen Mitteln, Nachweis und quantitative Bestimmung von UV-Filtern in kosmetischen Mitteln, HPLC-Verfahren, (Feb 2014) / DIN EN 16344 Cosmetics - Analysis of cosmetic products - Screening for UV-filters in cosmetic products and quantitative determination of 10 UV-filters by HPLC (2013-11)