Proficiency Tests
DLA
food
cosmetics
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Evaluation Report
proficiency test

DLA 54/2018

Cosmetic Products IV:

Fluoride

in Toothpaste

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

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Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report (19 May 2019) 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-Scharf (Technischer Leiter / Technical Manager) *- gezeichnet / signed M. Besler-Scharf* Alexandra Scharf MSc. (QM-Beauftragter / Quality Manager) *- gezeichnet / signed A. Scharf* Datum / Date: 19 May 2019
Unteraufträge *Subcontractors*	Falls im Rahmen der Eignungsprüfung eine Prüfung der Gehalte, Homogenität und Stabilität von EP-Parametern durchgeführt wurde, hat DLA diese im Unterauftrag vergeben. 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 *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 mixture of two common in commerce tooth pastes with sodium fluoride and a common in commerce toothpaste for children without fluoride from European Suppliers. Furthermore potassium sorbate was added as a preservative agent. The materials were mixed and homogenized.
Afterwards the samples were portioned to approximately 25 g into 28 mL plastic containers (HD-PE), sealed in metallised PET film bags and chronologically numbered.

Table 1: Composition of DLA-Samples

PT-Samples Toothpaste

Herbal Toothpaste with Fluoride

Ingredients: Aqua, Sorbitol, Hydrated Silica, Propylene Glycol, Cellulose Gum, Sodium C14-C16 Olefin Sulfonate, Disodium Pyrophosphate, Tetrasodium Pyrophosphate, Aroma, **Sodium Fluoride**, Chamomilla Recutita Flower Extract, Salvia Officinalis Leaf Extract, Commiphora Myrrha Resin Extract, Mentha Peperita Leaf Oil, Allantoin, Menthol, Sodium Saccharin, Lauryl Glycoside, Cl 77891, Cl 47005, Cl 42090

Toothpaste with Fluoride

Ingredients: Aqua, Sorbitol, Hydrated Silica, Glycerin, Potassium Nitrate, Cocamidopropyl Betaine, Aroma, Zinc Citrate, Xanthan Gum, Titanium Dioxide, Sodium Fluoride, Sodium Hydroxide, Sodium Saccharin, Sucralose, Limonene, Cinnamal, Eugenol

Toothpaste for Children without Fluoride

Ingredients: Aqua, Hydrated Silica, Glycerin, Xylitol, Propylene Glycol, Xanthan Gum, Titanium Dioxide, Aroma, Sodium Lauroyl Sarcosinate, Disodium EDTA, Sodium Chloride

Further ingredients

Ingredients: Potassium Sorbate

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

Table 2: Calculated amount according to labelled values of fluoride.

Ingredient	Amount (ppm)
Fluoride	1380 mg/kg

The composition (list of ingredients) and the amount of fluoride calculated according to the labelled values are given in table 1 and table 2 respectively.

2.1.1 Homogeneity

The calculation of the **repeatability standard deviations S_r of the participants** was used as an indicator of homogeneity. For fluoride the repeatability standard deviation was 3,87%. Thus the repeatability standard deviations is comparable to the precision data of respective standardized methods (e.g. ASU L 47.03-1, ASU L 49.00-7, s. 3.6.2) (vgl. Tab. 3) [18-19]. The repeatability standard deviations of the participants' results are given in the documentation in the statistic data (see 4.1).

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

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

2.1.2 Stability

Experience has shown that unopened toothpastes 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 41st week of 2018. The testing method was optional. The tests should be finished at 23rd November 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 tooth paste with herb extracts and the parameter fluoride (from sodium fluoride) to be determined.
The methods of analysis are optional.

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.

Out of 12 participants, 10 participants submitted their results in time. Two participants have not submitted any results.

3. Evaluation

3.1 Consensus value from participants (assigned value)

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

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

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

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

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

3.2 Robust standard deviation

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

3.3 Repeatability standard deviation

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

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

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

3.4 Reproducibility standard deviation

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

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

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

3.5 Exclusion of results and outliers

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

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

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

3.6 Target standard deviation (for proficiency assessment)

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

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

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.

In the present PT for valuation of <u>fluoride</u> the target standard deviation according to the general model of Horwitz was applied (see 3.6.1).

The corresponding participant results can be found in the documentation section.

3.6.1 General model (Horwitz)

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

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

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

3.6.2 Value by precision experiment

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

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

The values given in Table 3 relative repeatability standard deviation (RSD_r) and relative reproducibility standard deviation (RSD_R) were determined in collaborative trials using the specified methods. The in the table indicated resulting target standard deviation σ_{pt} is additionally given in the evaluation for information.

The German official ASU §64 method for the determination of fluoride in toothpaste (ASU K 84.00-23) gives a maximum deviation of 8,0% [20]. Reproducibility standard deviation and repeatability standard deviation are not reported.

Table 3: Relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviations (RSD_R) from precision experiments and resulting target standard deviations σ_{pt} [18-19]

Parameter	**Matrix**	**Mean values**	**RSD_r**	**RSD_R**	**σ_{pt}**	**Method / Literature**
Fluoride	Tea *	119 mg/kg	2,10%	6,96%	6,80%[1]	ASU [18]
Fluoride	Infant food	2,57 mg/kg	4,28%	10,1%	9,64%	ASU [19]
	Enteral supplement	1,28 mg/kg	6,25%	16,4%	15,8%	ASU [19]

[1] *used in evaluation (s. chapter 4)*
** mean of values from 4 tea samples*

3.6.3 Value by perception

The target standard deviation for proficiency assessment can be set at a value that corresponds to the level of performance that the coordinator would wish laboratories to be able to achieve [3].

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

Table 4 shows selected characteristics of participants results of the present PT in comparison to the previous year.

Table 4: Characteristics of the present PT (on dark gray) in comparison to the previous PT 2016 (SD = standard deviation, CV = coefficient of variation)

Parameter	**Matrix**	**robust Mean**	**rob. SD (S*)**	**rel. SD (VK_{S*}) [%]**	**Quotient S^*/σ_{pt}**	**DLA Report**
Fluoride	Toothpas-te	1300 mg/kg	53,3 mg/kg	4,10%	0,75	DLA 66/2016
Fluoride	Toothpas-te	1340 mg/kg	77,3 mg/kg	5,77%	1,1	DLA 54/2018

3.7 z-Score

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

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

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

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

The valid z-Score for each parameter is indicated as z-Score (σ_{pt}). The value indicated as z-Score (Info) only obtains a informative character. The both z-Scores were calculated with the different target standard deviations in accordance with 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].

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

The calculation is performed by:

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

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

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

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

For warning and action signals see 3.7.1.

3.9 Reproducibility cofficient of variation (CV_R)

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

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

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

3.10 Quotient $S^*/\sigma pt$

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 σ_{pt} does not exceed the value of 2.
A value > 2 means an insufficient precision, i.e. the analytical method is too variable, or the variation between the test participants is higher than estimated. Thus the comparability of the results is not given [3].

3.11 Standard uncertainty of the assigned value

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

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

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

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

4. Results

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

In the first table the characteristics are listed:

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

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

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

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

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

4.1 Fluoride in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	10
Number of outliers	-
Mean	1330
Median	1350
Robust Mean (X)	**1340**
Robust standard deviation (S*)	**77,3**
Number with 2 replicates	10
Repeatability SD (S_r)	51,4
Repeatability (CV_r)	3,87%
Reproducibility SD (S_R)	103
Reproducibility (CV_R)	7,77%
Target range:	
Target standard deviation σ_{pt}	**72,5**
Target standard deviation (for Information)	91,0
lower limit of target range	**1190**
upper limit of target range	**1480**
Quotient S/σ_{pt}*	*1,1*
Standard uncertainty $U_{(Xpt)}$	*30,5*
Results in the target range	*9*
Percent in the target range	*90%*

Comments to the statistic data:

The target standard deviation was calculated according to the general model of Horwitz. In addition, the target standard deviation was calculated for information according to 3.6.2 Evaluation of an experiment on precision (ASU §64 L 47.03-1).

The evaluation showed a normal to low variability of results. The quotient S*/σ_{pt} was below 2,0. The robust standard deviation as well as the repeatability and reproducibility standard deviations were in the range of previous PTs (see 3.6.3). The comparability of results is given.

The repeatability and reproducibility standard deviations were in the range of established values for the applied methods (see 3.6.2)

90% of the results were in the target range.

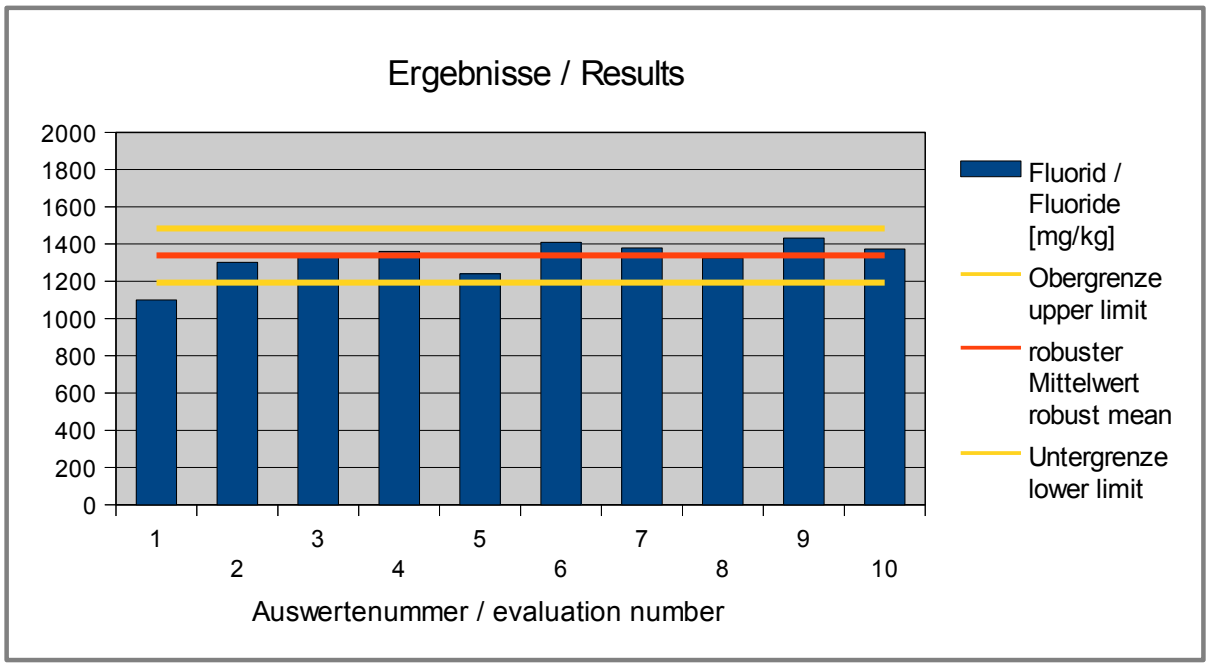

Abb. / Fig. 1: Ergebnisse Fluorid / Results fluoride

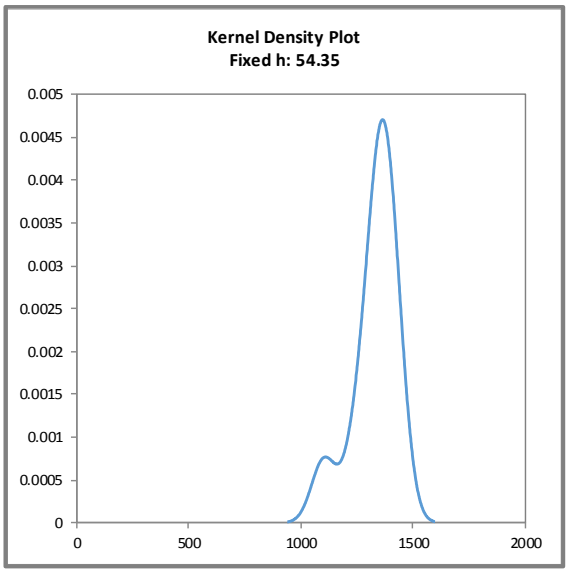

Abb. 2 Kerndichte-Schätzung der Ergebnisse für Fluorid
(mit h = 0,75 x σ_{pt} von X_{pt})

Fig. 2: Kernel density plot of fluoride results
(with h = 0,75 x σ_{pt} von X_{pt})

Comments:
The kernel density estimation shows a symmetrical distribution of results with a shoulder, which is due to an individual result outside the target range.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Fluorid / Fluoride [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	1100	-239	-3,3	-2,6	
2	1302	-36,6	-0,51	-0,40	
3	1342	3,35	0,046	0,037	
4	1360	21,4	0,29	0,23	
5	1240	-98,6	-1,4	-1,1	
6	1409	70,6	1,0	0,78	
7	1380	40,9	0,56	0,45	
8	1325	-13,6	-0,19	-0,15	
9	1432	93,4	1,3	1,0	
10	1374	35,4	0,49	0,39	

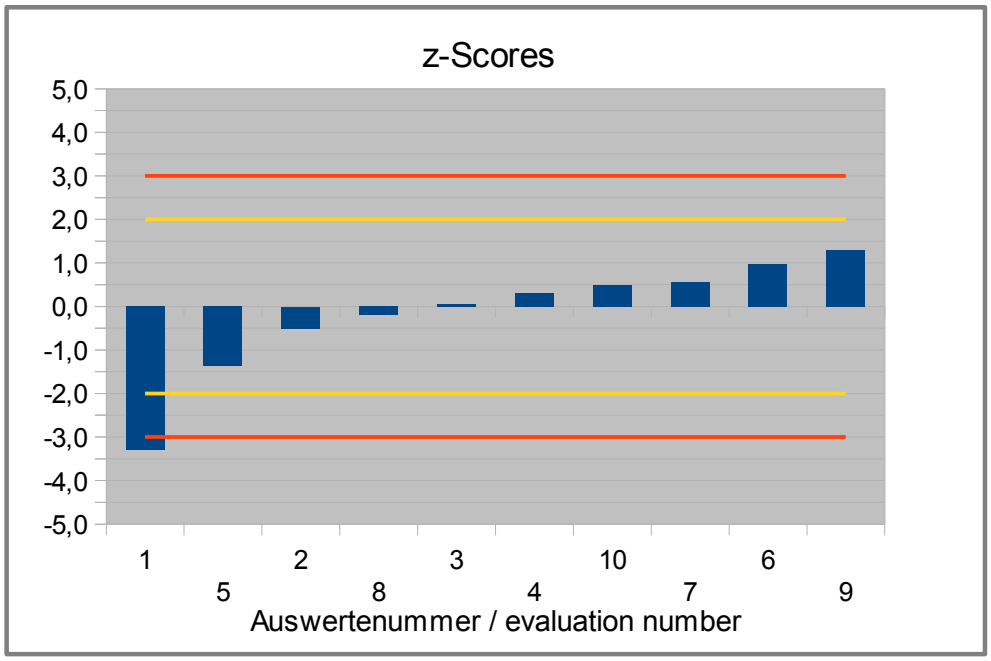

Abb. / Fig. 3: z-Scores Fluorid / fluoride

5. Documentation

5.1 Details by the participants

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

5.1.1 Primary Data

Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of ana-lysis	Result (Mean)	Result Sample I	Result Sample II	Limit of quantifica-tion	Incl. RR	Recovery rate
				day/month					yes/no	in %
1	mg/kg	1	59	23.11	1100	1000	1200	0,021	no	
2	mg/kg	22	38	20.11.	1302	1304	1299	< 0,02	yes	
3	mg/kg	13	47	31.10	1342	1330	1354	10	no	
4	mg/kg	16	44	13.11	1360	1340	1380	100	no	100
5	mg/kg	11	49	19.11	1240	1290	1190	-	-	-
6	mg/kg	5	55	16.11	1409,2	1410	1408,4	5		
7	mg/kg	14	46	06.11	1379,5	1389	1370	100	no	100
8	mg/kg	17	43	07.11	1325	1320	1330	20	no	
9	mg/kg	3	57	15.10.	1432	1434	1430	130	yes	96,5
10	mg/kg	56	4	24.10	1374	1380	1368	10	no	

5.1.2 Analytical Methods

Partici-pant	Method specification, as in test report / standard / literature	Remarks about sample preparation	Method description	Calibration and re-ference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
					yes / no	yes / no	
1	K84.06.01 -2(EG)		GC/MS with different conditions	yes		no	
2	§ 64 LFGB K 81.06.01-2		GC-FID	sodium fluoride	yes	yes	
3	ISE after distillation	sulfuric acid steam distillation	Ion-selective electrode	NaF		yes	
4	ASU 84.06.01/ 1984-05	Derivatization with triethylchlorosilane, extraction with xylene, cyclohexane as ISTD	Headspace-GC-FID	external calibration with ISTD	yes	yes	
5	in house method (SM-SZTL-003:2018)	-	-	-	no	no	-
6	HPIC-CD Internal method				no	yes	
7	official method (DM 22/12/86 II PAR 19) in GC-FID	selective derivatization in acidic conditions and extraction with an appropriate solvent.		NaF reference material - external standard		no	
8		mixed with TISAB IV	fluoride-sensitive electrode	external standard/ commercial mouthwash		yes / no	
9		homogenize, dissolve aliquot	fluoride-sensitive electrode		no	yes	
10	Ion-sensitive electrode	-	-	Fluoride-standard			

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:

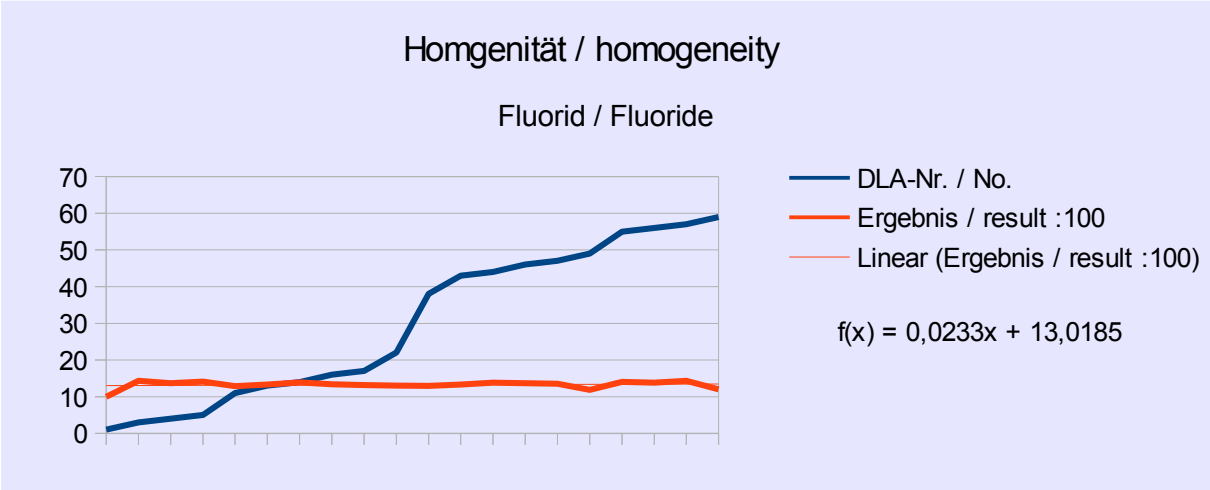

Abb./Fig. 4:
Trendfunktion Probennummern vs. Ergebnisse (1/100 dargestellt)
trend line function sample number vs. results (1/100 shown)

5.3 Information on the Proficiency Test (PT)

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

PT number	***DLA 54-2018***
PT name	***Cosmetic Products IV: Fluoride in Toothpaste***
*Sample matrix**	*Samples I + II:* ***Toothpaste / common in commerce ingredients***
Number of samples and sample amount	*2 identical samples I + II, 25 g each.*
Storage	*Samples I + II: cooled 2 - 10°C*
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative:* ***Fluoride***
Methods of analysis	*Analytical methods are optional*
Notes to analysis	*The analysis of PT samples should be performed like a routine laboratory analysis.* *In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights.*
Result sheet	*The results for sample I and II as well as the final results calculated as mean of the double determination (samples I and II) should be filled in the result submission file. The recovery rates, if carried out, has to be included in the calculation.*
Units	*mg/kg*
Number of significant digits	*at least 2*
Further information	*For information please specify:* – *Date of analysis* – *DLA-sample-numbers (for sample I and II)* – *Limit of detection* – *Assignment incl. Recovery* – *Recovery with the same matrix* – *Method is accredited*
Result submission	*The result submission file should be sent by e-mail to:* ***pt@dla-lvu.de***
Deadline	***the latest 23rd November 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	*Matthias Besler-Scharf, PhD*

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

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		AUSTRIA
		HUNGARY
		ITALY
		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 inter-laboratory comparisons
4. ASU §64 LFGB: Planung und statistische Auswertung von Ringversuchen zur Methoden-validierung / DIN ISO 5725 series part 1, 2 and 6 Accuracy (trueness and preci-sion) 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. Hor-witz; Analytical Chemistry, 54, 67-76 (1982)
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14. GMP+ Feed Certification scheme, Module: Feed Safety Assurance, chapter 5.7 Check-ing 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 Re-quirements, Appendix F, p. 2, AOAC Int (2016)
18. ASU §64 LFGB L 47.03-1 (1997) Untersuchung von Tee; Bestimmung des Fluoridgehal-tes; Potentiometrisches Verfahren (nach DIN 10807) [Determination of fluoride in tea, potentiometrically]
19. ASU §64 LFGB L 49.00-7 (2000) Bestimmung von Fluorid in diätetischen Lebensmitteln mit der ionensensitiven Elektrode [Determination of fluoride in dietetic food by ion selective electrode]
20. ASU § 64 LFGB K 84.06.01-2 (1984) Quantitative Bestimmung des Gesamtfluorids in Zahnpasten [Determination of total fluoride in toothpastes]