

Evaluation Report

proficiency test

DLA 66/2016

Cosmetic Products VI:

Fluoride in Toothpaste

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1. Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the verification and/or validation of the particular testing method [1, 5].

The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.

Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009 / ISO 13528:2015 [2, 3].

2. Realisation

2.1 Test material

The test material is a mixture of 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 for testing the homogeneity of the mixture. The materials were mixed and homogenized. Afterwards the samples were portioned to approximately 25 g into 20 mL plastic bottles (HD-PE) with screw cap and chronologically numbered.

Table 1: Composition of DLA-Samples

PT-Sample Toothpaste

Herbal Toothpaste with Fluoride

<u>Ingredients</u>: Aqua, Hydrated Silica, Sorbitol, Propylene Glycol, Xanthan Gum, Sodium C14-C16, Olefin Sulfonate, Aroma, Tetrapotassium Pyrophosphate, **Sodium Fluoride**, Sodium Saccharin, Mentha Arvensis Leaf Oil, Allantoin, Salvia Officinalis Leaf Extract, Chamomilla Recutita Flower Extract, Commiphora Myrrha Resin Extract, Zinc Chloride, Alcohol, Cl 74160, Cl 77492, Cl 77891

Toothpaste with Fluoride

<u>Ingredients</u>: Aqua, Hydrated Silica, Sorbitol, Glycerin, Sodium Lauryl Sulfate, Xanthan Gum, Aroma, Titanium Dioxide, PEG-6, **Sodium Fluoride**, Sodium Saccharin, Carrageenan, Limonene, CI 73360, CI 74160

Toothpaste for Children without Fluoride

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

additional ingredient:
Potassiume Sorbate

Table 2: Calculated amount according to labelled values of fluoride

Ingredient	Amount (ppm)
Fluoride	1290 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 homogeneity of bottled numbered DLA-samples was checked by 5-fold determination of sorbic acid by HPLC-UV. The repeatability standard deviation of 9,3 % is in the range of the allowed maximum deviation of 10% according to the german official method ASU $\S64$ K 84.00-23. Reproducibility standard deviation and repeatability standard deviation are not reported there [16]. The results of the homogeneity test are given in the documentation.

The calculation of the **repeatability standard deviation** S_r of the participants was also used as an indicator of homogeneity. It is 1,3% for fluoride. Therefore the repeatability standard deviation is similar to precision data of standardized methods for determination of fluoride (e.g. in food ASU L 47.03-1, ASU L 49.00-7, s. 3.6.2) (see Tab. 3) [18-19]. In toothpaste the allowed maximum deviation according to the german official method ASU §64 (K 84.00-23) is 8,0% [17]. The repeatability standard deviation of the participants' results is given in the table of statistic data (see 4.1).

Furthermore, the homogeneity was characterized by the **trend line function** of participants' results for chronological bottled single samples. The maximum deviation from the mean value of the trend line for fluoride was < 30% of the target standard deviation σ_{pt} (s. 5.2 homogeneity) and can therefore be regarded as low.

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].

2.2 Sample shipment and information to the test

Two portions of test material were sent to every participating laboratory in the $28^{\rm th}$ week of 2016. The testing method was optional. The tests should be finished at $9^{\rm th}$ September 2016 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 toothpaste with herbal flavor with sodium fluoride. Any suitable method can be used for the determination of the fluoride content.

The material is tested for homogeneity.

In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights.

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 participants submitted the result 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].

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_{Dti}) are made whenever possible.

The statistical evaluation is carried out for all the parameters for 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 Sr 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 Sr, also known as standard deviation within laboratories Sw, is performed by: [3, 4].

The relative repeatability standard deviation as a percentage of the mean value is indicated as coefficient of variation $CV_{\rm r}$ 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 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.

In the present PT for valuation of $\underline{fluoride}$ the target standard deviation according to the general model of Horwitz was applied (see 3.6.1).

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
$\sigma_R = 0,02c^{0,8495}$	$1,2 \times 10^{-7} \le c \le 0,138$	≥ 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. $1 \text{ mg/kg} = 1 \text{ ppm} = 10^{-6} \text{ kg/kg}$)

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 $\sigma_{P}t$ 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% \$17]. Reproducibility standard deviation and repeatability standard deviation are not reported.

<u>Table 3:</u> 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)

 $^{^{\}star}$ 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 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 (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

$$-2 \le z \le 2$$
.

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 \geq 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 ($\hat{\sigma}$) 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 $\sigma_{\text{\tiny D}}$ '.

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

$$-2 \le z' \le 2$$
.

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]:

$$CV_R = \underline{S_R} * \underline{100}$$

In contrast to the standard deviation as a measure of the absolute variability the $CV_{\mbox{\tiny K}}$ gives the relative variability within a data region. While a low $CV_{\mbox{\tiny R}}$, e.g. < 5-10% can be taken as evidence for a homogeneous set of results, a $CV_{\mbox{\tiny R}}$ 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 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 σ_{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 $v(x_{pt})/\sigma_{pt}$ 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^{x})
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 $(X_{pt} + 2\sigma_{pt})$ *
$\label{eq:Variation} \mbox{Variation coefficient $V_{\mbox{\tiny K}}$ 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:

Auswerte-	D	Abweichung	0		Hinweis
nummer	Parameter		z-Score	z-Score	
Evaluation	[Einheit / Unit]	Deviation	σpt	(Info)	Remark
number					

4.1 Fluoride in mg/kg

<u>Vergleichsuntersuchung</u> / <u>Proficiency Test</u>

Statistic Data	
Number of results	10
Number of outliers	0
Mean	1310
Median	1290
Robust Mean (X)	1300
Robust standard deviation (S*)	53,3
Number with 2 replicates	9
Repeatability SD (S _r)	16,8
Repeatability (CV_r)	1,28%
Reproducibility SD (S _R)	57,5
Reproducibility (CV _R)	4,37%
Target range:	
Target standard deviation σ_{Pt}	70,7
Target standard deviation (for Information)	88,4
lower limit of target range	1160
upper limit of target range	1442
Quotient S*/opt	0,75
Standard uncertainty U(Xpt)	21,1
Quotient $U(x_{pt})/\sigma_{pt}$	0,30
Results in the target range	10
Percent in the target range	100%

<u>Comments to the statistic data:</u>

The target standard deviation was calculated according to the general model of Horwitz.

The evaluation showed a low variability of results. The quotient S^{\star}/σ_{pt} was below 1,0. The robust standard deviation as well as 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.

The quotient $U(Xpt)/\sigma pt$ of 0,3 was low.

All results were in the target range.

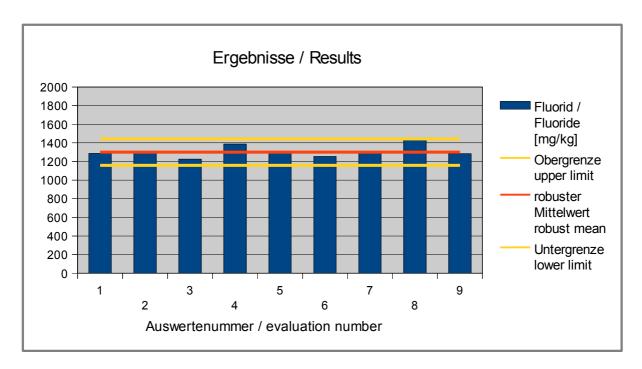
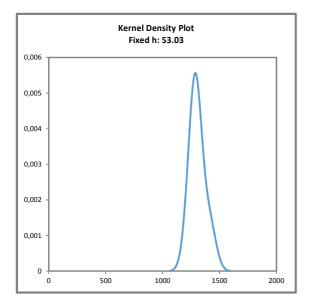


Abb. 1: Ergebnisse Fluorid
Fig. 1: Results fluoride



<u>Abb. 2:</u> Kerndichte-Schätzung der Ergebnisse für Fluorid (mit $h = 0.75 \times \sigma_{pt} \text{ von } X_{pt}$)

Fig. 2: Kernel density plot of
fluoride results
(with h = 0,75 x opt von Xpt)

Comments:

The kernel density estimation shows a normal distribution of results (s. fig. 2).

Ergebnisse der Teilnehmer: Results of Participants:

Auswerte- nummer	Fluorid / Fluoride	Abweichung [mg/kg]	z-Score	z-Score	Hinweis
Evaluation number	[mg/kg]	Deviation [mg/kg]	(o pt)	(Info)	Remark
1	1288	-12	-0,2	-0,1	
2	1292	-8	-0,1	-0,1	
3	1226 *	-74	-1,0	-0,8	
4	1387	87	1,2	1,0	
5	1310	10	0,1	0,1	
6	1254	-46	-0,6	-0,5	
7	1304	4	0,1	0,0	
8	1430	130	1,8	1,5	
9	1284	-16	-0,2	-0,2	
10	1290	-10	-0,1	-0,1	

 $^{^{\}star}$ mean calculated by DLA

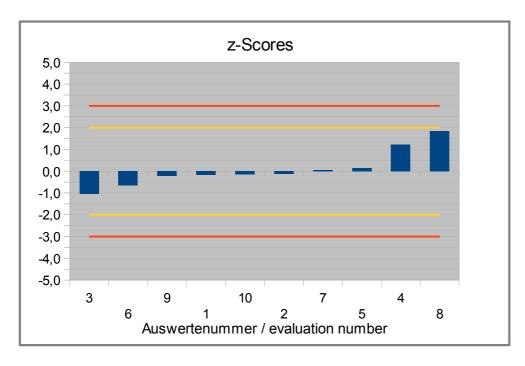


Abb. 3: Z-Scores Fluorid Fig. 3: Z-Scores fluoride

5. Documentation

5.1 Primary data

Parameter	Teilnehmer	Einheit	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestim- mungsgren- ze	Inkl. WF	Wiederfin- dungsrate [%]
Analyte	Participant	Unit	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of de- termination	Incl. RR	Recovery rate [%]
	1	mg/kg	45	28	29.08.16	1288	1279	1298		no	n.b.
	2	mg/kg	18	42	01.09.16	1292	1304	1280	10	no	-
	3	mg/kg	7	34		1224,49 / 1228,43	1212,95 / 1236,03	1232,56 / 1224,3	0,3	102,25 / 99,66 / 101,62 / 99,53	yes
Fluorid /	4	mg/kg	9	25	29.08.2016	1387,28	1385,66	1388,36	70	no	98
Fluoride	5	mg/kg	20	50	30.08.16	1310	1314	1306	100	100	no
	6	mg/kg	22	48	24.08.16	1254,33	1238,71	1269,94	33	no	107,2
	7	mg/kg	4	31	29.08.16	1304	1302	1306	<0,005 g/100g	no	
	8	mg/kg	13	36	02.08.16	1430	1457	1403	100	no	-
	9	mg/kg	40	11	10.08.16	1284	1280	1288			no
	10	mg/kg	15	37	20.07.16	1290	1290	1280	120	no	100

5.2 Homogeneity

5.2.1 Homogeneity of bottled PT-samples

Homogeneity test of sorbic acid by HPLC-UV:

Independant samples	mg/kg
1	466
2	398
3	447
4	458
5	516

Mean 457

Repeatability Standard Deviation 42,3 9,25%

5.2.2 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 item can be characterized with the help of the trend line function:

Fluoride				
Target standard deviation σ_{pt}	70,7			mg/kg
Sample numbers	4 - 50			
Total numbers of samples	20			
Slope	-1,89			
Trend line range	1288	_	1326	mg/kg
Deviation trend line	1307	±	19,0	mg/kg
Percent of opt	26,9	엉		

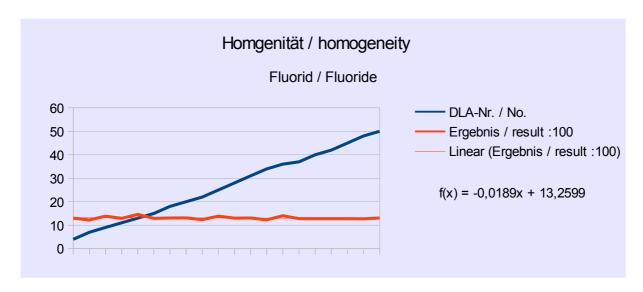


Abb. 4: Trendfunktion Probennummern / Fluorid Ergebnisse (1/100 dargestellt)

Fig. 4: trend line function sample number / fluoride results (1/100 shown)

5.3 Analytical Methods

Details by the participants

Parameter	Teilneh- mer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Wiederfindung mit gleicher Ma- trix	Methode ak- kreditiert	Sonstige Hinweise
Analyte	Participant	Method description	Sample preparation	Measuring method	Recovery with same matrix	Method ac- credited	Further remarks
	1		Direct determination wi- thout addition of Hcl	Titration		No	
	2	lonen Selective Elektrode	sulfuric acid acidified water vapor destillation	ISE	No	Yes	
	3	A portion of standard & sample were treated with 2M HCI to decrease the pH. Then incubate for 1hr at 45°C to free ionic bonds. 1M NaOH and TI-SAB II were added to adjust the pH and ionic strength. The potential of the supernatant was measured by ISE.	1 g of sample was dissolved with deionized water in a 100-mL volumetric flask	lon Selective Electrode (ISE)	Yes / No / Yes / No	Yes	
Fluorid / Fluoride	4	Potentiometry	water extraction	Potentiomety by Ion Selective Elektrode	Yes	Yes	
	5	official method (DM 22/12/86 II PAR 19) in GC-FID	selective derivatization in acidic conditions and extraction with an appropriate solvent.	official method (DM 22/12/86 II PAR 19) in GC-FID		No	
	6	ASU § 35 LMBG K 84.06.01 2(EG)	Samples homogenized with spatula	GC-FID	Yes	Yes	area accreditation
	7	§ 64 LFGB K 84.06.01-2		GC-FID		Yes	
	8	photometrically	Microdiffusion by perchloric acid	photometrically	-	Yes	
	9	HPIC Internal Method	Dilution in water	Conductometry	No	No	
	10	in-house method GC-FID	Homogenization, Silylation	GC-FID	Yes	Yes	

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		ITALY
		Germany
		FRANCE
		Germany
		PHILIPPINES
		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 Ananlytical 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)
 9. Protocol for the design, conduct and interpretation of method performance
- studies; W. Horwitz; Pure & Applied Chemistry, 67, 331-343 (1995)
- 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)
- 11. The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories; Pure Appl Chem, 78, 145 - 196 (2006)
- 12.AMC Kernel Density Representing data distributions with kernel density estimates, amc technical brief, Editor M Thompson, Analytical Methods Committee, AMCTB No 4, Revised March 2006 and Excel Add-in Kernel.xla 1.0e by Royal Society of Chemistry
- 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.ASU § 64 LFGB K 84.00-23 (1995) Nachweis und Bestimmung von Benzoesäure, 4-Hydroxybenzoesäure, Sorbinsäure, Salicylsäure und Propionsäure in kosmetischen Mitteln [Determination of benzoic acid, 4-hydroxy benzoic acid, sorbic acid, salicylic acid and propionic acid in cosmetic products]
- 17.ASU § 64 LFGB K 84.06.01-2 (1984) Quantitative Bestimmung des Gesamtfluorids in Zahnpasten [Determination of total fluoride in toothpastes]
- 18.ASU §64 LFGB L 47.03-1 (1997) Untersuchung von Tee; Bestimmung des Fluoridgehaltes; 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]