Evaluation Report
proficiency test

DLA 31/2019

Iodine and Fluorine:

in Salt

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

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EP-Koordinator *PT-Coordinator*	Dr. Matthias Besler-Scharf
Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report (18. November 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-Beauftragte / Quality Manager) *- gezeichnet / signed A. Scharf* Datum / Date: 18. November 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 / Contents

1. Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the verification and/or validation of the particular testing method [1, 5].
The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.
Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009 / ISO 13528:2015 [2, 3].

2. Realisation

2.1 Test material

The test material is a common in commerce iodized table salt with fluorine from a European supplier.
The contents of the packaging units were mixed and homogenized.

Afterwards the samples were portioned to approximately 200 g into metallised PET film bags and chronologically numbered.

The composition (list of ingredients) of the samples and the contents of iodine and fluorine is given in table 1 and 2.

Table 1: Composition of DLA-Samples

Iodized table salt
Ingredients: Boiling salt, potassium fluoride, potassium iodate, separating agent: sodium ferrocyanide.

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 amounts of parameters according to the manufacturers specification

Parameter	**Content per kg**
Iodine	20 mg
Fluorine	310 mg

2.1.1 Homogeneity

The calculation of the **repeatability standard deviations S_r of the participants** was used as an indicator of homogeneity. It is 2.8% for iodine and 8.6% for fluorine. Thus they were similar to corresponding repeatability standard deviations of precision data of the standardized methods (e.g. ASU-Method 00.00-93 and 47.03-1, s. 3.6.2) (see Table 2) [18-19]. The repeatability standard deviations of the participants' results are given in the documentation in the statistic data (see 4.1 to 4.2).

Furthermore, the homogeneity was graphically characterized for information by the **trend line function of participants' results for chronological bottled single samples** (s. 5.2.2 Homogeneity).

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

The experience with various DLA reference materials showed good storage stability with respect to the durability of the sample (spoilage) and the content of iodine and fluorine for samples with a comparable water activity (a_w value <0.5) and matrix. The sample material is therefore stable against microbial spoilage at room temperature and dry light-protected storage.

2.2 Sample shipment and information to the test

Two portions of test material were sent to every participating laboratory in the 30th week of 2019. The testing method was optional. The tests should be finished at 30th August 2019 the latest.

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

The two portions contain identical samples of iodized salt with fluorine. The analytical method for the determination of the parameters iodine and fluorine is 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.

All 13 participants submitted their results in time.

3. Evaluation

3.1 Consensus value from participants (assigned value)

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

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

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

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

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

3.2 Robust standard deviation

For comparison to the target standard deviation σ_{pt} (standard deviation for proficiency assessment) a robust standard deviation (S*) 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 the parameter fluorine the target standard deviation according to the general model of Horwitz was applied (see 3.6.1).

The target standard deviation of the evaluation by a precision experiment (s. 3.6.2) was used for the parameter iodine (ASU §64 methods L 00.00-93) [18].

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

3.6.1 General model (Horwitz)

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

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

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

3.6.2 Value by precision experiment

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

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

The relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviation (RSD_R) given in Table 2 were determined in ring tests using the indicated methods.
The resulting target standard deviations σ_{pt}, which were identified there, were used to evaluate the results and to provide additional information for the statistical data.

Table 2: Relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviations (RSD_R) according to selected evaluations of tests for precision and the resulting target standard deviation σ_{pt} [18-19]

Parameter	**Matrix**	**Mean (mg/kg)**	**RSD_r (%)**	**RSD_R (%)**	**σ_{pt} (%)**	**Method / Literature**
Iodine	Cod meat	4,15	0,7	8,9	39,5	ICP-MS/ [18] ASU 00.00-93
Iodine	Iodized salz	19,8	6,4	15	13,3[1]	ICP-MS/ [18] ASU 00.00-93
Iodine	Seaweed	40,1	0,9	6,2	2,84	ICP-MS/ [18] ASU 00.00-93
Fluorine	Tea	150	1,76	4,69	6,02	Potentiometrisch/[19] ASU 47.03-1
Fluorine	Tea	113	1,65	9,15	16,1	Potentiometrisch/[19] ASU 47.03-1
Fluorine	Tea	152	1,98	6,14	7,80[1]	Potentiometrisch/[19] ASU 47.03-1

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

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 or 3.6.2 was regarded suitable.

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

Tabelle 3: Characteristics of the present PT (on grey) in comparison to the previous PT from 2017 (SD = standard deviation, CV = coefficient of variation)

Parameter	**Matrix (Powder)**	**robust Mean**	**rob. SD (S*)**	**rel. SD (CV_{S*}) [%]**	**Quotient S*/σpt**	**DLA-report**
Iodine	Table salt	18,5	2,60	14,1	1,0	DLA 31/2017
Iodine	Table salt	23,2	2,72	11,7	0,82	DLA 31/2019
Fluorine	Table salt	200	41,9	21,0	1,8*	DLA 31/2017
Fluorine	Table salt	314	65,9	21,0	2,0*	DLA 31/2019

** with target standard deviation σpt'*

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.

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

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

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_i) 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 ($U_{(xpt)}$) [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_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 gives the relative variability within a data region. While a low CV, e.g. <5-10% can be taken as evidence for a homogeneous set of results, a CV of more than 50% indicates a "strong inhomogeneity of statistical mass", so that the suitability for certain applications such as the assessment of exceeded maximum levels or the performance evaluation of the participating laboratories possibly can not be done [3].

3.10 Quotient S*/σ_{pt}

Following the HorRat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation S* and target standard deviation σ_{pt} does not exceed the value of 2.
A value > 2 means an insufficient precision, i.e. the analytical method is too variable, or the variation between the test participants is higher than estimated. Thus the comparability of the results is not given [3].

3.11 Standard uncertainty of the assigned value

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

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

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

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

4. Results

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

In the first table the characteristics are listed:

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

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

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

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

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

4.1 Iodine in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	11
Number of outliers	-
Mean	23,8
Median	22,7
Robust Mean (X_{pt})	**23,2**
Robust standard deviation (S*)	**2,72**
Number with 2 replicates	10
Repeatability SD (S_r)	0,643
Repeatability (CV_r)	2,80%
Reproducibility SD (S_R)	2,77
Reproducibility (CV_R)	12,0%
Target range:	
Target standard deviation σ_{pt}	**3,32**
Target standard deviation (for Information)	2,31
lower limit of target range	**16,6**
upper limit of target range	**29,8**
Quotient S/σ_{pt}*	*0,82*
Standard uncertainty $U_{(Xpt)}$	*1,02*
Results in the target range	*10*
Percent in the target range	*91%*

Comments:

The target standard deviation was calculated using data from a precision experiment (ASU §64 L 00.00-93)(3.6.2). Additionally the target standard deviation according to the model of Horwitz (s. 3.6.1) is given for information.

The distribution of results showed a low variability. The quotient S/σ_{pt} was below 1,0. The robust standard deviation was in the range of previous PTs (see 3.6.3). The comparability of results is given.*

The repeatability and reproducibility standard deviation were in the range of of established values for the used determination methods (s. 3.6.2).

91% of results were in the target range.

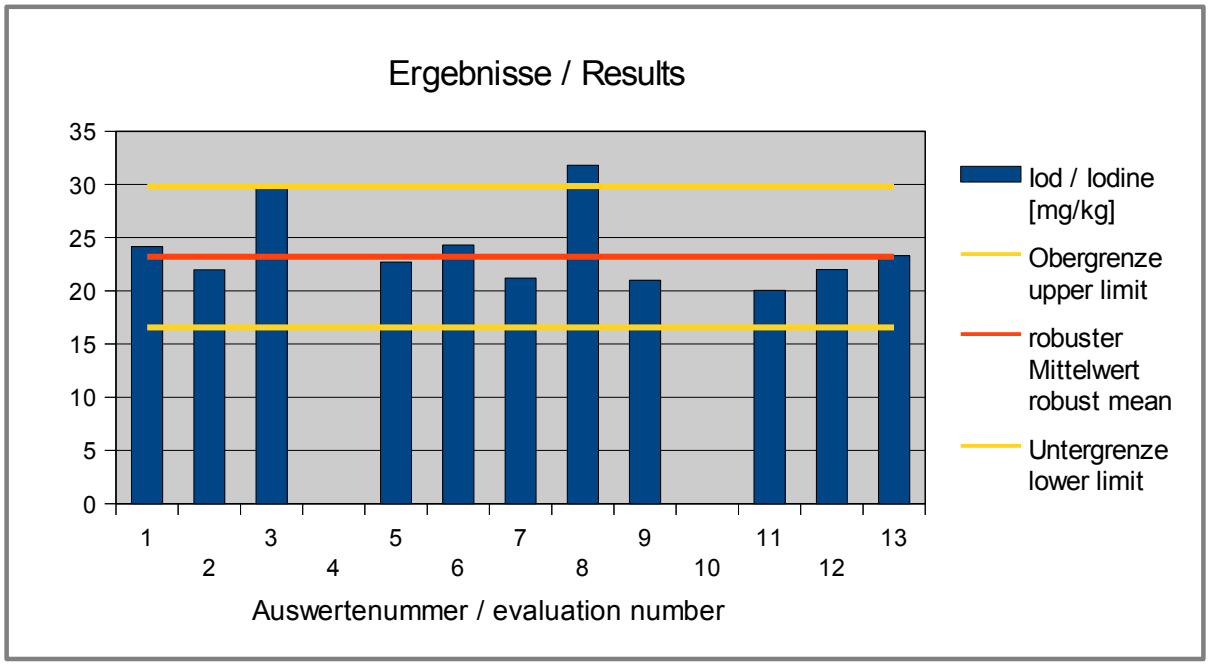

Abb. / Fig. 1: Ergebnisse Iod / Results iodine

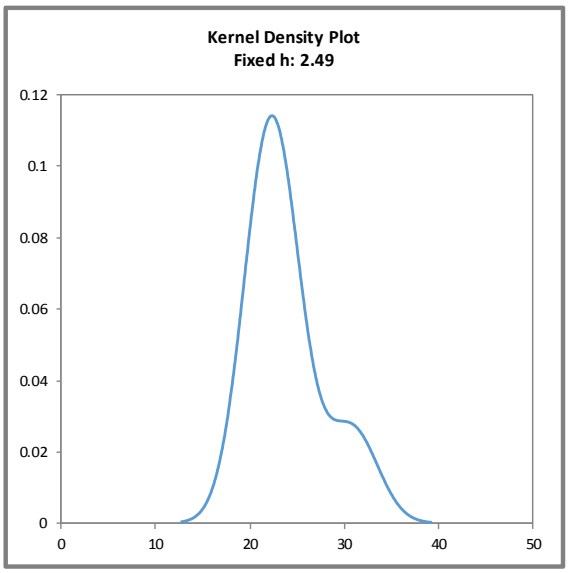

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x σ_{pt} von X_{pt})

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

Comment:
The kernel density shows a symmetrical distribution of results with a slight side peak at approx. 31 mg/kg, due to two result outside or at the upper target range.

Ergebnisse der teilnehmenden Institute:
Results of Participants:

Auswerte-nummer Evaluation number	Iod / Iodine [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	24,2 *	0,97	0,29	0,42	
2	22,0	-1,23	-0,37	-0,53	
3	29,7	6,47	1,9	2,8	
4					
5	22,7	-0,50	-0,15	-0,22	
6	24,3	1,10	0,33	0,47	
7	21,2	-2,01	-0,61	-0,87	
8	31,8	8,60	2,6	3,7	
9	21,0	-2,20	-0,66	-0,95	
10					
11	20,1 *	-3,15	-0,95	-1,4	
12	22,0	-1,20	-0,36	-0,52	
13	23,3	0,10	0,03	0,04	

* Mean calculated by DLA

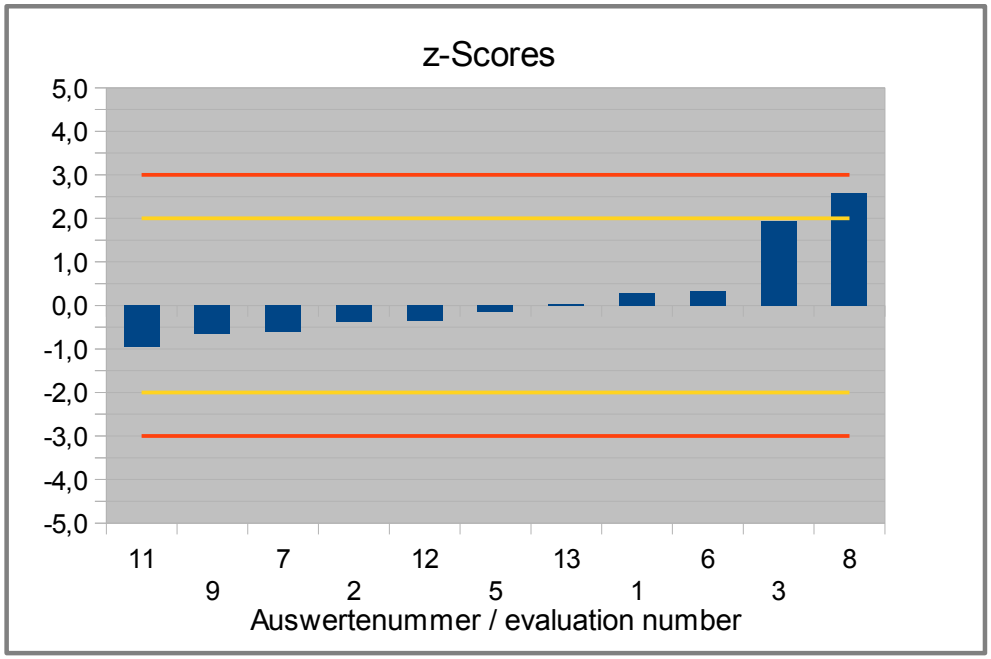

Abb. / Fig. 3: z-Scores Iod / Iodine

4.2 Fluorine in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	11
Number of outliers	-
Mean	314
Median	317
Robust Mean (X_{pt})	**314**
Robust standard deviation (S*)	**65,9**
Number with 2 replicates	11
Repeatability SD (S_r)	27,0
Repeatability (CV_r)	8,62%
Reproducibility SD (S_R)	61,1
Reproducibility (CV_R)	19,5%
Target range:	
Target standard deviation σ_{pt}'	**32,6**
Target standard deviation (for Information)	18,8
lower limit of target range	**249**
upper limit of target range	**379**
Quotient S^*/σ_{pt}'	*2,0*
Standard uncertainty $U_{(Xpt)}$	*24,8*
Results in the target range	*7*
Percent in the target range	*64%*

Comments:

The target standard deviation was calculated according to the model of Horwitz (s. 3.6.1). Additionally the target standard deviation using data from precision experiments (ASU §64 L 47.03-1) is given for information.

The distribution of results showed an increased variability. The quotient S^*/σ_{pt} was at 3,1. Therefore the valuation was done by z'-scores considering the standard uncertainty. The quotient S^*/σ_{pt}' was then below 2,0. The robust standard deviation was in the range of previous PTs (see 3.6.3). The comparability of results is given.

The repeatability and reproducibility standard deviation were in the range of of established values for the used determination methods (for other matrices) (s. 3.6.2).

64% of results were in the target range.

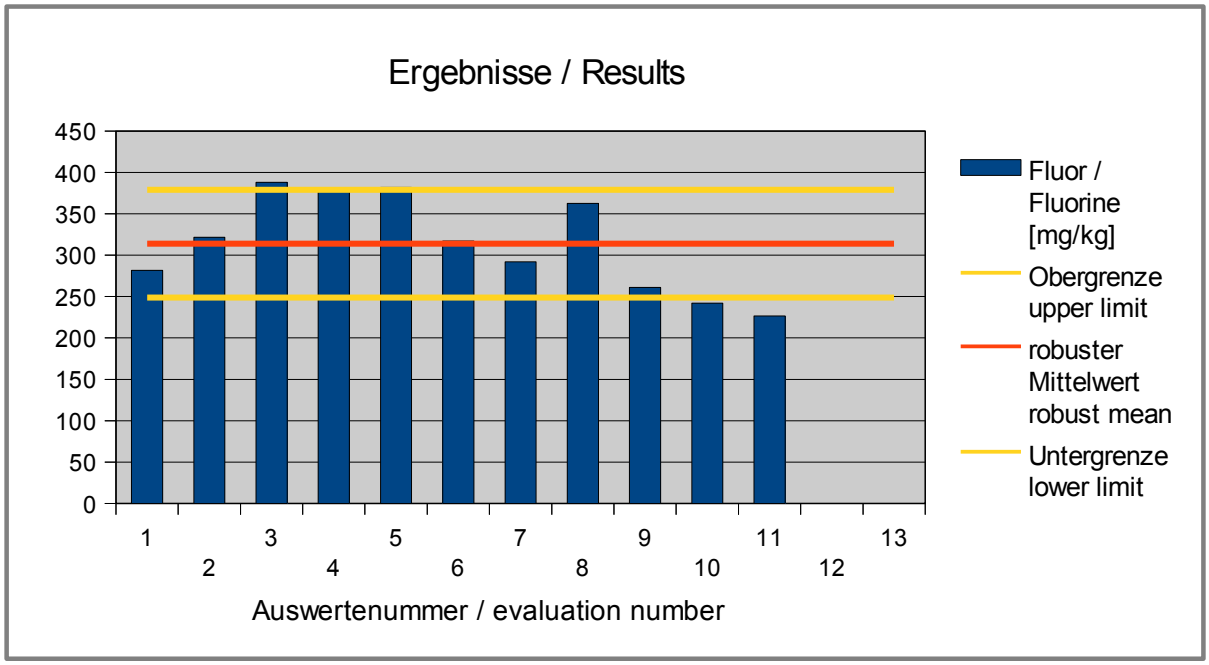

Abb. / Fig. 4: Ergebnisse Fluor / Results fluorine

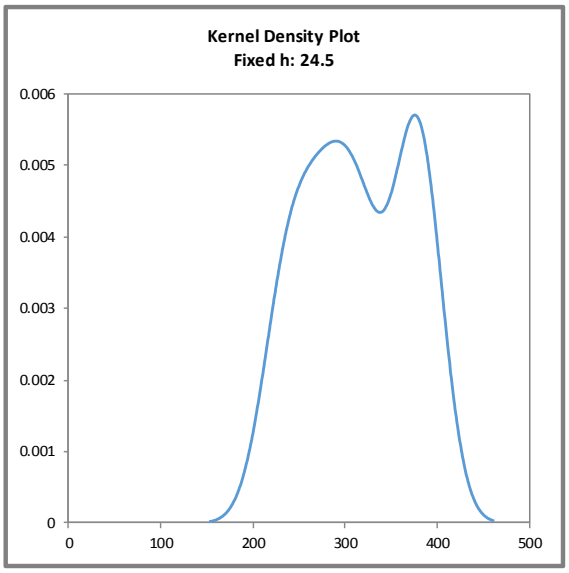

Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

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

Comment:
The kernel density showed a relatively broad distribution of results with an additional maximum at approx. 380 mg/kg.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Fluor / Fluorine [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	282 *	-32,2	-1,0	-1,7	
2	322	7,8	0,24	0,42	
3	388	74,2	2,3	4,0	
4	378	64,2	2,0	3,4	
5	382	68,2	2,1	3,6	Averaging calculation unsuitable, difference of single values > 2 σpt'; z'-scores: sample 1 = 0,77 and sample 2 = 3,4
6	317	3,2	0,10	0,17	
7	292	-21,8	-0,67	-1,2	
8	363	48,7	1,5	2,6	
9	261	-52,8	-1,6	-2,8	
10	242	-71,8	-2,2	-3,8	
11	227 *	-87,3	-2,7	-4,7	
12					
13					

* Mean calculated by DLA

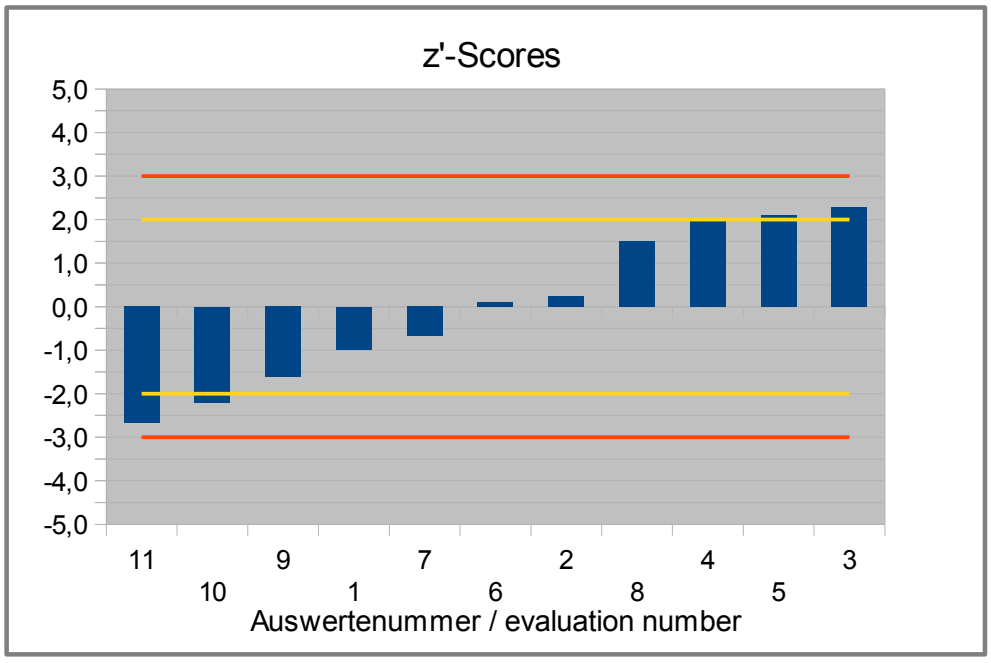

Abb. / Fig. 6: z´-Scores Fluor / fluorine

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

Para-meter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quantifi-cation	Incl. RR	Recovery rate	Method description as in test report / norm / literature
					Day/Month					yes / no	in %	
Iod / Iodine	1	mg/kg	11		19. Sep	23,96	23,85	24,06		No		MET-CENAN-DECYTA-015 Quantitative determination of iodine in salt. Ed. N°08.2018
	1	mg/kg		38	19. Sep	24,38	24,28	24,48		No		MET-CENAN-DECYTA-015 Quantitative determination of iodine in salt. Ed. N°08.2018
	2	mg/kg	Sample No. 03	Sample No. 46	19.09.19	21,97	22,05	21,89				PV-AC-096
	3	mg/kg	21	28		29,67	29,96	29,38	< 0,10	no		DIN EN 15111 (2007-06)
	4	mg/kg										
	5	mg/kg	20	29	16.09.19	22,7	22,9	22,6	7,3	no		LAV 25-5208.01; potentiometric
	6	mg/kg	16	33	12.08.	24,3	24,7	23,9	0,086	no		§ 64 L 00.00-93:2008-12 modified
	7	mg/kg	2	47	09.09.19	21,19	21,56	20,82	1,9	no	99,43	in house method/ Schweizerisches Lebensmittelhandbuch
	8	mg/kg	14	35	08.08.	31,8	30,62	32,98	5	no	99,7-101	Determination of iodine in iodized salt with ICP-OES (house method)
	9	mg/kg	22	27	14.08.19	21	21,2	20,8	0,5	no	-	DIN 38405D4
	10	mg/kg										
	11	mg/kg	8	41	21.08.		21,2	18,9	1,2	no	100	TGL 21820/05, Nr.2.9; Dez. 1977
	12	mg/kg	42	7	23.08.19	22	22	21	0,1	no		DIN EN 15111
	13	mg/kg	31/2019	31/2019	08.08.	23,3	23,3	23,3	2	no	-	Titration

Para-meter	Parti-cipant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quantifi-cation	Incl. RR	Recovery rate	Method description as in test report / norm / literature
					Day/Month					yes / no	in %	
Flour / Fluorine	1	mg/kg	11		19. Sep	292,09	290,35	293,82		No		MET-CENAN-DECYTA-017 Determination of fluorine in salt and water. Potentiometric selective ion method. Ed. N° 02.2016
	1	mg/kg		38	19. Sep	271,17	268,6	273,74		No		MET-CENAN-DECYTA-017 Determination of fluorine in salt and water. Potentiometric selective ion method. Ed. N° 02.2016
	2	mg/kg	Sample No. 03	Sample No. 46	16.09.19	321,66	324,84	318,47				PV-AC-E-185
	3	mg/kg	21	28		388	412	363	<5,00	no		DIN EN 16279
	4	mg/kg	12	37	19.09.19	378	394	362	100mg/kg	no		sample was solved in water and measured by HPLC with Conductivity detector and sup-pression (mobile phase Na2CO3 in water, column shodex IC SI-52 4E 250*4mm* 5µm)
	5	mg/kg	20	29	17.09.19	382	339	425	50	no		LAV 25-5210.01; potentiometric
	6	mg/kg	16	33	06.08.	317	328	306	13	no		Ion-sensitive electrode, German standard method
	7	mg/kg	2	47	05.09.19	292	308	275	5	no		ASU § 64 LFGB L 59.11-18, 1986-11, modified, potentiometric method
	8	mg/kg	14	35	22.08.	362,5	344,5	380,4	4	no	103	DIN 38405-4 1985-07 Determination with ion-selective electrode fluorid
	9	mg/kg	22	27	14.08.19	261	247	274	0,5	no	-	DIN38405D33
	10	mg/kg	9	40	15.08. / 05.09.	242	250	235	200	yes		internal method GC P5211_10_008 (2018-02)
	11	mg/kg	8	41	22.08.		242	211	10	no	101	ASU § 64 LFGB L 59.11-18; Nov.1986
	12	mg/kg										
	13	mg/kg	-	-	-	-	-	-	-	-	-	-

5.1.2 Analytical Methods

Parameter	Participant	Sample preparation and processing	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
					yes / no	yes / no	
Iod / Iodine	1	Sample dissolved in water	Volumetric	Internal control sample	no	yes	
	1	Sample dissolved in water	Volumetric	Internal control sample	no	yes	
	2					yes	Determination and specification as potassium iodate
	3		ICP-MS			yes	
	4						
	5					yes	
	6	Extraction with TMAH, weight ~ 0,25 g				yes	
	7	50 g salt are diluted in dest. water by heating	titrimetric	potassium iodate	yes	yes	
	8	1% sample solution in 0.05% TMAH	ICP-OES (axial)	certified iodide standards in matrix-adapted solution (1% NaCl in 0.05% TMAH)	yes	yes	
	9	homogenization; dissolve in water	Photometry	external; KIO3	no	yes	
	10						
	11		iodometric determination		no	yes	
	12	according to DIN	ICP-MS	from 1 g / l iodide solution		yes	
	13	100 g Sample	Titration with sodium thiosulfate	-	no	no	-

Parameter	Participant	Sample preparation and processing	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
					yes / no	yes / no	
Flour / Fluorine	1	Sample dissolved in water	Selective ion	Internal control sample	no	no	
	1	Sample dissolved in water	Selective ion	Internal control sample	no	no	
	2		Fluoride-selective electrode			no	Determination and specification as fluoride
	3		Elektrode			no	
	4			standard material VWR, inhouse reference material		yes	
	5					yes	In our view, the two subsamples (despite mixing before analysis) are not homogeneous in terms of fluoride content. The average content of sample I was determined with a 7-fold determination with a rel. Std.dev. of 9.54% and of sample II with a 3-fold determination with a rel. std. dev. of 4.21%.
	6			reference solution: Roth IC standard solution fluoride		yes	
	7	weight 20 g/l, Dilution 1:4, 50 ml used for determination	ISE, Modification: Extension of the matrix to salt	each fluoride standard solution for ion chromatography, 1000 mg / l	no	yes	
	8	careful manual mixing of the sample in porcelain dish, solution of the sample to 5 g / l, otherwise according to specified DIN standard		Calibration: certified standard solution after dilution; Recovery: certified standard solution after dilution	no	yes	
	9	homogenization; dissolve in water	ISE	external; NaF	no	yes	
	10		GC-FID with int. Std.	5-pts. calibration with int. std. and ref. Material	yes	yes	
	11				no	yes	
	12						
	13	-	-	-	-	-	-

5.2 Homogeneity

5.2.1 Trend line function of the participants results

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

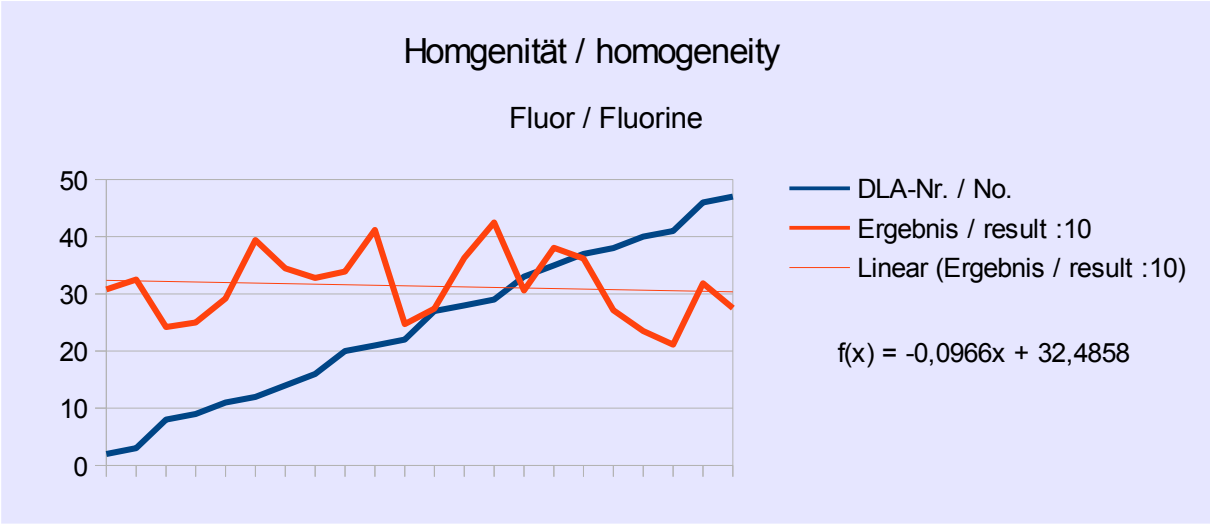

Abb./Fig. 7:
Trendfunktion Probennummern vs. Fluor Ergebnisse (1/10 dargestellt)
trend line function sample number vs. fluorine results (1/10 shown)

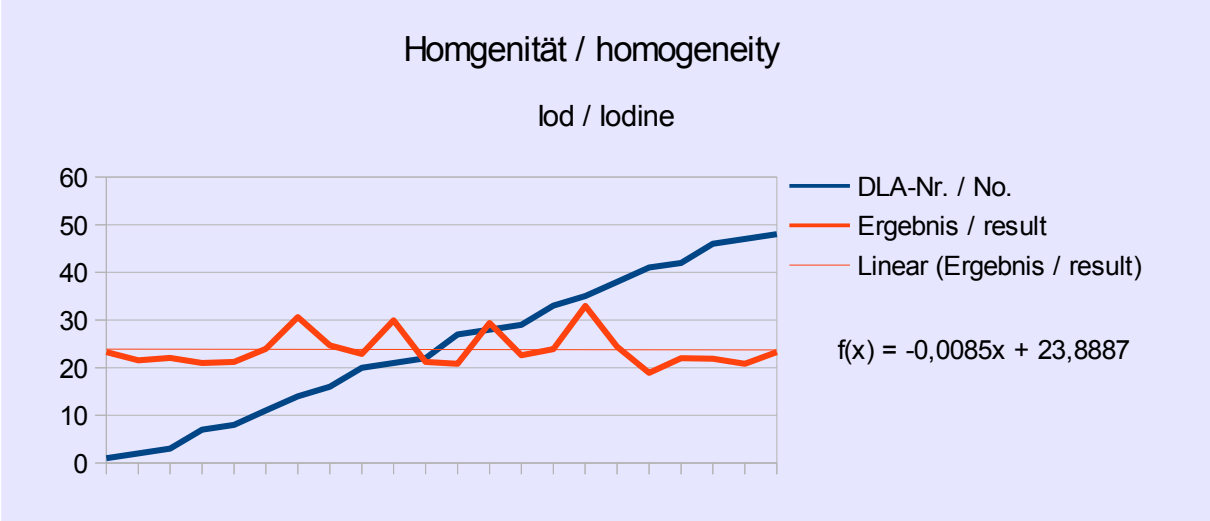

Abb./Fig. 8:
Trendfunktion Probennummern vs. Iod Ergebnisse
trend line function sample number vs. iodine results

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 31-2019***
PT name	***Iodine and Fluorine in Salt***
*Sample matrix**	***Samples I + II:*** *Iodine salt with fluoride / Ingredients: boiling salt, potassium fluoride, potassium iodate, separating agent: sodium ferrocyanide*
Number of samples and sample amount	*2 identical samples I + II, 200 g each*
Storage	*Samples I + II:* ***room temperature***
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative:* ***Iodine and Fluorine***
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 20th September 2019.***
Evaluation report	*The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.*
Coordinator and contact person of PT	*Matthias Besler-Scharf PhD*

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

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		AUSTRIA
		Germany
		Germany
		Germany
		Germany
		Germany
		PERU
		AUSTRIA
		Germany
		Germany
		Germany
		Germany
		Germany

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

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

7. Index of references

1. DIN EN ISO/IEC 17025:2005; Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien / General requirements for the competence of testing and calibration laboratories
2. DIN EN ISO/IEC 17043:2010; Konformitätsbewertung – Allgemeine Anforderungen an Eignungsprüfungen / Conformity assessment – General requirements for proficiency testing
3. ISO 13528:2015 & DIN ISO 13528:2009; Statistische Verfahren für Eignungsprüfungen durch Ringversuche / Statistical methods for use in proficiency testing by interlaboratory comparisons
4. ASU §64 LFGB: Planung und statistische Auswertung von Ringversuchen zur Methodenvalidierung / DIN ISO 5725 series part 1, 2 and 6 Accuracy (trueness and precision) of measurement methods and results
5. Verordnung / Regulation 882/2004/EU; Verordnung über über amtliche Kontrollen zur Überprüfung der Einhaltung des Lebensmittel- und Futtermittelrechts sowie der Bestimmungen über Tiergesundheit und Tierschutz / Regulation on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules
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7. The International Harmonised Protocol for the Proficiency Testing of Ananlytical Laboratories ; J.AOAC Int., 76(4), 926 – 940 (1993)
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16. Homogeneity and stability of reference materials; Linsinger et al.; Accred Qual Assur, 6, 20-25 (2001)
17. AOAC Official Methods of Analysis: Guidelines for Standard Method Performance Requirements, Appendix F, p. 2, AOAC Int (2016)
18. ASU § 64 LFGB L 00.00-93 Bestimmung von Iod in Lebensmitteln, ICP-MS-Verfahren (Dezember 2008) [Determination of iodine in foods, ICP-MS method]
19. ASU § 64 LFGB L 47.03-1 Untersuchung von Tee, Bestimmung des Fluoridgehaltes, Potentiometrisches Verfahren (September 1997) [Analysis of tea, determination of the fluorine content, potentiometric method]
20. ASU § 64 LFGB L 49.00-7 Bestimmung von Fluorid in diätetischen Lebensmitteln, ionensensitive Elektrode (Juli 2000) [Determination of fluoride in dietetic foods, ion-sensitive electrode]
21. Schweizer Lebensmittel-Buch, Kochsalz 07 Jodid-Bestimmung (titrimetrisch) [Swiss Book of Foodstuffs, boiling salt 07 determination of iodine, titration]
22. Schweizer Lebensmittel-Buch, Kochsalz 08 Fluorid-Bestimmung (photometrisch)[Swiss Book of Foodstuffs, boiling salt 08 determination of fluoride, photometric]
23. Schweizer Lebensmittel-Buch, Kochsalz 09 Fluorid-Bestimmung (elektrometrisch) [Swiss Book of Foodstuffs, boiling salt 09 determination of fluoride, electrometric]