Proficiency Tests

DLA

food
cosmetics
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Evaluation Report

proficiency test

DLA 31/2017

Iodine and Fluorine in Salt

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

EP-Anbieter *PT-Provider*	**DLA - Dienstleistung Lebensmittel Analytik GbR** Gesellschafter: Dr. Gerhard Wichmann und Dr. Matthias Besler Waldemar-Bonsels-Weg 170, 22926 Ahrensburg, Germany Tel. ++49(0)171-1954375 Fax. ++49(0)4102-9944976 eMail. proficiency-testing@dla-lvu.de
EP-Nummer *PT-Number*	DLA 31/2017
EP-Koordinator *PT-Coordinator*	Dr. Gerhard Wichmann
Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report : 23 October 2017
EP-Bericht Freigabe *PT-Report Authorization*	Dr. Matthias Besler (Technischer Leiter / Technical Manager) - *gezeichnet / signed M. Besler* Dr. Gerhard Wichmann (QM-Beauftragter / Quality Manager) - *gezeichnet / signed G. Wichmann* Datum / Date: 23 October 2017
Unteraufträge *Subcontractors*	Die Prüfung der Gehalte, Homogenität und Stabilität von EP-Parametern wird von DLA im Unterauftrag vergeben. The analysis of the content, homogeneity and stability of PT-parameters are subcontracted by DLA.
Vertraulichkeit *Confidentiality*	Die Teilnehmerergebnisse sind im EP-Bericht in anonymisierter Form mit Auswertenummern benannt. Daten einzelner Teilnehmer werden ausschließlich nach vorheriger Zustimmung des Teilnehmers an Dritte weitergegeben. Participant result are named anonymously with evalutation 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 salt products (table salt, iodine salt with iodine and fluoride and iodized table salt) from European suppliers and a microtracer premix (wheat flour, microtracer iron particles (FSS red lake) for homogeneity verification.
The raw materials were sieved, combined, homogenized and then sieved again.

Approximately 20 kg of the material was packaged in about 200 grams in metallized PET film bags. The portions were numbered chronologically.

Table 1: Values of iodine and fluorine calculated from the information given by the manufacturers (declared contents):

Parameter	Content per mg/kg	Rob. mean LVU 31-2017
Iodine Fluorine	18 mg/kg 248 mg/kg	18,5 mg/kg 200 mg/kg

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

2.1.1 Homogeneity

The **mixture homogeneity before bottling** was examined 10-fold by **microtracer analysis.** It is a standardized method that is part of the international GMP certification system for feed [14].

Before mixing dye coated iron particles of µm size are added to the sample and the number of particles is determined after homogenization in taken aliquots. The evaluation of the mixture homogeneity is based on the Poisson distribution using the chi-square test. A probability of ≥ 5 % is equivalent to a good homogeneous mixture and of ≥ 25% to an excellent mixture [14, 15]. The microtracer analysis of the present PT sample showed probability of 63%. Additionally particle number results were converted into concentrations, statistically evaluated according to normal distribution and compared to the standard deviation according to Horwitz. This gave a HorRat value of 0,9. The results of microtracer analysis are given in the documentation.

The calculation of the **variation coefficient** of the repeatability standard deviation (CV_r) was used as an indicator of homogeneity. It is 8,3% for iodine and 8,5% for fluorine. The coefficient of variation CV_r is thus comparable to the precision data of the official method, see 3.6.2. The repeatability standard deviation of the participants is given at the characteristics (4.1).

Furthermore, the homogeneity for iodine was characterized by the **trend line function of participants' results for chronological bottled single samples.** The maximum deviations for iodine from the mean value of the trend line was in the range of 37% of the target standard deviation σ_{pt}´ (s. 5.2 homogeneity) and is to be judged as acceptable.

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

2.1.2 Stability

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 27th week of 2017. The testing method was optional. The tests should be finished at September 1st 2017 the latest.

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

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

Further information see 5.3.

2.3 Results

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

The finally calculated concentrations as average of duplicate determinations of both numbered samples was 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 method, information on the limit of quantification, the date of the analysis and general points to the method.

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 14 participants, 13 participants submitted at least one result in time.

3. Evaluation

3.1 Consensus values from participants (Assigned value)

The robust mean of the submitted results was used as assigned value (X) („consensus value from participants") providing a normal distribution. The calculation was done according to algorithm A as described in annex C of ISO 13528 [3].

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

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

The statistical evaluation is carried out for all the parameters for a minimum of 7 values are present.

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

3.2 Robust standard deviation

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

3.3 Repeatability standard deviation

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

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

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

3.4 Reproducibility standard deviation

The reproducibility standard deviation S_R represents a inter-laboratory estimate of the standard deviation for the determination of each parameter on the bases of (outlier free) individual participant results. It takes into account both the repeatability standard deviation S_r and the within-laboratory standard deviation S_S. Reproducibility standard deviations of PT´s may differ from reproducibility standard deviations of ring trials, because the participating laboratories of a PT generally use different internal conditions and methods for determining the measured values.

In the present evaluation, the specification of the reproducibility standard deviation, therefore, does not refer to a specific method, but characterizes approximately the comparability of results between the laboratories, assumed the effect of homogeneity and stability of the sample are negligible.

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

The relative reproducibility standard deviation as a percentage of the mean value is indicated as coefficient of variation CV_R in the table of statistical characteristics in the results section in case single results from participants are available. Its meaning is explained in more detail in 3.9.

3.5 Exclusion of results and outliers

Before statistical evaluation obvious blunders, such as those with incorrect units, decimal point errors, and results for a another proficiency test item can be removed from the data set [2]. Even if a result clearly deviates from the robust mean (e.g. factor >10) and has an influence on the robust statistics, a result can be excluded from statistical evaluation [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 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 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.

For the valuation of iodine the target standard deviation from a precision experiment (s. 3.6.2) was applied. For information, the target standard deviation of the general model according to Horwitz (see 3.6.1) was given.

For the valuation of fluorine the target standard deviation from the general model of Horwitz (s. 3.6.1) was applied. Due to the increased variability of fluorine the standard uncertainty was considered by evaluating with z´-scores (see 3.8). For information, the target standard deviation of a precisions experiment (see 3.6.2) was given.

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 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 deviation (RSD_R) according to selected evaluations of tests for precision and the resulting target standard deviation σ_{pt} [16 - 17]

Parameter	Matrix	Mean (mg/kg)	RSD_r (%)	RSD_R (%)	σ_{pt} (mg/kg)	Method / Literature
Iodine	Cod meat	4,15	0,7	8,9	1,64	ICP-MS/ 16
Iodine	Iodine salt	19,8	6,4	15	2,64[1]	ICP-MS/ 16
Iodine	Seaweed	40,1	0,9	6,2	1,14	ICP-MS/ 16
Fluorine	Tea	150	1,76	4,69	9,04	Potentiometric/ 17
Fluorine	Tea	113	1,65	9,15	18,2	Potentiometric/ 17
Fluorine	Tea	152	1,98	6,14	12,0[1]	Potentiometric/ 17

[1] values used *in the evaluation (see section 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 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

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

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

3.7.1 Warning and action signals

In accordance with the norm ISO 13528 it is recommended that a result that gives rise to a *z*-score above 3,0 or below −3,0, shall be considered to give an "action signal" [3]. Likewise, a *z*-score above 2,0 or below −2,0 shall be considered to give a "warning signal". A single "action signal", or "warning signal" in two successive PT-rounds, shall be taken as evidence that an anomaly has occurred which requires investigation. For example a fault isolation or a root cause analysis through the examination of transmission error or an error in the calculation, in the trueness and precision must be performed and if necessary appropriate corrective measures should be applied [3].

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

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 σ_{pt}'.

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

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

For warning- and action-signals see 3.7.1.

3.9 Reproducibility coefficient of variation (CV)

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^*/σ_{pt}

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

3.11 Standard uncertainty

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

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

If $U_{(Xpt)} \leq 0{,}3\ \sigma_{pt}$ the standard uncertainty of the consensus value needs not to be included in the interpretation of the results of the PT [3]. A clear exceeded the value of 0.3 is an indication that the target standard deviation was possibly set too low for the standard uncertainty of the assigned value.

The quotient $U(X_{pt})/\sigma_{pt}$ is reported in the characteristics of the test.

4. Results

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

In the first table the characteristics are listed:

Statistic Data
Number of results
Number of outliers
Mean
Median
Robust mean(X_{pt})
Robust standard deviation (S^*)
Number with 2 replicates
repeatability standard deviation (S_r)
Repeatability (Cv_r) in %
reproducibility standard deviation (S_R)
Reproducibility (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 $U(X_{pt})$
Quotient $U(X_{pt})/\sigma_{pt}$ or $U(X_{pt})/\sigma_{pt}'$
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	**Parameter [Einheit/ Unit]**	**Abweichung**	**Z´-Score** σ_{pt}'	**z-Score** (Info)	**Hinweis**
Evaluation number		**Deviation**			**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	13
Number of outliers	1
Mean	18,1
Median	18,0
Robust Mean (X)	**18,5**
Robust standard deviation (S*)	**2,60**
Number with 2 replicates	13
Repeatability SD (S_r)	1,50
Repeatability (CV_r)	8,29%
Reproducibility SD (S_R)	3,82
Reproducibility (CV_R)	21,2%
Target range:	
Target standard deviation σ_{pt}	**2,64**
Target standard deviation (for Information)	1,90
lower limit of target range	**13,2**
upper limit of target range	**23,7**
Quotient S/σ_{pt}*	*1,0*
Standard uncertainty $U_{(Xpt)}$	*0,901*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,34*
Results in the target range	*12*
Percent in the target range	*92,3%*

Comments:

For the valuation the target standard deviation from a precision experiment (s. 3.6.2) was applied. For information, the target standard deviation of the general model according to Horwitz (see 3.6.1) was given.

The distribution of the results showed an normal variability. The quotient S^*/σ_{pt} was 1,0. The comparability of results is given.

Repeatability- and reproducibility standard deviation are in the range of established values for the methods used (see 3.6.2).

The quotient $U(X_{pt})/\sigma_p$ (0,34) is not increased.

92% of the results were in the target area.

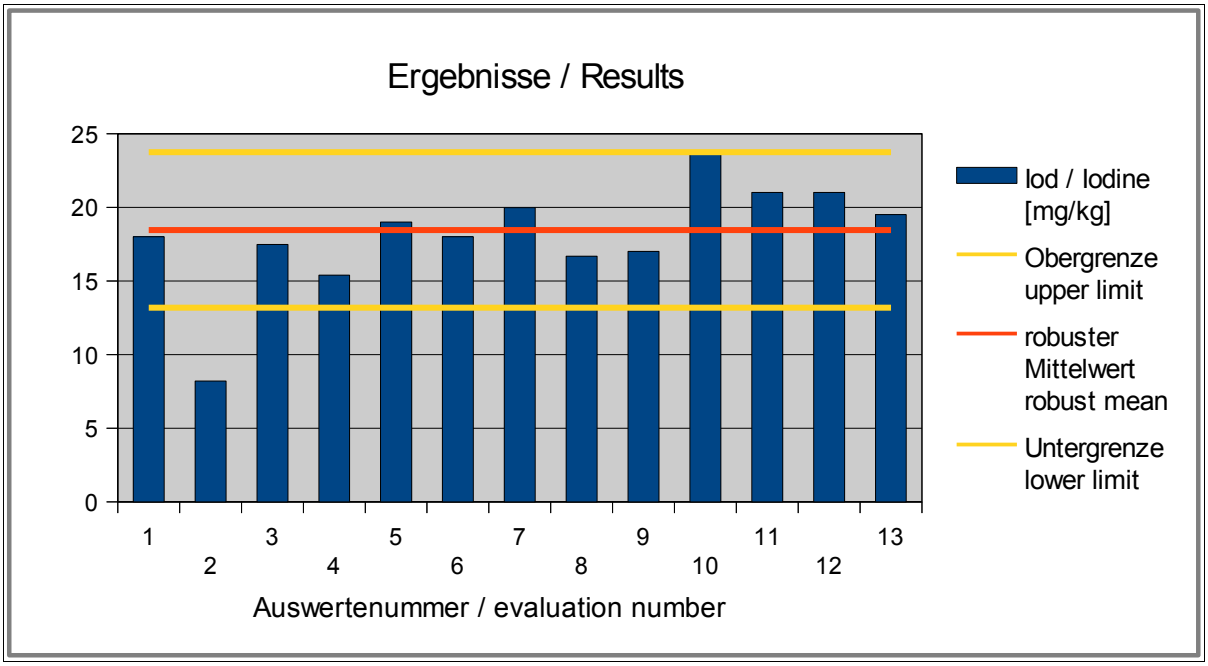

Abb. / Fig. 1: Ergebnisse Iod / Results iodine

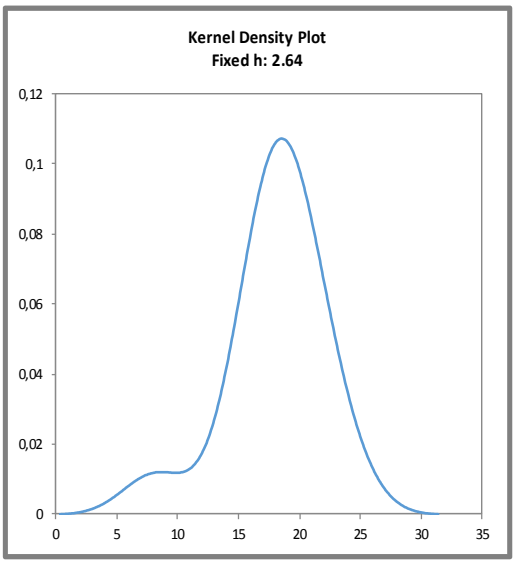

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = σ_{pt} von X_{pt}

Kernel density plot of results with h = σ_{pt} of X_{pt}

Comment:
The kernel density shows a normal distribution of results with a slight side peak at 8 mg/kg, due to the result outside the target range (outlier).

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	18,0	-0,457	-0,17	-0,24	
2	8,20	-10,3	-3,9	-5,4	Ausreisser / Outlier
3	17,5*	-0,977	-0,37	-0,51	
4	15,4	-3,06	-1,2	-1,6	
5	19,0	0,543	0,21	0,29	
6	18,0	-0,457	-0,17	-0,24	
7	20,0	1,52	0,58	0,80	
8	16,7	-1,79	-0,68	-0,94	
9	17,0	-1,46	-0,55	-0,77	
10	23,6	5,14	1,9	2,7	
11	21,0	2,54	1,0	1,34	
12	21,0	2,54	1,0	1,34	
13	19,5	1,04	0,40	0,55	

** Mean calculated by DLA*

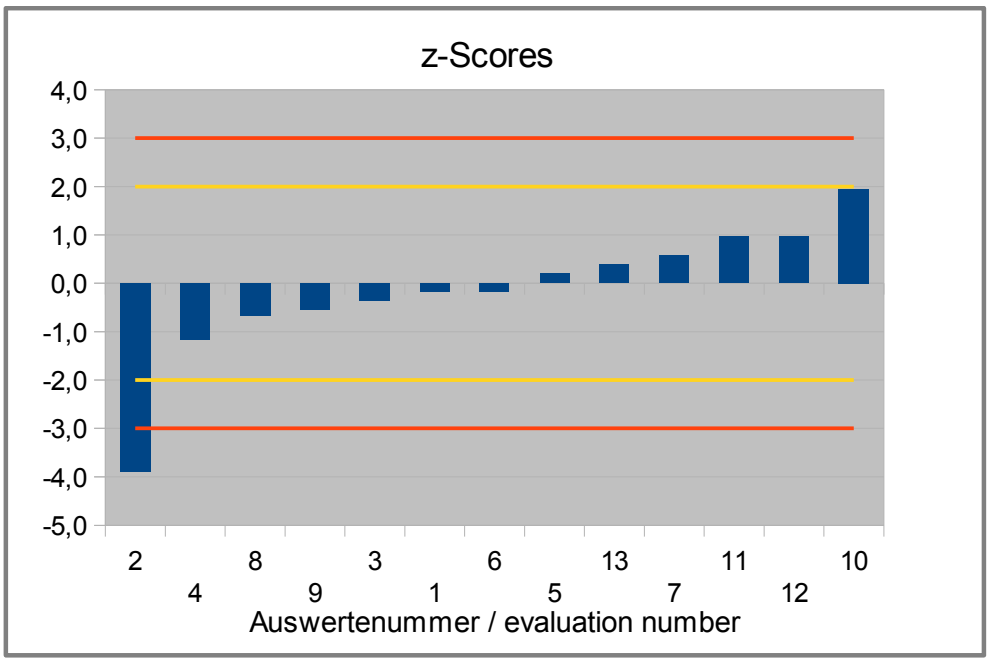

Abb. / Fig. 3: Z-Scores Iod / Iodine

4.2 Fluorine in mg/kg

Vergleichsuntersuchung / Proficiency Test

Kenndaten	
Anzahl der Messergebnisse	8
Anzahl der Ausreißer	0
Mittelwert	201
Median	203
Robuster Mittelwert (X_{pt})	**200**
Robuste Standardabweichung (S*)	**41,9**
Anzahl mit 2 Wiederholmessungen	8
Wiederholstandardabweichung (S_r)	16,9
Variationskoeffizient (VK_r)	8,45%
Vergleichsstandardabweichung (S_R)	40,1
Variationskoeffizient (VK_R)	20,0%
Zielkenndaten:	
Zielstandardabweichung σ_{pt}´	**23,5**
Zielstandardabweichung (zur Information)	11,9
Untere Grenze des Zielbereichs	**153**
Obere Grenze des Zielbereichs	**247**
Quotient S/σ_{pt}´*	*1,8*
Standardunsicherheit $U_{(Xpt)}$	*18,5*
Quotient $U_{(Xpt)}/\sigma_{pt}$´	*0,79*
Ergebnisse im Zielbereich	*6*
Prozent im Zielbereich	*75,0%*

Comments:

For the valuation the target standard deviation from the general model of Horwitz (s. 3.6.1) was applied. Due to the increased variability (quotient S*/σ_{pt} was 2,9) the standard uncertainty was considered by evaluating with z´-scores (see 3.8). For information, the target standard deviation of a precision experiment (see 3.6.2) was given.

The quotient S*/σ_{pt}´ was below 2,0. The comparability of results is given.

Repeatability- and reproducibility standard deviation are in the range of established values for the methods used (see 3.6.2).

The quotient $U(X_{pt})/\sigma_{pt}$´ (0,79) is increased, but is acceptable on the basis of the other characteristics and the use of different methods.

75% of the results were in the target area.

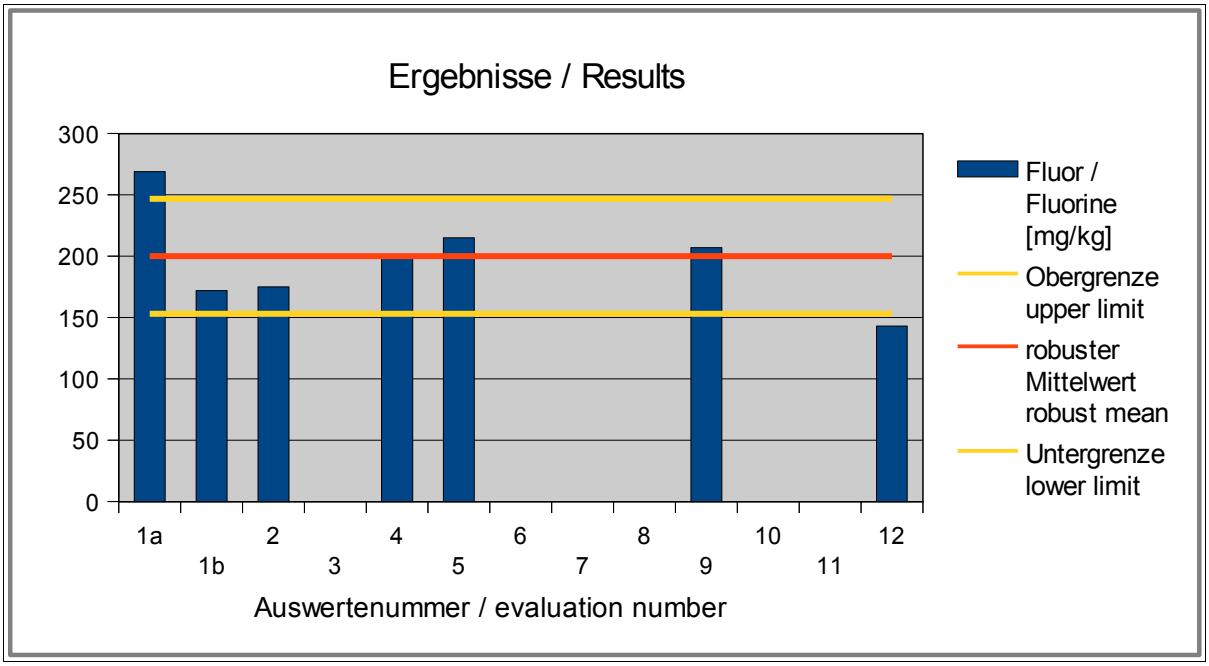

Abb. / Fig. 4: Ergebnisse Fluor / Results fluorine

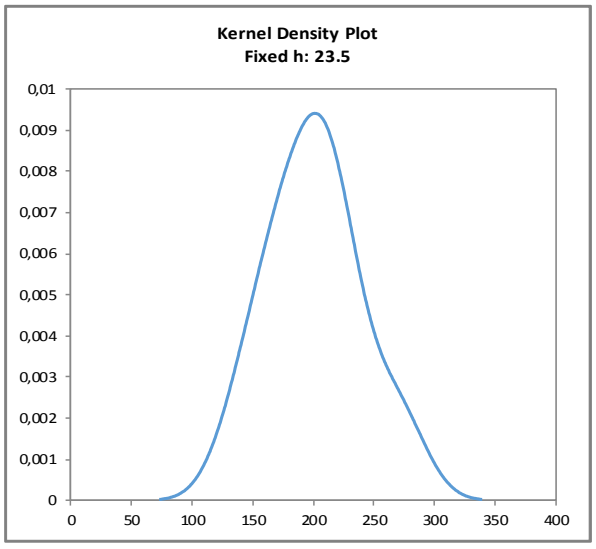

Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse mit h = σ_{pt}´ von X_{pt}

Kernel density plot of results with h = σ_{pt}´ of X_{pt}

Comment:
The kernel density shows a normal distribution of results with a slight shoulder at 270 mg/kg, due to the result outside the target range.

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
1a	269	69,0	2,9	5,8	
1b	172	-28,0	-1,2	-2,4	
2	175	-25,0	-1,1	-2,10	
3					
4	199	-0,978	-0,042	-0,082	
5	215	15,0	0,64	1,27	
6					
7					
8					
9	207	7,02	0,30	0,59	
10					
11					
12	143	-57,0	-2,4	-4,80	
13	226	26,0	1,1	2,19	

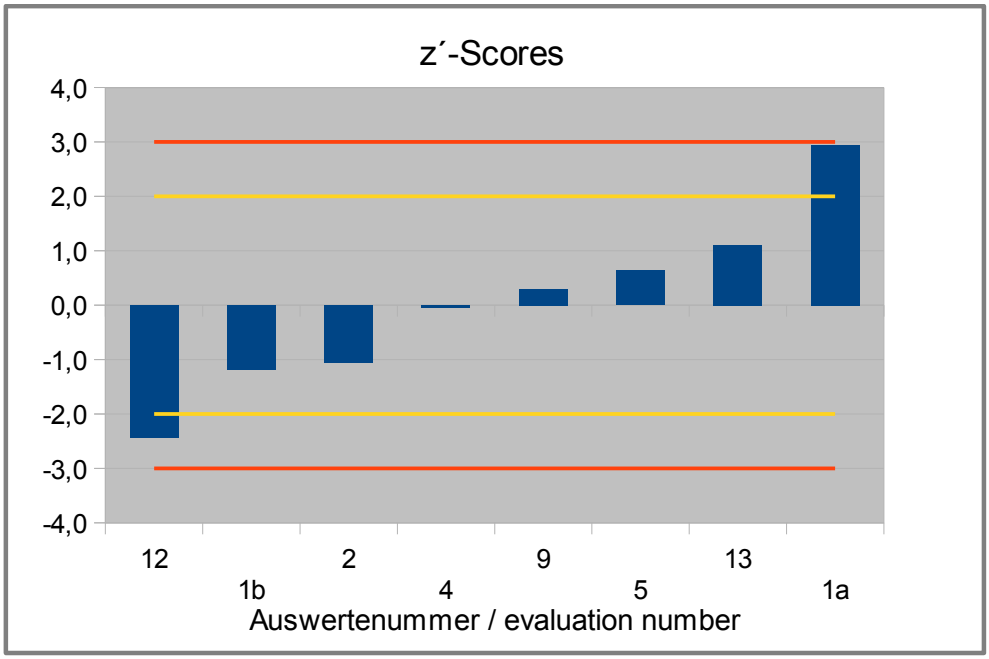

Abb. / Fig. 6: Z´-Scores Fluor / fluorine

5. Documentation

5.1 Details by participants

5.1.1 Primary data

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

5.1.1.1 Iodine

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/ month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	3	69	22.8.	18,0	18,6	17,5	0,9	no	
2	7	65	02.08.17	8,20	8,12	8,27	0,1	no	-
3	10	62	21.08.17		17,45	17,5	none	no	no
4	19	53	28.08.17	15,4	15,3	15,5	7,3	no	
5	16	56	11.08.17	19	20	18	0,075	no	
6	05	67	11/08	18	20	16	3,5	no	91
7	46	26	23.08.17	19,98	20,05	19,9	0,1	yes	100
8	23	49	15.08.	16,67	16,48	16,85	1,9	no	99,12
9	17	55	28.07.17	17	17,1	16,9		no	92,3
10	34	38	02.08.17	23,6	24,3	22,8	0,2	no	
11	22	50	18.07.17	21	23,7	18,3	0,05	no	102,4
12	11	61	20.07.17	21	20	22	0,2	no	-
13	14	58	19.07.17	19,5	20,1	18,9	0,1	no	-

5.1.1.2 Fluorine

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantificati-on	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1a	3	69	24.08.17	269	276	261	40	yes	100
1b	3	69	22.08.17	172	180	164	4	no	
2	7	65	24.08.17	175	153	196	0,15	no	-
3	10	62	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.
4	19	53	29.08.17	199	199	200	50	no	
5	16	56	15.08.17	215	235	195	20	no	
6	05	67							
7	46	26							
8	23	49	n.a.						
9	17	55	26.07.17	207	216	198		no	
10	34	38							
11	22	50							
12	11	61	20.07.17	143	142	143	5	no	-
13	14	58	21.07.17	226	232	214	1	no	-

5.1.2 Analytical methods

5.1.2.1 Iodine

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	**Method description**	**Sample preparation**	**Measuring method**	**Calibration and reference matreial**	**Recovery with same matrix**	**Method accredited**	**Further remarks**
					ja / nein	ja / nein	
1	ICP-MS					yes	
2	Iodine in foodstuffs (ICP-MS) acc. DIN EN 15111, mod.	see column „Measuring method"	Mod.: mix a predilution, no ultracentrifugation	Method with internal standard	no	yes	
3	In-house method	none		no	no	yes	
4	LAV 25-5208.01; potentiometric					yes	
5	§ 64 L 00.00-93:2008-12 modified	Extraction with TMAH, weight ~ 0,25 g			no	yes	Both samples were homogenized separatly with Universal Mill typ IKA M20; values different - it is not assumed from two identical samples.
6	EuSalt/AS 002-2005	weight of salt 50g	titrimetrical method	no	yes	yes	Titrated sample of salt solution had unusal colour before we added 1 ml of starch solution indicator*
7	EN 15111	dissolve in H2O; than alkaline extraction at increased temperature	ICP-MS	Potassium iodate	yes	yes	-
8	In-house method, schweiz. Lebensmittelhandbuch	50 g sample has been solved by heat in dest. water.	titrimetrical method	Potassium iodate	yes	yes	Heavy sediment and slight turbit. After the additon of potassiumiodide the solution gets green-grey-brown instead of amber-coloured. The transition point is slow and difficult to see. After the titration remains a fine dark magnetic sediment*
9	In-house method	50 g salt in 500 ml paltic piston and use 100 ml for determination.	Titration with sodium thiosulfate solution	Dope 50 g NaCl with 30 mg/kg potassium iodate solution	yes	yes	
10	iodometric	grinding				yes/no	
11	DIN EN 15111	Extraction	ICP-MS	5µg/l - 50µg/L	no	yes	Recovery with BCR063R (milk powder)
12	DIN 15111	-	-	0, 10, 50, 100 µg/kg, milk powder	-	yes	no
13	i.A.a. DIN 38405-D33	Prepatation of a stock solution	Photometric	KJO3 p.a.	-	yes	

* DLA used 16 mg/kg Microtracer (Microtracer ferrous particles/FSS-red lake; with the dye E 129 (0,1 - 0,2 mg/kg)) for homogeneity testing.

5.1.2.2 Fluorine

Teilnehmer	Methodenbeschrei-bung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode ak-kreditiert	Sonstige Hinweise
Participant	**Method description**	**Sample preparation**	**Measuring method**	**Calibration and reference matreial**	**Recovery with same matrix**	**Method ac-credited**	**Further remarks**
					ja / nein	ja / nein	
1a	HPLC-CD					yes	
1b	ione sensitive electrode					no	
2	Fluoride in foodstuffs (ion sensitive electrode) acc. L49.00-07, mod.	see column „Measuring method“	Mod.: Matrix also selected foods, dissolve without ultrasonic bath, triple standard addition, using a titrator.	Standard addition	no	yes	
3	not analysed	not analysed		not analysed	not analysed	not analysed	
4	LAV 25-5210.01; potentiometric					yes	
5	Ion-sensitive elektrodes, Deutsches Einheitsverfahren; deviation: Matrix table salt				yes	yes	Both samples were homogenized separatly with Universal Mill typ IKA M20; values different - it is not assumed from two identical samples.
6							
7							
8							
9	In-house method	50 g salt in 500 ml plastic piston; dilution 1:10; for determination used 25 ml	n. § 64 LFGB L 59.11-27; updated August 2013	Fluoride standard solution 1000 mg/l F	no	no	
10							
11							
12	-	-	-	table salt	-	-	no
13	i.A.a. DIN 38405-D4	prepare a stock solution	ISE	NaF p.a.	-	yes	

5.2 Homogeneity

5.2.1 Homogeneity testing before PT

Microtracer Homogeneity Test
DLA 31-2017

Weight whole sample	20,0	kg
Microtracer	FSS-rot lake	
Particle size	75 – 300	µm
Weight pro particle	2,0	µg
Addition of tracer	16,1	mg/kg

Result of analysis:

Sample	Weight [g]	Particle number	Particle [mg/kg]
1	10,89	90	16,5
2	12,32	103	16,7
3	10,03	85	16,9
4	9,74	81	16,6
5	8,52	72	16,9
6	10,04	82	16,3
7	8,3	60	14,5
8	10,81	64	11,8
9	10,75	85	15,8
10	9,03	72	15,9

Poisson distibution		
Number of samples	10	
Degree of freedom	9	
Mean	79,4	Partikel
Standard deviation	7,92	Partikel
χ^2 (CHI-Quadrat)	7,11	
Probability	**63**	%
Recovery rate	98,5	%

Nrmal distribution		
Number of samples	10	
Mean	15,8	mg/kg
Standard deviation	1,58	mg/kg
rel. Standard deviation	10,0	%
Horwitz Standard deviation	10,6	%
HorRat-Value	**0,9**	
Recovery rate	98,5	%

5.2.2 Comparison of sample number/test results and trend line

By comparison of the **increasing sample numbers** and the measurement results of iodine, the homogeneity of the chronological bottled PT item can be characterized with the help of the trend line function:

Iodine				
Target standard deviation σ_{pt}	1,90			mg/kg
Sample numbers	3 - 69			
Total numbers of samples	26			
Slope	-0,0557			
Trend line range	18,8	-	17,4	mg/kg
Deviation trend line	18,1	±	0,70	mg/kg
Percent of σpt	36,8	%		

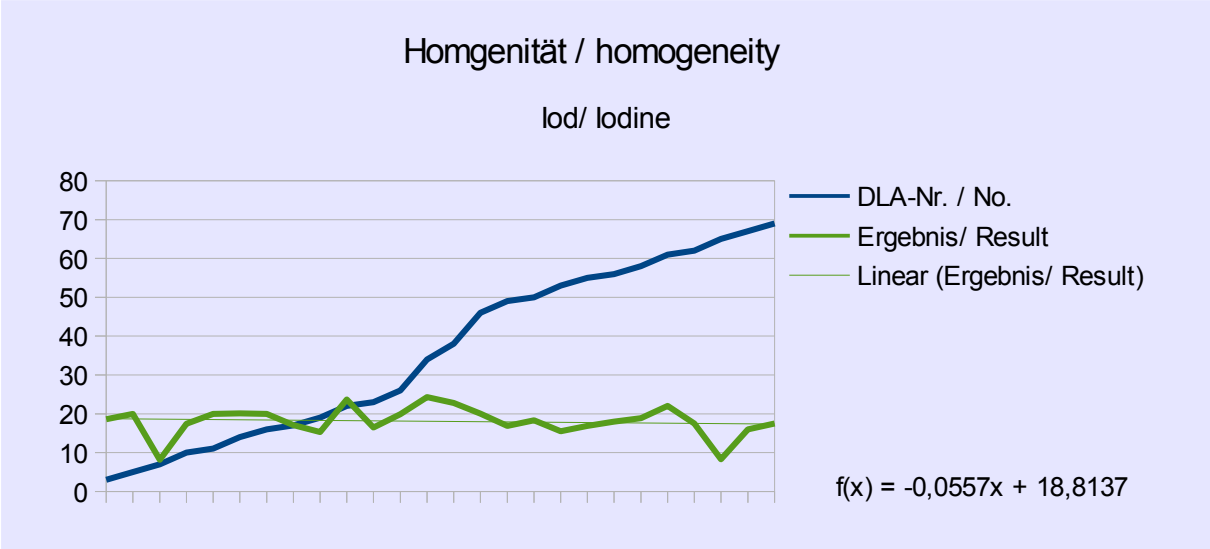

Abb./Fig. 7:
Trendfunktion Probennummern vs. Ergebnisse
trend line function sample number vs. results

5.3 Sample cover letter: Information on the Proficiency Test (PT)

Before the PT, the participants are given the following information in the sample cover letter:

Information on the Proficiency Test (PT)

PT number	***DLA 31-2017***
PT name	***Iodine and Fluorine in Salt***
*Sample matrix**	*Samples A + B:* ***Salt***
Number of samples and sample amount	*2 identical samples A + B, 200 g each.*
Storage	*Samples A + B: 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 A and B as well as the final results calculated as mean of the double determination (samples A and B) 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 A and B)* – *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 01st September 2017***
Evaluation report	*The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.*
Coordinator and contact person of PT	*Dr. Gerhard Wichmann*

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

6. Index of participant laboratories

Teilnehmer/ Participant	Ort/ Town	Land/ Country
		Austria
		Austria
		Germany
		Germany
		Germany
		France
		Germany
		Germany
		Germany
		Germany
		Lithuania
		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 literature

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 L 00.00-93 Bestimmung von Iod in Lebensmitteln, ICP-MS-Verfahren (Dezember 2008)
17. ASU § 64 LFGB L 47.03-1 Untersuchung von Tee, Bestimmung des Fluoridgehaltes, Potentiometrisches Verfahren (September 1997)
18. ASU § 64 LFGB L 49.00-7 Bestimmung von Fluorid in diätetischen Lebensmitteln, ionensensitive Elektrode (Juli 2000)
19. Schweizer Lebensmittel-Buch, Kochsalz 07 Jodid-Bestimmung (titrimetrisch)
20. Schweizer Lebensmittel-Buch, Kochsalz 08 Fluorid-Bestimmung (photometrisch)
21. Schweizer Lebensmittel-Buch, Kochsalz 09 Fluorid-Bestimmung (elektrometrisch))