Proficiency Tests

DLA

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Evaluation Report

proficiency test

DLA 25/2017

Mycotoxins: Aflatoxins + Ochtatoxin A in Spice Mixture

Dienstleistung Lebensmittel Analytik GbR
Waldemar-Bonsels-Weg 170
22926 Ahrensburg, Germany

proficiency-testing@dla-lvu.de
www.dla-lvu.de

Coordinator: Dr. G. Wichmann

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 25/2017
EP-Koordinator *PT-Coordinator*	Dr. Gerhard Wichmann
Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report : 26 July 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: 26 July 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 with a natural content of aflatoxins and ochratoxin A is a spice mixture (curry powder, paprika, tragacanth root powder, rice flour, corn flour). To the mixture were further added microtracer iron particles (FSS red lake) for homogeneity verification.

The raw materials were ground, sieved, combined, homogenized and then sieved again.

Approximately 4 kg of the material was packaged in about 50 grams in metallized PET film bags. The portions were numbered chronologically.

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]. An evaluation of the filters was not possible due to overlapping colour effects.

The homogeneity of the bottled numbered DLA samples was checked by a 5-fold determination of ochratoxin A by means of HPLC/ immunoaffinity processing (ASU §64 L 15.00-1/1). The repeatability standard deviation is with 6,6% in the range of repeatability standard deviations of the methods ASU §64 L 15.03-1 [22] and ASU §64 L 30.00-5 [23] for the determination of ochratoxin A, which is in the range of 5,6% to 20,1%, see 3.6.2. The results of the homogeneity tests are given in the documentation, see 5.2.1.

The calculation of the **variation coefficient** of the repeatability standard deviation (CV_r) was used as an indicator of homogeneity. It is 9,5% for aflatoxin B1, 8,8% for total aflatoxin and 6,4% for ochratoxin A. The coefficient of variation CV_r is thus comparable to the precision data of the official methods, see 3.6.2 (see table 1)[19, 20, 22, 23]. The repeatability standard deviation of the participants is given at the characteristics (4.1 – 4.3).

Furthermore, the homogeneity for ochratoxin A was characterized by the **trend line function of participants' results for chronological bottled single samples**. The maximum deviations for ochratoxin A from the mean value of the trend line was in the range of 10% of the target standard deviation *σpt* (s. 5.2 homogeneity) and is to be judged 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].

2.1.2 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 aflatoxins and ochratoxin A for samples with a comparable dry mass (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 20th week of 2017. The testing method was optional. The tests should be finished at March 30th 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.

All 11 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 aflatoxin B1, total aflatoxins and ochratoxin A the target standard deviation from the general model of Horwitz/ Thompson (s. 3.6.1) was applied. Due to the increased variability of total aflatoxins and aflatoxin B1 the standard uncertainty was considered by evaluating with z´-scores (see 3.8).

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)

The general model of Horwitz/ Thompson is used for the concentration range < 120 µg/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 1 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 1: 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} [19, 20, 22, 23]

parameter	matrix	mean (µg/kg)	RSD_r	RSD_R	σ_{pt}	Method/ Literature
Aflatoxin B1	corn	14,9	5,8%	10%	0,072	HPLC/19
Aflatoxin B1	peanut butter	5,26	14,9%	30%	0,22	HPLC/19
Aflatoxin B1	peanut butter	0,80	6%	32%	0,13	HPLC/20
Aflatoxin B1	paprika	0,84	14%	19%	0,13	HPLC/20
Aflatoxin B1	paprika	1,39	10%	17%	0,12	HPLC/20
Total Aflat.	corn	24,5	7,3%	11,7%	0,16	HPLC/19
Total Aflat.	peanut butter	8,42	17%	30%	0,43	HPLC/19
Total Aflat.	peanut butter	1,3	6%	34%	0,52	HPLC/20
Total Aflat.	paprika	0,90	17%	34%	0,49	HPLC/20
Total Aflat.	paprika	2,0	12%	28%	0,41	HPLC/20
Ochratoxin A	sultans	11,4	5,6%	14,3%	4,68	HPLC/23
Ochratoxin A	barley	14,4	7,9%	26,5%	8,83	HPLC/22
Ochratoxin A	corn	16,3	20,1%	28,4%	8,38	HPLC/22

The values from the grayed-out lines were used for the calculation of the target standard deviation σ_{pt} from tests for precision, which are specified for information in the evaluation (see under 4.1, 4.2 and 4.3),

3.6.3 Value by perception

In the present PT DLA 25-2017 curry powder was to be tested for the parameters ochratoxin A (OTA), aflatoxin B1 or total aflatoxins. According to EU Regulation 1881/2006 [23] the following maximum levels are set for aflatoxins and ochratoxin A:

Section 2: Mycotoxins

	Foodstuffs (1)	Maximum levels (µg/kg)		
2.1	**Aflatoxins**	B_1	Sum of B_1, B_2, G_1 and G_2	M_1
2.1.14.	Following species of spices: *Capsicum* spp. (dried fruits thereof, whole or ground, including chillies, chilli powder, cayenne and paprika) *Piper* spp. (fruits thereof, including white and black pepper) *Myristica fragrans* (nutmeg) *Zingiber officinale* (ginger) *Curcuma longa* (turmeric) Mixtures of spices containing one or more of the abovementioned spices	5,0	10,0	—

2.2	**Ochratoxin A**	
'2.2.11.	Spices, including dried spices	
	Piper spp. (fruits thereof, including white and black pepper) *Myristica fragrans* (nutmeg) *Zingiber officinale* (ginger) *Curcuma longa* (turmeric)	15 µg/kg
	Capsicum spp. (dried fruits thereof, whole or ground, including chillies, chilli powder, cayenne and paprika)	20 µg/kg
	Mixtures of spices containing one of the abovementioned spices	15 µg/kg'

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.

Table 2 shows selected characteristics of participants results of the present PT in comparison to the previous years.

Table 2: Characteristics of the present PT (on blue-grey) in comparison to previous PTs since 2015 (SD = standard deviation, CV = coefficient of variation)

Parameter	rob. mean (µg/kg)	rob. SD (S*) (µg/kg)	rel. SD (VK_r) [%]	rel. SD (VK_R) [%]	Target-SD (σ_{pt}) (µg/kg)	Quotient S^*/σ_{pt}	DLA-report
Aflat. B1	0,79	0,483	9,52%	54,6%	0,274	1,8	25-2017
Total Aflat.	1,55	1,27	5,59%	132%	0,655	1,9	25-2017
OTA	34,1	9,05	6,38%	42,7%	7,50	1,2	25-2017
Aflat. B1	1,80	0,723	21,4	64,5	0,397	1,8	24-2016
Total Aflat.	2,29	1,15	18,9	53,7	0,666	1,7	24-2016
OTA	42,1	27,9	11,4	55,3	14,8	1,9	24-2016
Aflat. B1	1,76	0,914	-	-	0,559	1,6	19-2015
Total Aflat.	2,01	1,21	-	-	0,695	1,7	19-2015
OTA	45,6	31,9	-	-	16,1	2,0	19-2015

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 / **Evaluation number**	**Parameter [Einheit/ Unit]**	**Abweichung** / **Deviation**	**Z´-Score** σ_{pt}´	**z-Score** (Info)	**Hinweis** / **Remark**

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

4.1 Aflatoxin B1 in µg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	0,785
Median	0,735
Robust Mean (X)	**0,785**
Robust standard deviation (S*)	**0,483**
Number with 2 replicates	8
Repeatability SD (S_r)	0,0747
Repeatability (CV_r)	9,52%
Reproducibility SD (S_R)	0,429
Reproducibility (CV_R)	54,6%
Target range:	
Target standard deviation σ_{pt}´	**0,274**
Target standard deviation (for Information)	0,127
lower limit of target range	**0,236**
upper limit of target range	**1,33**
Quotient S/σ_{pt}´*	*1,8*
Standard uncertainty $U_{(Xpt)}$	*0,213*
Quotient $U_{(Xpt)}/\sigma_{pt}$´	*0,78*
Results in the target range	*7*
Percent in the target range	*88%*

Comments:

The target standard deviation was evaluated using the model of Horwitz/ Thompson. The distribution of results showed an increased variability. Valuation was done considering the standard uncertainty by z'-score.

The target standard deviation "for information" was calculated from values by perception (ASU §64 L 23.05-2)[20], see 3.6.2.

The distribution of the results showed an increased variability. The quotient S^*/σ_{pt}´ was 1,8. The robust standard deviation is comparable to those of prior PT´s (see 3.6.3). 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 $U(X_{pt})/\sigma_{pt}$ (0,78) is increased, but is acceptable on the basis of the other characteristics and the use of different methods.

88% of the results were in the target area.

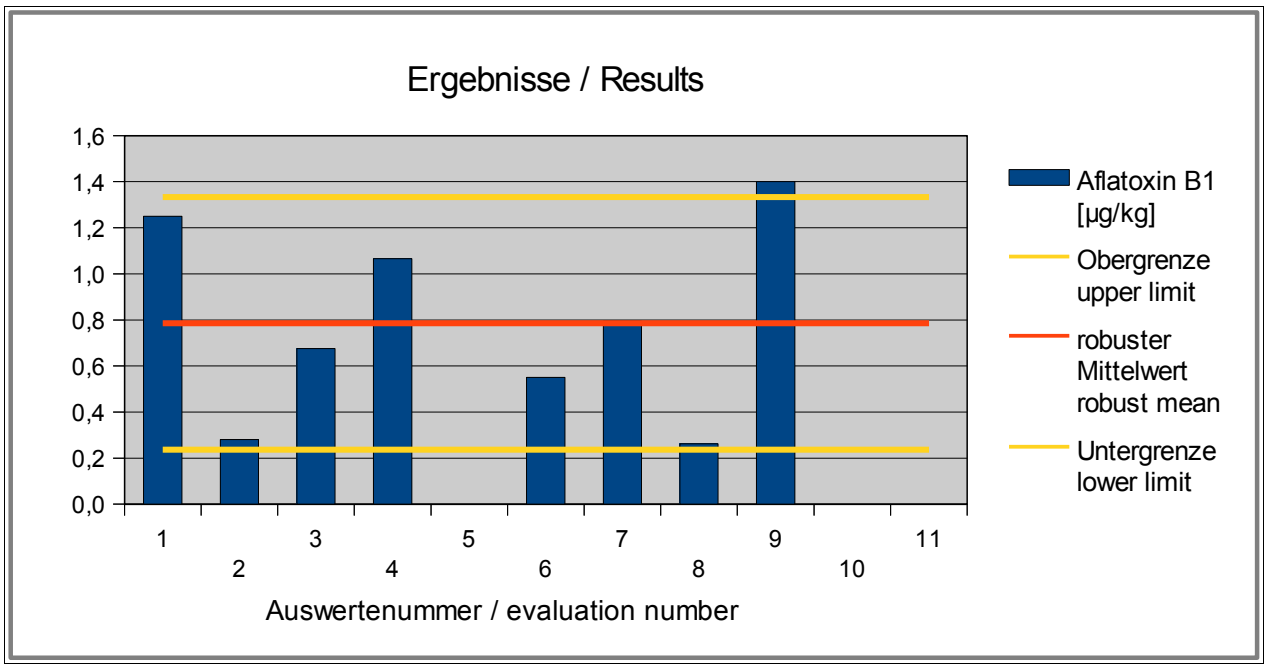

Abb. / Fig. 1: Ergebnisse/ Results aflatoxin B1

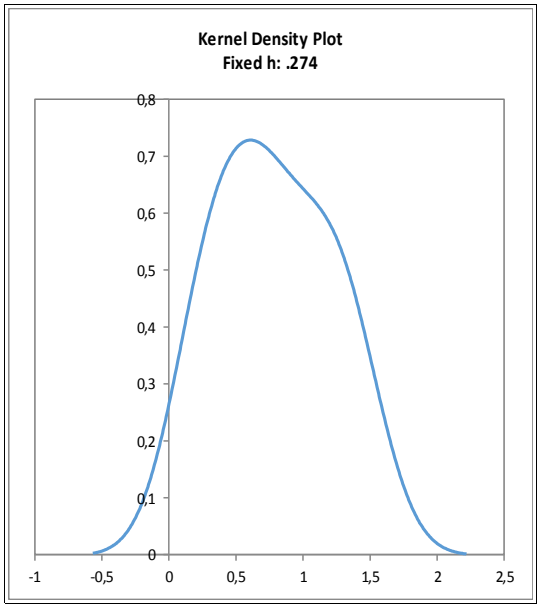

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = σ_{pt} von X_{pt} (0,274 µg/kg)

Kernel density plot of results with h = σ_{pt} *of* X_{pt} (0,274 µg/kg)

Comment:
The kernel density shows a normal distribution of results with a slight shoulder at 1,4 µg/kg, due to the result outside the target range.

Ergebnisse der teilnehmenden Institute:
Results of Participants:

Auswerte-nummer Evaluation number	Aflatoxin B1 [µg/kg]	Abweichung [µg/kg] Deviation [µg/kg]	z´-Score $(\sigma_{pt})'$	z-Score (Info)	Hinweis Remark
1	1,25	0,465	1,7	3,7	
2	0,281	-0,504	-1,8	-4,0	
3	0,675	-0,110	-0,4	-0,9	
4	1,07	0,280	1,0	2,2	
5					
6	0,55*	-0,235	-0,86	-1,8	
7	0,795	0,010	0,037	0,081	
8	0,262	-0,523	-1,9	-4,1	
9	1,40	0,615	2,2	4,8	
10					
11					

** Mean calculated by DLA*

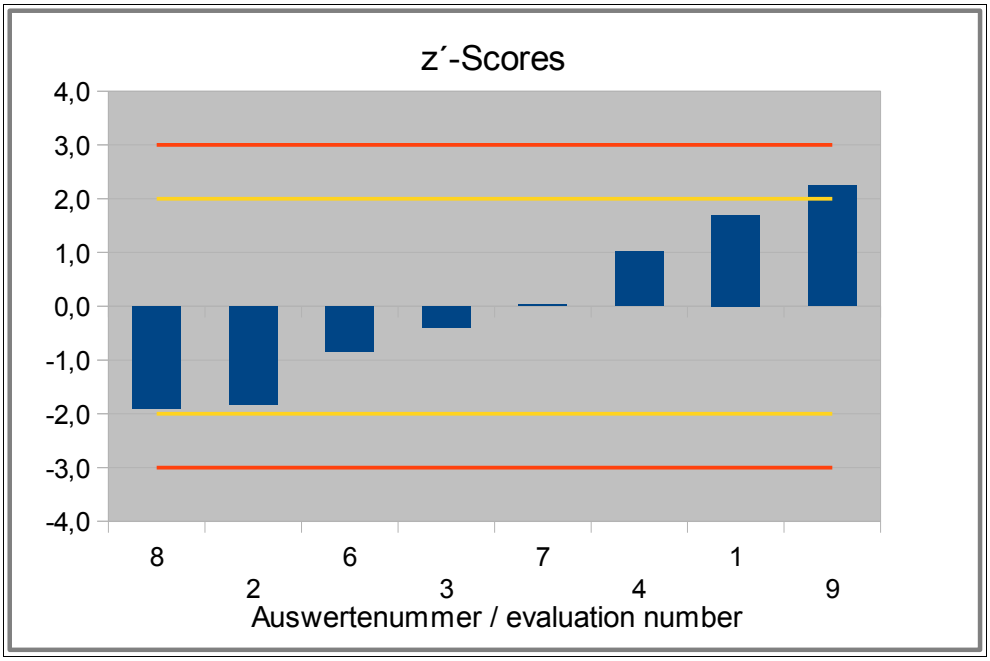

Abb. / Fig. 3: Z-Scores aflatoxine B1

4.2 Total aflatoxins in µg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	7
Number of outliers	1
Mean	1,27
Median	0,845
Robust Mean (X)	**1,10**
Robust standard deviation (S*)	**0,55**
Number with 2 replicates	7
Repeatability SD (S_r)	0,112
Repeatability (CV_r)	8,82%
Reproducibility SD (S_R)	0,879
Reproducibility (CV_R)	69,0%
Target range:	
Target standard deviation σ_{pt}´	**0,357**
Target standard deviation (for Information)	0,295
lower limit of target range	**0,392**
upper limit of target range	**1,82**
Quotient S/σ_{pt}´*	*1,5*
Standard uncertainty $U_{(Xpt)}$	*0,261*
Quotient $U_{(Xpt)}/\sigma_{pt}$´	*0,73*
Results in the target range	*6*
Percent in the target range	*86%*

Comments:

The target standard deviation was evaluated using the model of Horwitz/ Thompson. The distribution of results showed an increased variability. Valuation was done considering the standard uncertainty by z'-score.

The target standard deviation "for information" was calculated from values by perception (ASU §64 L 23.05-2)[20], see 3.6.2.

The distribution of the results showed an increased variability. The quotient S^*/σ_{pt}´ was 1,5. The robust standard deviation is comparable to those of prior PT´s (see 3.6.3). 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 $U(X_{pt})/\sigma_{pt}$´ (0,73) is increased, but is acceptable on the basis of the other characteristics and the use of different methods.

86% of the results were in the target area.

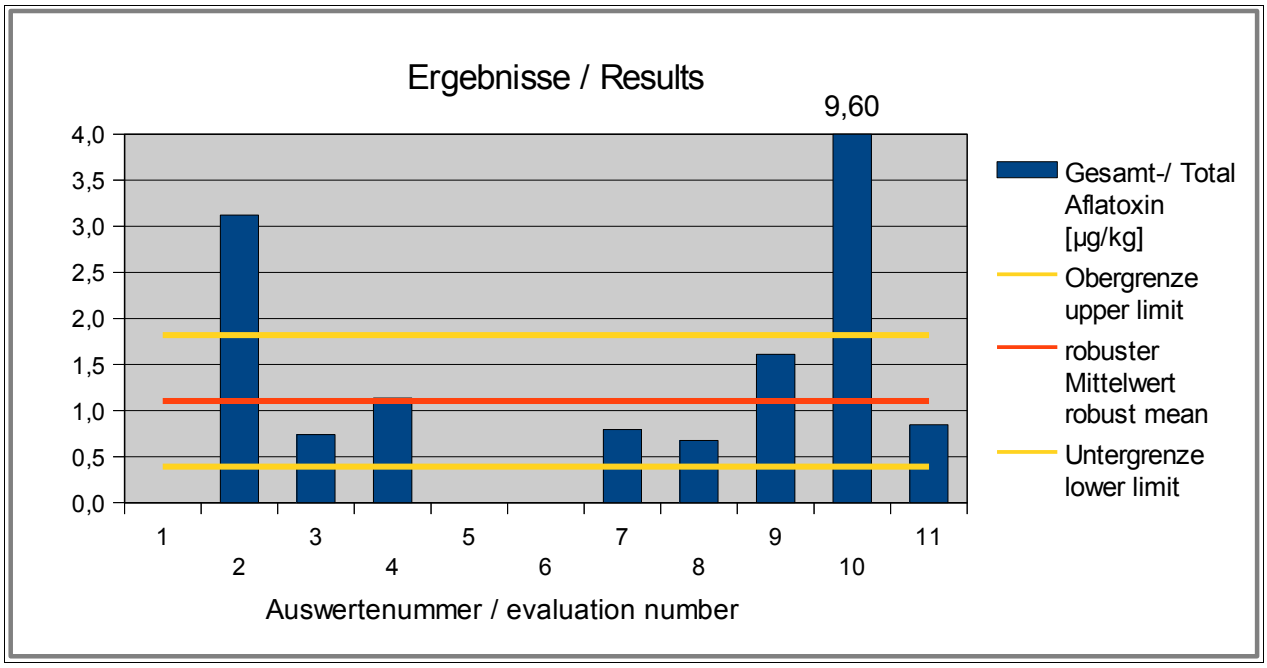

Abb. / Fig. 4: Ergebnisse Gesamt- / Results Total-Aflatoxin

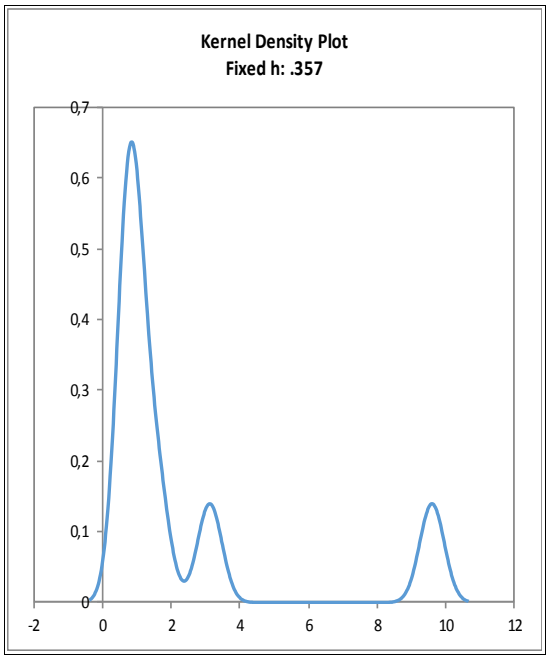

Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse mit h = σ_{pt} von X_{pt} (0,357 µg/kg)

Kernel density plot of results with h = σ_{pt} of X_{pt} (0,357 µg/kg)

Comment:
The kernel density shows a normal distribution of results with two side-peaks at 3,1 and 9,6 µg/kg, which are due to the two outliers.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Gesamt-/ Total Aflatoxin [µg/kg]	Abweichung [µg/kg] Deviation [µg/kg]	z´-Score (σ_{pt})´	z-Score (Info)	Hinweis Remark
1					
2	3,12	2,0	5,7	6,8	Ausreisser / Outlier
3	0,74	-0,4	-1,0	-1,2	
4	1,14	0	0,084	0,10	
5					
6					
7	0,80	0	-0,87	-1,1	
8	0,68	-0,4	-1,2	-1,5	
9	1,61	0,5	1,4	1,7	
10	9,60	8,5	(>12)	(>20)	Ausreisser / Outlier; Farktor 10?; wurde von der Auswertung ausge-schlossen
11	0,845*	-0,3	-0,73	-0,88	

**** Mean calculated by DLA***

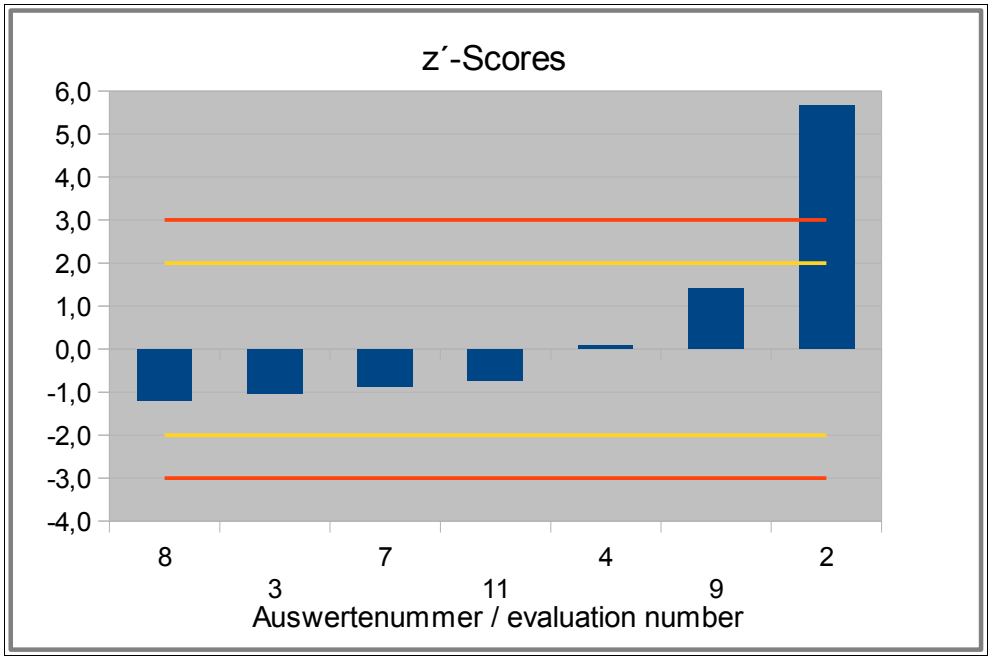

Abb. / Fig. 6: Z´-Scores Gesamt-/ Total-Aflatoxin

4.3 Ochratoxin A in µg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	10
Number of outliers	1
Mean	37,1
Median	33,0
Robust Mean (X)	**34,1**
Robust standard deviation (S*)	**9,05**
Number with 2 replicates	10
Repeatability SD (S_r)	2,37
Repeatability (CV_r)	6,38%
Reproducibility SD (S_R)	15,9
Reproducibility (CV_R)	42,7%
Target range:	
Target standard deviation σ_{pt}	**7,50**
Target standard deviation (for Information)	8,38
lower limit of target range	**19,1**
upper limit of target range	**49,1**
Quotient S/σ_{pt}*	*1,2*
Standard uncertainty $U_{(Xpt)}$	*3,58*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,48*
Results in the target range	*9*
Percent in the target range	*90%*

Anmerkungen zu den Kenndaten:
The target standard deviation was evaluated using the model of Horwitz/ Thompson.

The target standard deviation "for information" was calculated from values by perception (ASU §64 L 15.03-1)[22], see 3.6.2.

The distribution of the results showed a normal variability. The quotient S^*/σ_{pt} was 1,2. The robust standard deviation is comparable to those of prior PT´s (see 3.6.3). 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 $U(X_{pt})/\sigma_{pt}$ (0,48) is slightly above 0,3, but is acceptable on the basis of the other characteristics and the use of different methods.

90% of the results were in the target area.

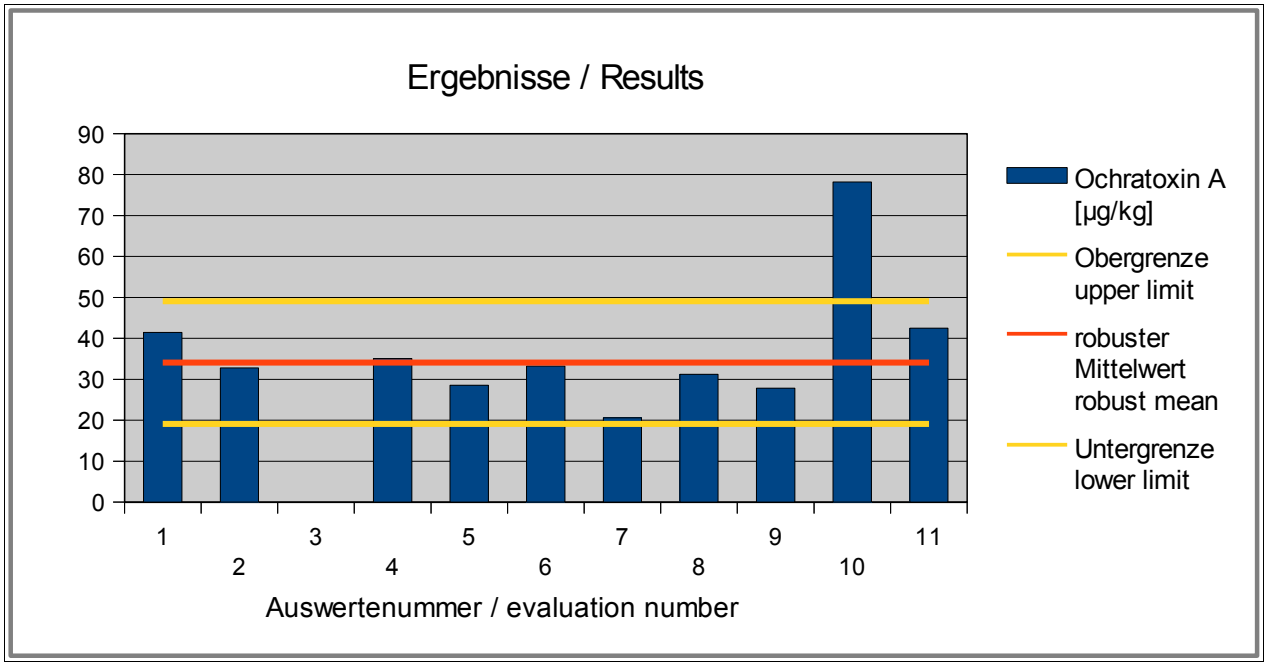

Abb. / Fig. 7: Ergebnisse/ Results Ochratoxin A

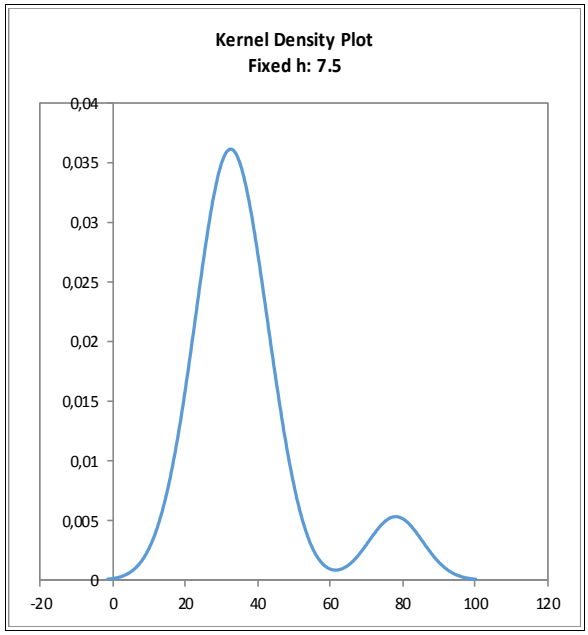

Abb. / Fig. 8:
Kerndichte-Schätzung der Ergebnisse mit h = σ_{pt} von X_{pt} (7,5 µg/kg)

Kernel density plot of results with h = σ_{pt} of X_{pt} (7,5 µg/kg)

Comment:
The kernel density shows a normal distribution of results with a sidepeak at 80 µg/kg, which is due to the outlier.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Ochratoxin A [µg/kg]	Abweichung [µg/kg] Deviation [µg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	41,5	7,39	1,0	0,88	
2	32,8	-1,31	-0,17	-0,16	
3					
4	35,1	1,01	0,13	0,12	
5	28,6	-5,54	-0,74	-0,66	
6	33,2	-0,89	-0,12	-0,11	
7	20,6	-13,5	-1,8	-1,6	
8	31,2	-2,89	-0,39	-0,34	
9	27,8	-6,29	-0,84	-0,75	
10	78,2	44,1	5,9	5,3	Ausreisser / Outlier
11	42,5	8,41	1,1	1,0	

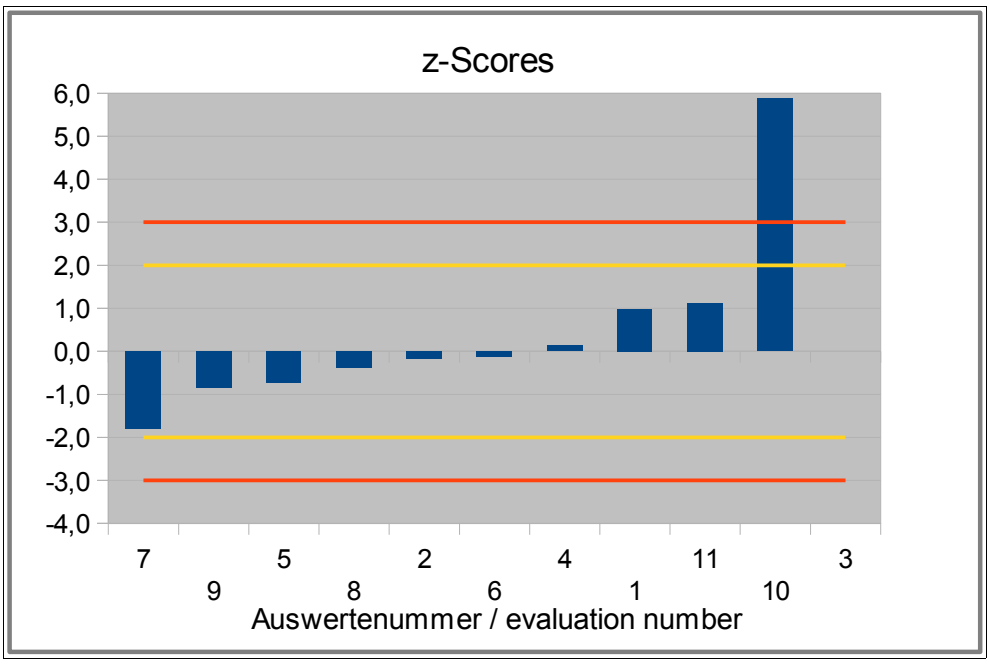

Abb. / Fig. 9: Z-Scores Ochratoxin A

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 Aflatoxin B1

Teilnehmer	Probe A DLA Nr.	Probe B DLA Nr.	Datum der Analyse	Ergebnis	Ergebnis Probe A	Ergebnis Probe B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate
Participant	Sample A DLA no.	Sample B DLA no.	Date of analysis	Result	Result samole A	Result sample B	Limit of determination	Incl. RR	Recovery-rate
			day/ month	µg/kg	µg/kg	µg/kg	µg/kg	yes/no	in %
1	14	61	27.06.17	1,25	1,25	1,25	0,2	yes	100
2	8	67	08.06.17	0,281	0,316	0,246		no	80
3	5	70	27.06.17	0,675	0,66	0,69		no comparable data for spice mixture	85% for peanut
4	30	45	08.06.17	1,065	1,19	0,94	0,1	yes	65,4
5	10	65	27.06.17	not determined	not determined	not determined	1 ug/kg	no	
6	15	60	22/06	< LOQ	0,6	0,5	1,6	yes	85
7	7	68	22.06.17	0,795	0,816	0,774	0,1	no	96
8	33	42	08.06.17	0,262	0,289	0,235			
9	2	73	06.06.	1,40	1,36	1,44	0,15	no	74
10	32	43							
11	22	53							

5.1.1.2 Total Aflatoxin

Teilnehmer	Probe A DLA Nr.	Probe B DLA Nr.	Datum der Analyse	Ergebnis	Ergebnis Probe A	Ergebnis Probe B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate
Participant	Sample A DLA no.	Sample B DLA no.	Date of analysis	Result	Result samole A	Result sample B	Limit of determination	Incl. RR	Recovery-rate
			day/ month	µg/kg	µg/kg	µg/kg	µg/kg	yes/no	in %
1	14	61							
2	8	67	08.06.17	3,123	3,274	2,971		no	80
3	5	70		0,74	0,73	0,75		no comparable data for spice mixture	85% for peanut
4	30	45	08.06.17	1,135	1,26	1,01	0,4	ja	---
5	10	65	27.06.17	not determined	not determined	not determined	1 ug/kg	no	
6	15	60	22/06	0,0	0,0	0,0			
7	7	68	22.06.17	0,795	0,816	0,774	0,1	no	96
8	33	42	08.06.17	0,676	0,691	0,661			
9	2	73	06.06.	1,61	1,54	1,67	n.a.	no	n.a.
10	32	43	02.06.17	9,6	9,7	9,4	2	no	
11	22	53	06./27./28 .06.	<1	0,87	0,82	1	no	

5.1.1.3 Aflatoxin B2

Teilnehmer	Probe A DLA Nr.	Probe B DLA Nr.	Datum der Analyse	Ergebnis	Ergebnis Probe A	Ergebnis Probe B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate
Participant	Sample A DLA no.	Sample B DLA no.	Date of analysis	Result	Result samole A	Result sample B	Limit of determinatio n	Incl. RR	Recovery-rate
			day/ month	µg/kg	µg/kg	µg/kg	µg/kg	yes/ no	in %
1	14	61	27.06.17						
2	8	67	08.06.17	0,281	0,316	0,245		no	80
3	5	70		0,065	0,07	0,06		no comparable data for spice mixture	85% for peanut
4	30	45	08.06.17	0,11	0,13	< 0,1	0,1	yes	69,2
5	10	65	27.06.17	not determined	not determined	not determined	1 ug/kg	no	
6	15	60	22/06	< LOQ	0,1	0,1	0,5	yes	85
7	7	68	22.06.17	<0.1	<0.1	<0.1	0,1	no	100
8	33	42	08.06.17	0,052	0,045	0,058			
9	2	73	06.06.	0,21	0,18	0,23	0,1	no	86
10	32	43							
11	22	53							

5.1.1.4 Aflatoxin G1

Teilnehmer	Probe A DLA Nr.	Probe B DLA Nr.	Datum der Analyse	Ergebnis	Ergebnis Probe A	Ergebnis Probe B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate
Participant	Sample A DLA no.	Sample B DLA no.	Date of analysis	Result	Result samole A	Result sample B	Limit of determination	Incl. RR	Recovery-rate
			day/ month	µg/kg	µg/kg	µg/kg	µg/kg	yes/ no	in %
1	14	61	27.06.17						
2	8	67	08.06.17	0,635	0,708	0,562		no	80
3	5	70	-	-	-	-		no comparable data for spice mixture	85% for peanut
4	30	45	08.06.17	< 0,1	< 0,1	< 0,1	0,1	yes	84,9
5	10	65	27.06.17	not determined	not determined	not determined	1 ug/kg	no	
6	15	60	22/06	< LOD	0,0	0,0	1,6	yes	74
7	7	68	22.06.17	<0.1	<0.1	<0.1	0,1	no	98
8	33	42	08.06.17	0,363	0,357	0,368			
9	2	73	06.06.	< LOQ	< LOQ	< LOQ	0,15	no	n.a.
10	32	43							
11	22	53							

5.1.1.5 Aflatoxin G2

Teilnehmer	Probe A DLA Nr.	Probe B DLA Nr.	Datum der Analyse	Ergebnis	Ergebnis Probe A	Ergebnis Probe B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate
Participant	Sample A DLA no.	Sample B DLA no.	Date of analysis	Result	Result samole A	Result sample B	Limit of determination	Incl. RR	Recovery-rate
			day/ month	µg/kg	µg/kg	µg/kg	µg/kg	yes/ no	in %
1	14	61	27.06.17						
2	8	67	08.06.17	1,926	1,934	1,918		no	80
3	5	70	-	-	-	-		no comparable data for spice mixture	85% for peanut
4	30	45	08.06.17	< 0,1	< 0,1	< 0,1	0,1	yes	67,4
5	10	65	27.06.17	not determined	not determined	not determined	1 ug/kg	no	
6	15	60	22/06	< LOQ	0,3	0,4	0,5	yes	68
7	7	68	22.06.17	<0.1	<0.1	<0.1	0,1	no	72
8	33	42	08.06.17	< 0,010	< 0,010	< 0,010			
9	2	73	06.06.	< LOQ	< LOQ	< LOQ	0,1	no	n.a.
10	32	43							
11	22	53							

5.1.1.6 Ochratoxin A

Teilnehmer	Probe A DLA Nr.	Probe B DLA Nr.	Datum der Analyse	Ergebnis	Ergebnis Probe A	Ergebnis Probe B	Bestimmungs-grenze	Inkl. WF	Wiederfin-dungsrate
Participant	Sample A DLA no.	Sample B DLA no.	Date of analysis	Result	Result samole A	Result sample B	Limit of determinatio n	Incl. RR	Recovery-rate
			day/ month	µg/kg	µg/kg	µg/kg	µg/kg	ye/ no	in %
1	14	61	27.06.17	41,48	42,28	40,67	1	yes	100
2	8	67	08.06.17	32,78	34,66	30,9		no	80
3	5	70							
4	30	45	08.06.17	35,1	33,7	36,5	1	yes	68,3
5	10	65	27.06.17	28,55	30,5	26,6	1 ug/kg	no	
6	15	60	22/06	33,2	36,2	30,2	4	yes	94
7	7	68	01.06.17	20,6	20,7	20,5	1	no	95
8	33	42	13.06.17	31,2	30,1	32,2	2		
9	2	73	12.06.	27,8	27,6	28	2	no	79
10	32	43	02.06.17	78,2	79,5	76,9	2	no	
11	22	53	06./28./29 .6./30.6.	42,5	40	45	2	no	

5.1.2 Analytical methods

5.1.2.1 Aflatoxin B1

Teil-nehmer	Methodenbeschreibung	Probenvorberei-tung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfin-dung mit gleicher Matrix	Methode akkredi-tiert	Sonstige Hinweise
Parti-cipant	Method description	Sample preparati-on	Measuring me-thod	Calibration and reference material	Recovery with same matrix	Method accredi-ted	Further re-marks
					yes/no	yes/no	
1		Extraction with ACN/H2O; cleaning with MycoSep	LC-MS/MS	Call. with std Fa. ROMER-Labs	yes	yes	Internal std: 13C17 Aflatoxin B1
2	In-house method, LC-MS/MS			yes	yes	yes	
3	Determination HPLC with IAC				no	no	Routine analyse only for peanuts
4	PV 2.019/004-07	---	---	---	yes	yes	---
5	internal method	IAC clean up	PFP chromatography with MS/MS detection	External calibration, Ochratoxin A and Aflatoxins B1, B2, G1, G2	no	yes	
6		IAC	HPLC-FLD	ext. Calibration	no	yes	
7	Extraction: 10.0 g sample + 1 g NaCl, Extraction with 600 ml MeOH/H2O (80+20 v/v). Extract filtered. 5 ml sample extract with 20 ml TWEEN-20 10% sol. diluted. Than IAC-cleaning and elution of the Toxins in methanol. The eluate completed with dest. Water to 5.0 ml and the solution filtered. The quantitativ determination with RP-C18 HPLC and fluorescence detection (Ex 362 nm, Em 440 nm) after electrochemical postcolumn derivatisation (COBRA cell).	see method indications	SLMB 1374	Method extern standard. Refernce material: Aflatoxin B1 2.0 mg/ml in CH3CN, Sigma-Aldrich, 34029 Oekanal, 2 ml; Aflatoxin B2 0.5 mg/ml in CH3CN, Sigma-Aldrich, 34034, Oekanal, 2 ml; Aflatoxin G1 2.0 mg/ml in CH3CN, Sigma-Aldrich, 34032, Oekanal, 2 ml; Aflatoxin G2 0.5 mg/ml in CH3CN, Sigma -Aldrich, 34033, Oekanal, 2 ml; Ochratoxin A solution 10 mg/ml in CH3CN, Sigma -Aldrich, 34037, Oekanal, 2 ml	yes	yes	
8	ASU L 15.00-2 mod.	AflaStar-IAC COIAC 1000	HPLC (Fluorescence detection)	DLA 16-2014		yes	
9	In-house method, following Ph. Eur.	n.a.	HPLC-FLD	n.a.	yes	yes	n.a.
10							
11							

IAC = Immunoaffinity column

5.1.2.2 Gesamt-Aflatoxine

Teil-nehmer	Methodenbes-chreibung	Proben-vorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfind-ung mit gleicher Matrix	Methode akkredit-iert	Sonstige Hinweise
Parti-cipant	Method descrip-tion	Sample prepara-tion	Measuring method	Calibration and reference material	Recovery with same matrix	Method ac-credited	Further remarks
					yes/ no	ja / nein	
1							
2	In-house method, LC-MS/MS			yes	yes	yes	
3	Determination HPLC with IAC				no	no	Routine analyse only for peanuts
4	PV 2.019/004-07	---	---	---	yes	yes	---
5	Internal method	Cleaning with IAC	PFP Chromatography with MS/MS detection	External calibration, Ochratoxin A and Aflatoxins B1, B2, G1, G2	no	yes	
6							calculation parameters
7					yes	yes	
8	ASU L 15.00-2 mod.	AflaStar-IAC COIAC 1000	HPLC (Fluorescence detector)	DLA 16-2014		yes	
9	In-house method following Ph. Eur.	n.a.	HPLC-FLD	n.a.	yes	yes	n.a.
10		2,5g / 25ml 70% methanol	ELISA			no	The strongly coloured matrix (curcuma powder?) had been very disturbed both in ELISA and in HPLC!
11	Veratox® HS Aflatoxin-Kit	Extraction with Säule Neogen					

IAC = Immunoaffinity column

5.1.2.3 Ochratoxin A

Teil-nehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference material	Recovery with same matrix	Method accredited	Further remarks
					ja / nein	ja / nein	
1		Extraction with ACN/H2O; cleaning with MycoSep	LC-MS/MS	call. with std. Fa. ROMER-Labs	yes	yes	Internal std: 13C20 Ochratoxin A
2	In-house method, LC-MS/MS			yes	yes	yes	
3							
4	PV 2.019/001-07	---	---	---	yes	yes	---
5	Internal method	cleaning with IAC	PFP Chromatography with MS/MS detection	External calibration, Ochratoxin A and Aflatoxins B1, B2, G1, G2	no	yes	
6		IAC	HPLC-FLD	ext. Calibration	no	yes	
7	Extraction: 10 g sample with 80 ml extraction sol. (MeOH/ 3% Natriumhydrogencarbonatlsg. 50+50 v/v). Extraction and filter with glass filter (alternativly centrifuging). Wash 10 ml filtrate with CH2Cl2. Dilute 5 ml aqueous phase with 100 ml PBS-buffer sol. Than IAC (ca. 1 drops/s). Elution with methanol, drying at Rotavapor. Dissolve residue in 0.500 ml mobile phase. Quantitative determination with RP-C18 HPLC und Fluorescence detection (Ex 330 nm, Em 470 nm)	see method data	SLMB 1387		yes	yes	
8	ASU L 15.00-1/1 mod.	OchraStar-IAC COIAC 2000	HPLC (Fluorescence detektor)	DLA 16-2014		yes	
9	Method according to Ph. Eur.	n.a.	HPLC-FLD	n.a.	yes	yes	n.a.
10		5g / 40ml 50% Methanol	ELISA			no	The strongly coloured matrix (curcuma powder?) had been very disturbed both in ELISA and in HPLC!
11	Veratox® Ochratoxin-Kit						

IAC = Immunoaffinity column

5.2 Homogeneity

5.2.1 Homogeneity of the bottled PT-samples

Homogeneity test using the determination of Ochratoxin A by means of HPLC/ immunoaffinity processing (ASU §64 L 15.00-1 / 1):

Samples:

PT-material after bottling
(Ochratoxin A)

Wiederholmessungen	µg/kg	
# 06	33,7	
# 17	30,7	
# 29	32,3	
# 54	34,6	
# 72	29,4	
Mean:	32,1	
Repeated standard deviation:	2,1	≙ 6,6 %

5.2.2 Comparison of sample number/test results and trend line

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

Ochratoxin A			
Target standard deviation σ_{pt}	7,50		
Sample numbers	2 - 73		
Total numbers of samples	18		
Slope	0,113		
Trend line range	33,6	-	31,6
Deviation trend line	32,6	±	1,0
Percent of σpt	13,6	%	

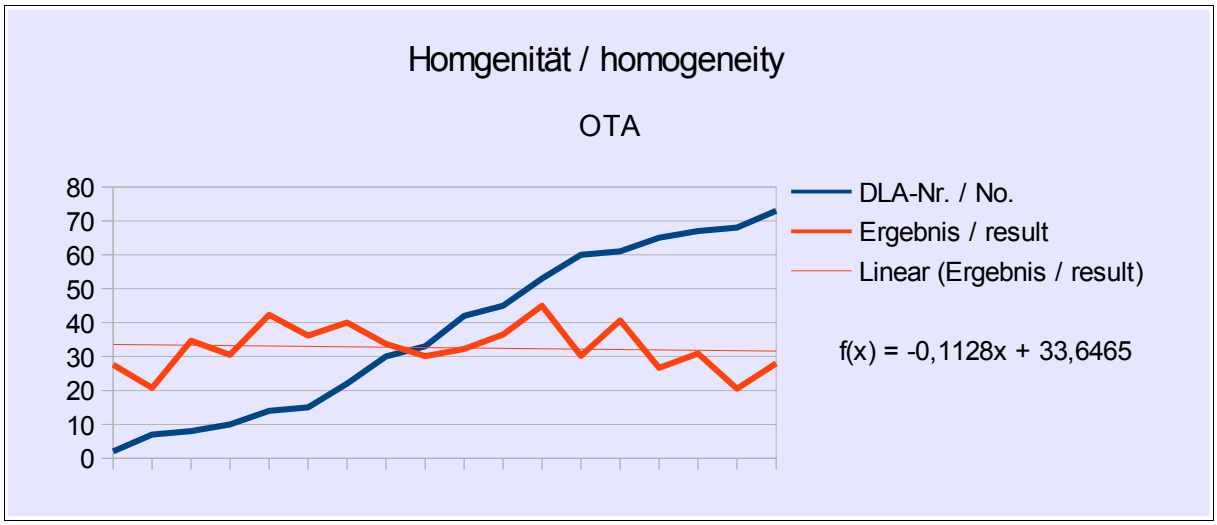

Abb./Fig. 10:
Trendfunktion Probennummern vs. Ergebnisse
trend line function sample number vs. results

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 25-2017***
PT name	***Aflatoxins + Ochratoxin A in Spice Mixture***
*Sample matrix**	*Samples A + B:* ***Spice Mixture***
Number of samples and sample amount	*2 identical samples A + B, 50 g each.*
Storage	*Samples A + B: cooled 2 - 10°C*
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative:* ***Aflatoxin B1, B2, G1, G2 + Ochratoxin A***
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	*µg/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* ***June 30th 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
		Switzerland
		Deutschland
		USA
		Deutschland
		Switzerland
		Deutschland
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[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

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