Proficiency Tests
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Evaluation Report
proficiency test

DLA 36/2017

Determining the quality of spice: Dry matter, total ash, acid insoluble ash and volatile oil in spice

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

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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 evaluation numbers in the PT report. Data of individual participants will be passed on to third parties only with prior consent of the participant.

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1. Introduction

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

2. Realisation

2.1 Test material

The test material is a mixture (from European suppliers) of the spice caraway (whole seeds) with the spice fennel (whole seeds) for homogeneity verification.
Fennel content in the mixture: 1,25%.

The raw materials were combined and homogenized.

Approximately 4 kg of the material was packaged in about 100 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 **Tracer analysis**. It is a standardized method that is part of the international GMP certification system for feed [14].

Before mixing, fennel seeds 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 and based on the normal distribution using the HorRat value. For the evaluation according to Poisson: A probability of ≥ 5 % is equivalent to a good homogeneous mixture and of ≥ 25% to an excellent mixture [14, 15]. For the evaluation according to the normal distribution: According to [16, 17], the HorRat values between 0,3 and 1,3 are to be accepted under repeatability conditions (measurements within the laboratory).

The tracer analysis of the present PT sample showed probability of 100%. 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 1,1. The results of tracer 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 0,45% for dry matter, 0,96% for total ash and 3,82% for volatile oil. 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 to 4.4).

Furthermore, the homogeneity was characterized by the **trend line function of participants' results for chronological bottled single samples**. The maximum deviations for total ash from the mean value of the trend line was in the range of 20% 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) 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 34th week of 2017. The testing method was optional. The tests should be finished at October 20th 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 10 participants, 9 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 evaluation of acid insoluble ash and volatile oil the target standard deviation of a precision experiment (see 3.6.2/ table 2) was applied. For information, the target standard deviation of the general model according to Horwitz (see 3.6.1) was given.

For the evaluation of dry matter and total ash the target standard deviation from the general model of Horwitz (s. 3.6.1) was applied. For information, the target standard deviation of a precisions experiment (see 3.6.2) was given.

The specified statistical data for the evaluation of "Acid insoluble ash" are given only for information, since only 5 participant results were available.

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} [18 – 20, 22].

Parameter	Matrix	Mean (g/100g)	RSD_r (%)	RSD_R (%)	σ_{pt} (g/100g)	Method / Literature
Vol. oil	Oregano	1,91	9,2	27,2	0,95	18/ Distillation
Vol. oil	Clove	14,0	14,0	26,3	0,87	18/ Distillation
Vol. oil	Black pepper	2,62	11,7	30,3	1,05[1]	18/ Distillation
Water/ (dry matter)	Nutmeg	6,0 (94,0)	5,17	9,17	7,59[1]	19/ Distillation
Water/ (dry matter)	Parsley	4,8 (95,2)	7,08	15,8	13,5	19/ Distillation
Mass loss	Coffee essence	3,24	3,3	9,6	8,40	22/ drying 95°C
Mass loss	Coffee essence	3,77	4,7	8,2	6,76	22/ drying 95°C
Mass loss	Coffee essence	4,58	2,3	8,9	7,89	22/ drying 95°C
Total ash	Oregano	8,96	7,6	11,3	0,55	20/gravimetric
Total ash	Clove	5,06	3,6	4,8	0,23[1]	20/gravimetric
Total ash	Black pepper	4,49	4,19	8,19	0,42	20/gravimetric
Acid insol. ash	Oregano	0,99	44,1	57,3	0,13[1]	20/gravimetric
Acid insol. ash	Clove	0,041	168	331	0,82	20/gravimetric
Acid insol. ash	Black pepper	0,079	73,4	134	0,33	20/gravimetric

[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].

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 Dry matter in g/100g

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	90,2
Median	89,9
Robust Mean (X)	**90,2**
Robust standard deviation (S*)	**1,24**
Number with 2 replicates	7
Repeatability SD (S_r)	0,409
Repeatability (CV_r)	0,453%
Reproducibility SD (S_R)	1,17
Reproducibility (CV_R)	1,29%
Target range:	
Target standard deviation σ_{pt}	**1,83**
Target standard deviation (for Information)	7,59
lower limit of target range	**86,6**
upper limit of target range	**93,9**
Quotient S/σ_{pt}*	*0,68*
Standard uncertainty $U_{(Xpt)}$	*0,549*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,30*
Results in the target range	*8*
Percent in the target range	*100%*

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. For information, the target standard deviation from a precision (ASU § 64 LFGB L 53.00-8) experiment was given.

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

Repeatability- and reproducibility standard deviation are considered low.

The quotient $U(X_{pt})/\sigma_p$ (0,30) is not increased.

100% of the results were in the target area.

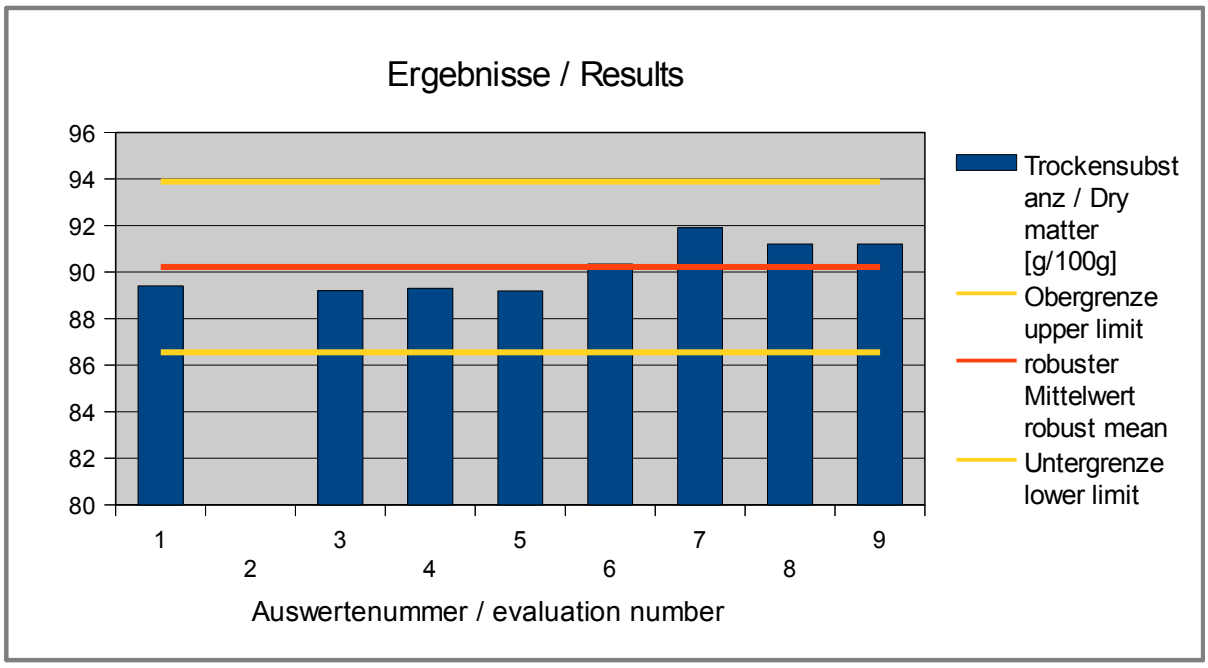

Abb. / Fig. 1: Ergebnisse Trockensubstanz / Results dry matter

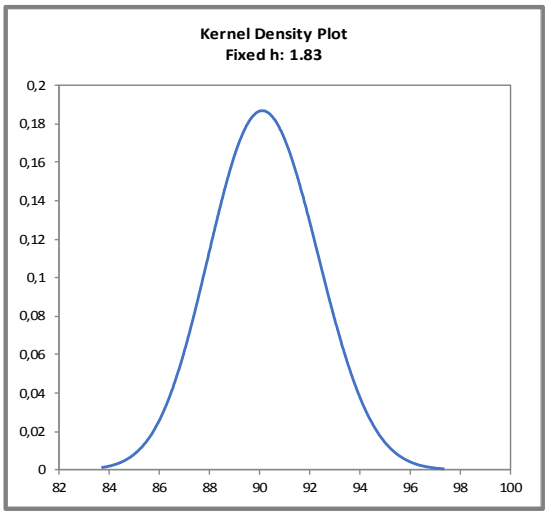

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = σ_{pt} von X_{pt}

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

Comment:
The kernel density shows a normal distribution of the results.

Ergebnisse der teilnehmenden Institute:
Results of Participants:

Auswerte-nummer Evaluation number	Trockensubstanz / Dry matter [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	89,4	-0,819	-0,45	-0,11	
2					
3	89,2	-1,02	-0,56	-0,13	
4	89,3	-0,919	-0,50	-0,12	
5	89,2	-1,03	-0,56	-0,14	
6	90,4*	0,131	0,072	0,017	
7	91,9	1,69	0,92	0,22	
8	91,2	0,981	0,54	0,13	
9	91,2	0,981	0,54	0,13	

** Mean calculated by DLA*

Abb. / Fig. 3: Z-Scores Trockensubstanz / dry matter

4.2 Total ash in g/100g

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	9
Number of outliers	0
Mean	5,55
Median	5,54
Robust Mean (X)	**5,55**
Robust standard deviation (S*)	**0,230**
Number with 2 replicates	8
Repeatability SD (S_r)	0,0528
Repeatability (CV_r)	0,956%
Reproducibility SD (S_R)	0,219
Reproducibility (CV_R)	3,97%
Target range:	
Target standard deviation σ_{pt}	**0,172**
Target standard deviation (for Information)	0,226
lower limit of target range	**5,21**
upper limit of target range	**5,89**
Quotient S/σ_{pt}*	*1,3*
Standard uncertainty $U_{(Xpt)}$	*0,096*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,56*
Results in the target range	*9*
Percent in the target range	*100%*

Comments:

For the valuation the target standard deviation from the general model of Horwitz (s. 3.6.1) was applied. For information, the target standard deviation of a precision experiment (ASU §64 53.00-4) was given.

The quotient S^*/σ_{pt} was 1,3. The comparability of results is given.

Repeatability- and reproducibility standard deviation are low.

The quotient $U(X_{pt})/\sigma_{pt}$ (0,56) is over 0,3, but is acceptable on the basis of the other characteristics and the use of different methods.

100% of the results were in the target area.

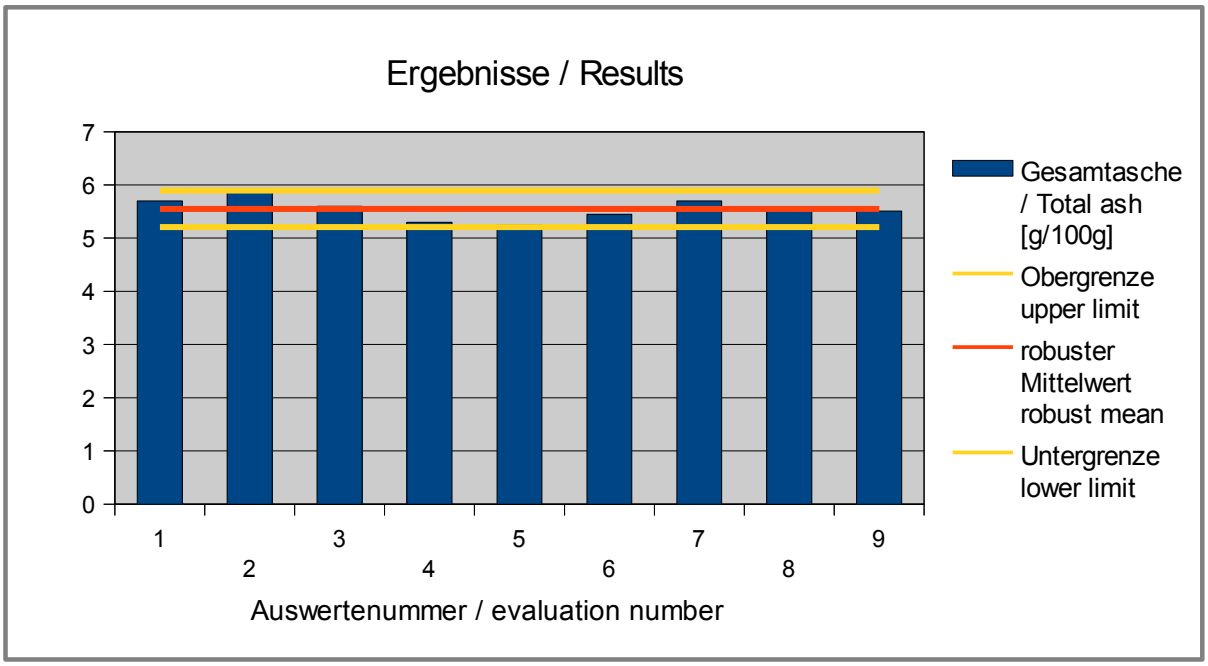

Abb. / Fig. 4: Ergebnisse Gesamtasche / Results total ash

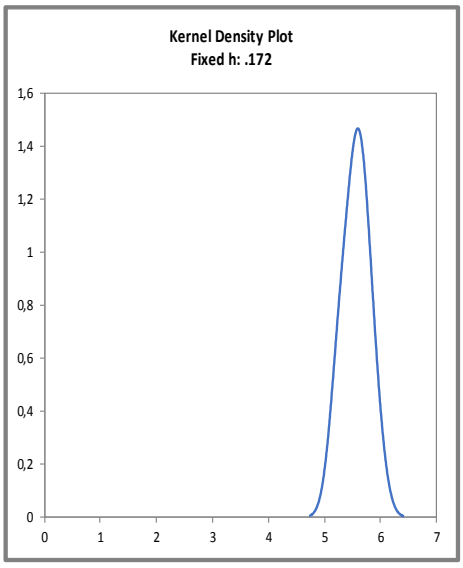

Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse mit h = σ_{pt} von X_{pt}

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

Comment:
The kernel density shows a normal distribution of results.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Gesamtasche / Total ash [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	5,70	0,150	0,88	0,67	
2	5,90	0,350	2,0	1,6	
3	5,60	0,0503	0,29	0,22	
4	5,30	-0,250	-1,5	-1,1	
5	5,25	-0,297	-1,7	-1,3	
6	5,45*	-0,100	-0,58	-0,44	
7	5,70	0,150	0,88	0,67	
8	5,54	-0,0097	-0,06	-0,04	
9	5,51	-0,0397	-0,23	-0,18	

** Mean calculated by DLA*

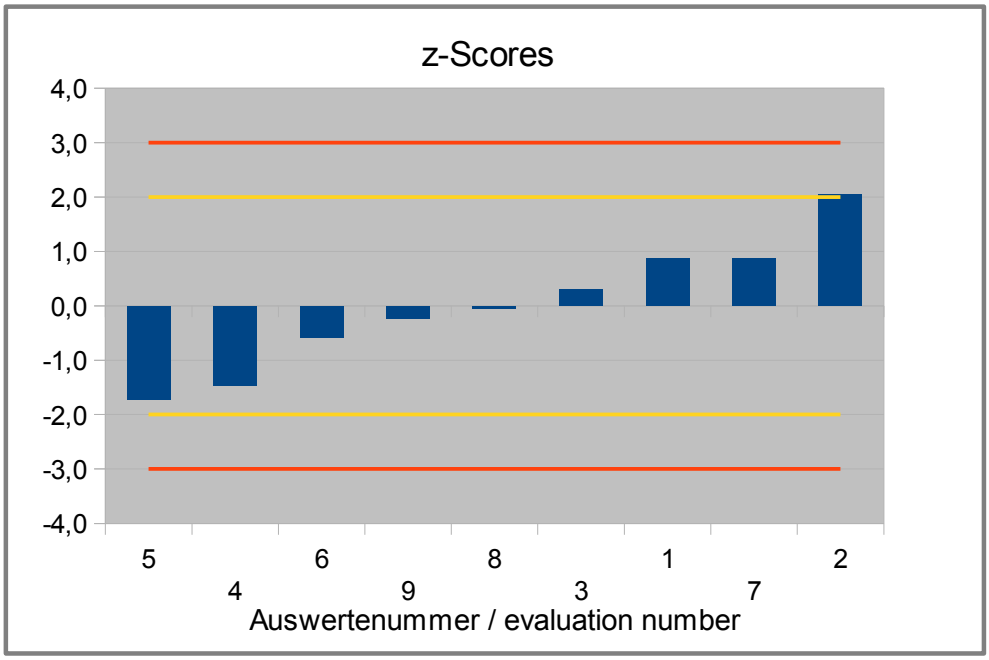

Abb. / Fig. 6: Z-Scores Gesamtasche / total ash

4.3 Acid insoluble ash in g/100g

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	0,102
Median	0,065
Robust Mean (X)	**0,102**
Robust standard deviation (S*)	**0,0929**
Number with 2 replicates	4
Repeatability SD (S_r)	0,00815
Repeatability (CV_r)	7,92%
Reproducibility SD (S_R)	0,0813
Reproducibility (CV_R)	79,0%
Target range:	
Target standard deviation σ_{pt}	**0,0492**
Target standard deviation (for Information)	0,00577
lower limit of target range	**0,00395**
upper limit of target range	**0,201**
Quotient S/σ_{pt}*	*1,9*
Standard uncertainty $U_{(Xpt)}$	*0,052*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*1,1*
Results in the target range	*5*
Percent in the target range	*100%*

Comments:

The calculated statistical data are given only informative, since only 5 results were available for the evaluation.

For the evaluation the target standard deviation of a precision experiment (ASU §64 53.00-4) was applied. For information, the target standard deviation from the general model of Horwitz (s. 3.6.1) was given.

The distribution of the results showed acceptable variability for the method and the proximity to the limit of determination. The quotient S^*/σ_{pt} was 1,9. The comparability of results is given (due to the small number of participants "with reservations"). The Repeatability standard deviation should be considered inconspicuous and the reproducibility standard deviation as high, but comparable to the ASU values.
The quotient $U(X_{pt})/\sigma_{pt}$ (1,1) is increased.

100% of the results were in the target area. For three participants the result was below the limit of quantitation of 0,1 g/100g.

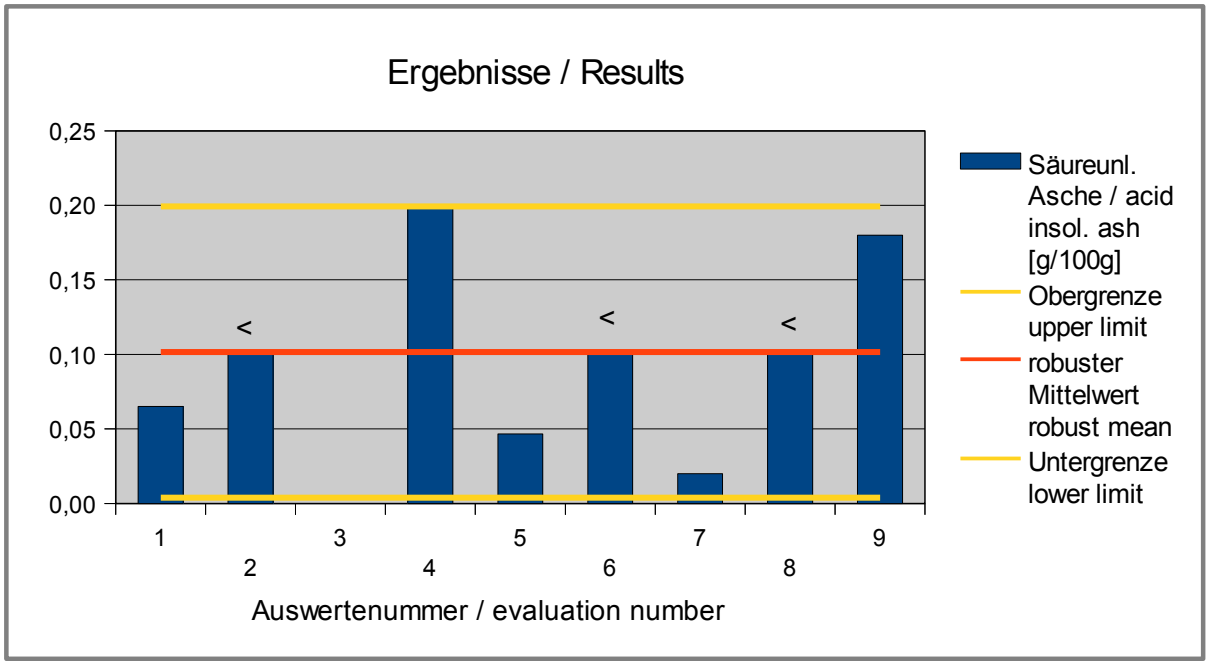

Abb. / Fig. 7: Ergebnisse Säureunlösliche Asche / Results acid insoluble ash

Abb. / Fig. 8:
Kerndichte-Schätzung der Ergebnisse

Kernel density plot of results

Comment:
The kernel density could not be performed due to the small number of participants.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Säureunl. Asche / acid insol. ash [g/100g]	Abweichung [g/100g] Deviation [g/100g]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,0650	-0,200	-1,6	-15	
2	< 0,1				
3					
4	0,200	-0,0645	-0,51	-5,0	
5	0,0466	-0,218	-1,7	-17	
6	< 0,1*				
7	0,0200	-0,245	-1,9	-19	
8	<0,1				
9	0,180	-0,0845	-0,66	-6,5	

** Mean calculated by DLA*

The calculated statistical data are given only informative, since only 5 results were available for the evaluation.

4.4 Volatile oil in ml/100g DM

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	7
Number of outliers	1
Mean	3,87
Median	3,51
Robust Mean (X)	**3,59**
Robust standard deviation (S*)	**0,939**
Number with 2 replicates	7
Repeatability SD (S_r)	0,139
Repeatability (CV_r)	3,82%
Reproducibility SD (S_R)	0,917
Reproducibility (CV_R)	25,3%
Target range:	
Target standard deviation σ_{pt}	**1,05**
Target standard deviation (for Information)	0,118
lower limit of target range	**1,50**
upper limit of target range	**5,68**
Quotient S/σ_{pt}*	*0,90*
Standard uncertainty $U_{(Xpt)}$	*0,444*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,42*
Results in the target range	*6*
Percent in the target range	*85,7%*

Comments:

For the evaluation the target standard deviation of a precision experiment (ASU §64 53.00-10) was applied. For information, the target standard deviation from the general model of Horwitz (s. 3.6.1) was given.

The quotient S^*/σ_{pt} was 0,90. The comparability of results is given.

Repeatability- and reproducibility standard deviation should be considered inconspicuous.

The quotient $U(X_{pt})/\sigma_{pt}$ (0,42) is over 0,3, 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.

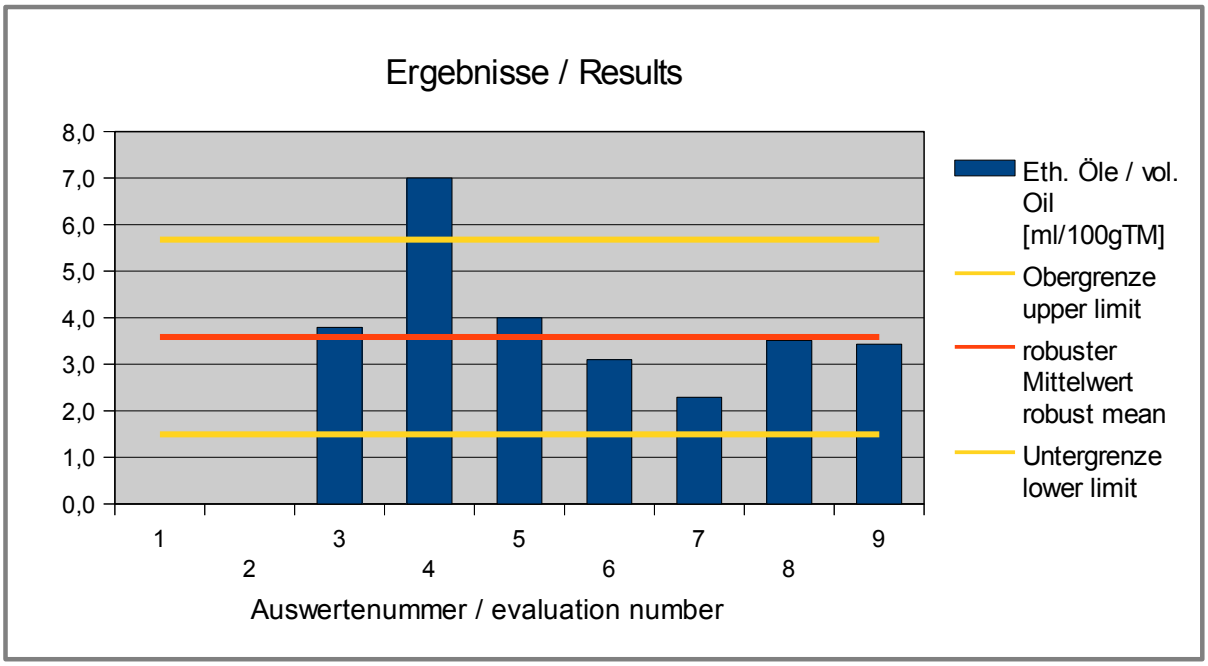

Abb. / Fig. 9: Ergebnisse Etherische Öle / Results volatile oil

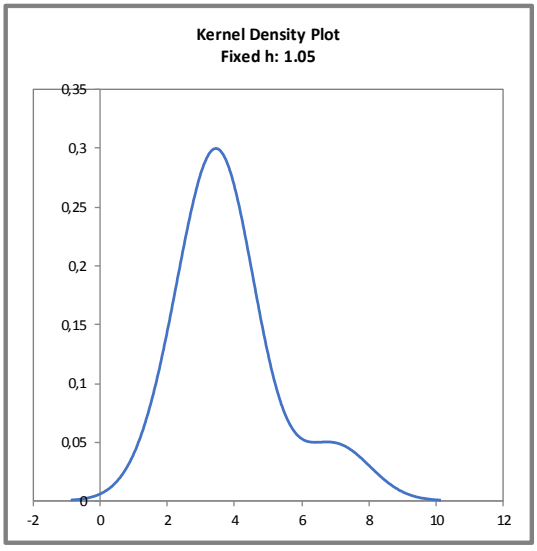

Abb. / Fig. 10:
Kerndichte-Schätzung der Ergebnisse mit h = σ_{pt} von X_{pt}

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 7 ml/100gDM, due to the result outside the target range (outlier).

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Eth. Öle / vol. Oil [ml/100gTM]	Abweichung [ml/100gTM] Deviation [ml/100gTM]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1					
2					
3	3,79	0,204	0,19	1,7	
4	7,00	3,41	3,3	29	Ausreisser / Outlier
5	4,00	0,414	0,40	3,5	
6	3,10*	-0,486	-0,47	-4,1	
7	2,29	-1,30	-1,2	-11	
8	3,51	-0,0764	-0,073	-0,65	
9	3,43	-0,156	-0,15	-1,3	

** Mean calculated by DLA*

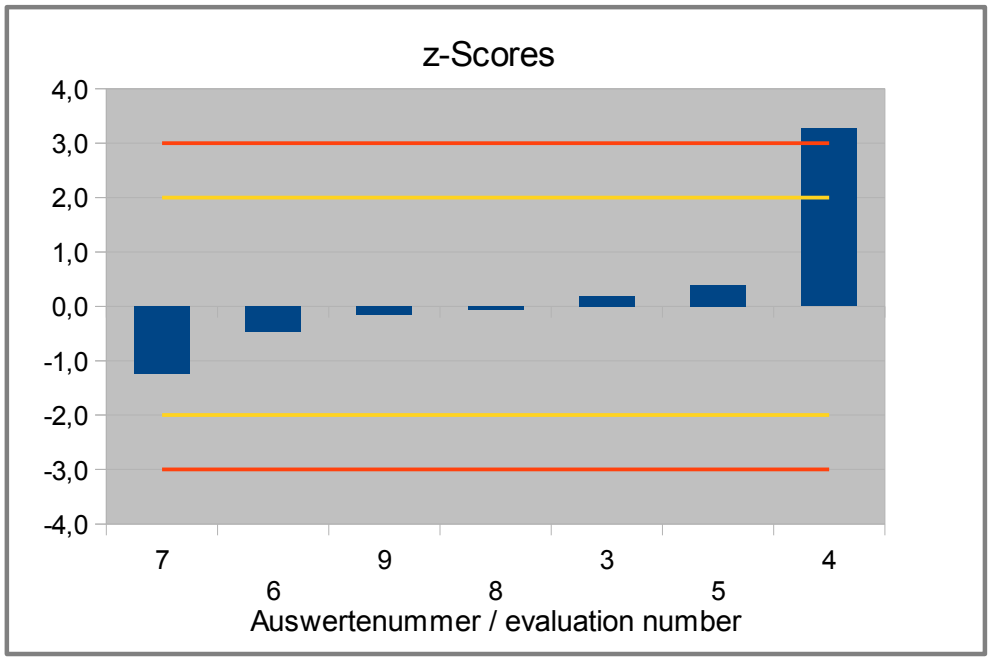

Abb. / Fig. 11: Z-Scores Etherische Öle / volatile oil

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 Dry matter

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestim-mungsgrenze	Inkl. WF	Wiederfin-dungsrate [%]
Participant	**Sample No. A**	**Sample No. B**	**Date of analysis**	**Result (Mean)**	**Result A**	**Result 2**	**Limit of quantifica-tion**	**Incl. RR**	**Recovery rate** [%]
			Day/Month	g/100g	g/100g	g/100g	g/100g	yes/no	in %
1	18	22	30. Aug	89,4				no	
2	11	29	-	-	-	-	-	-	-
3	5	35	October	89,2	89,2	89,2		no	
4	1	39	29/08	89,3	89,2	89,4	0,1	no	
5	6	34	20.09.	89,19	89,36	89,03	k.A.	no	-
6	7	33	29. Aug		91	89,7			
7	9	31		91,91	91,91	91,91		no	-
8	2	38	7.9.	91,2	90,85	91,55	3g/100g		
9	13	27	07. Sep	91,2	91,14	91,27	no	no	100

5.1.1.2 Total ash

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestim-mungsgrenze	Inkl. WF	Wiederfin-dungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result 2	Limit of quantifica-tion	Incl. RR	Recovery rate [%]
			Day/Month	g/100g	g/100g	g/100g	g/100g	yes/no	in %
1	18	22	21. Sep	5,7				no	
2	11	29	14.09.2017	5,9	5,9	5,9	0,1	no	-
3	5	35	October	5,60	5,57	5,63		no	
4	1	39	29/08	5,3	5,21	5,31	0,1	no	
5	6	34	22.09.	5,253	5,192	5,313	k.A.	no	-
6	7	33	29. Aug		5,5	5,4			
7	9	31		5,70	5,7	5,7		no	-
8	2	38	8.9.	5,54	5,54	5,54	0,1g/100g		
9	13	27	07. Sep	5,51	5,55	5,47	no	no	100

5.1.1.3 Acid insoluble ash

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestim-mungsgrenze	Inkl. WF	Wiederfin-dungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result 2	Limit of quantifica-tion	Incl. RR	Recovery rate [%]
			day/month	g/100g	g/100g	g/100g	g/100g	yes/no	in %
1	18	22	22. Sep	0,065				no	
2	11	29	14.09.2017	<0,1	<0,1	<0,1	0,1	no	-
3	5	35	October	0	0	0		no	
4	1	39	30/08	0,2	0,18	0,16	0,1	no	
5	6	34	26.09.	0,04659	0,04379	0,04939	k.A.	no	-
6	7	33	29. Aug		<0.1	<0.1	0,1		
7	9	31		0,02	0,02	0,02		no	-
8	2	38	8.9.	<0,1	<0,1	<0,1	0,1g/100g		
9	13	27	08. Sep	0,18	0,17	0,18	no	no	100

5.1.1.4 Volatile oil

Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result 2	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	g/100g DM	g/100g DM	g/100g DM	g/100g DM	yes/no	in %
1	18	22							
2	11	29	-	-	-	-	-	-	-
3	5	35	October	3,79	3,58	3,99		no	
4	1	39	30/08	7	7	7	0,5	no	
5	6	34	18.09.	4,0	3,9	4,2	k.A.	no	-
6	7	33	29. Aug		3,1	3,1			
7	9	31		2,29	2,29	2,29		no	-
8	2	38	7.9.	3,51	3,52	3,5	0,1nl/100gDM		
9	13	27	07. Sep	3,43	3,41	3,44	0,05	no	100

5.1.2 Analytical methods

5.1.2.1 Dry matter

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
					yes/no	yes/no	
1		deleted	gravimetric			yes	
2	-	-	-	-	-	-	-
3	26.11.03 1a					yes	
4	gravimetric					yes	
5	residual moisture with Moisture Analyzer	the sample was cold-grinding over a rotor mill (with liquid nitrogen), Particle size < 800 µm.	-	Calibration on 07.01.17 with Cumol	no	no	
6	azeotropic					no	sample A =no.7; sample B=no.33
7			Drying at 103°C	keine	-		
8	Acc. to DIN 10229		Volumetric			yes	
9	Rapid method	no	Thermogravimetry, Halogen heating modul	internal Calibration	no	yes	Specification of dry matter, water content is 100-dry matter

5.1.2.2 Total ash

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
					yes/no	yes/no	
1	§ 64 LFGB 53.00-4	deleted	gravimetric			yes	
2	§ 64 LFGB L 53.00-4	-	-	-	-	yes	
3	53.00 4					yes	
4	gravimetric					yes	
5	ISO 928	the sample was cold-grinding over a rotor mill (with liquid nitrogen), Particle size < 800 µm.	Temperature 550 °C	-	no	no	
6	gravimetric					no	
7	ASU L53.00-4 1996-02		gravimetric	no	-	yes	
8	§64 LFGB L06.00-4, mod.		gravimetric			yes	
9	ASU L. 53.00-4	sample homogenization	gravimetric	no	no	yes	Sample A = no. 13; sample B = no. 27

5.1.2.3 Acid insoluble ash

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
					yes/no	yes/no	
1	§ 64 LFGB 53.00-4	deleted	gravimetric			yes	
2	§ 64 LFGB L 53.00-4	-	-	-	-	yes	
3	53.00 4					yes	
4	gravimetric					yes	
5	ISO 930	the sample was cold-grinding over a rotor mill (with liquid nitrogen), Particle size < 800 µm.	Temperature 550 °C	-	no	no	
6	gravimetric					no	
7	ASU L53.00-4 1996-02		gravimetric	no	-	yes	
8	ISO 930		gravimetric			yes	
9	ASU L. 53.00-4	sample homogenization	gravimetric	no	no	yes	

5.1.2.4 Volatile Oil

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
					yes/no	yes/no	
1							not tested
2	-	-	-	-	-	-	-
3	53.00 10					yes	
4	Destillation					no	
5	DIN 10228 (according to ISO 6571)	the sample was cold-grinding over a rotor mill (with liquid nitrogen), Particle size < 800 µm.	-	Calibration on 07.01.17 with Cumol	no	no	
6	volumetric					no	
7	ASU L53.00-10 2010-09		steam distillation	no	-	no	
8	§64 LFGB L53.000-10, mod.		Volumetrie			yes	
9	ASU L. 53.00-10 (Sept 2010)	steam distillation	Volumetrie	no	no	yes	Calculation with deteminded water results

5.2 Homogeneity

5.2.1 Homogeneity testing before PT

DLA 36-2017

Weight whole sample	4,00	kg
Tracer	Fennel seeds	
Weight pro particle	8000	µg
Addition of tracer	12500	mg/kg

Result of analysis: (Number of fennel seeds = partikcle)

Sample	Weight [g]	Particle number	Particle [mg/kg]
1	19,28	27	11203
2	21,53	30	11147
3	20,60	26	10097
4	21,06	29	11016
5	21,75	32	11770
6	20,65	29	11235
7	21,54	30	11142
8	19,68	29	11789
9	20,54	29	11295
10	22,40	31	11071

Poisson distribution		
Number of samples	10	
degree of freedom	9	
Mean	29,2	Particle
Standard deviation	1,22	Particle
χ^2 (CHI-Quadrat)	0,46	
Probability	**100**	%
Recovery rate	89	%

Normal distribution		
Number of samples	10	
Mean	11177	mg/kg
Standard deviation	465	mg/kg
rel. Standard deviation	4,2	%
Horwitz Standard deviaton	3,9	%
HorRat Value	**1,1**	
Recovery rate	89	%

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:

Total ash				
Target standard deviation σ_{pt}	0,172			g/100g
Sample numbers	1 - 39			
Total numbers of samples	16			
Slope	0,00363			
Trend line range	5,49	-	5,55	g/100g
Deviation trend line	5,5	±	0,0319	g/100g
Percent of σpt	18,5	%		

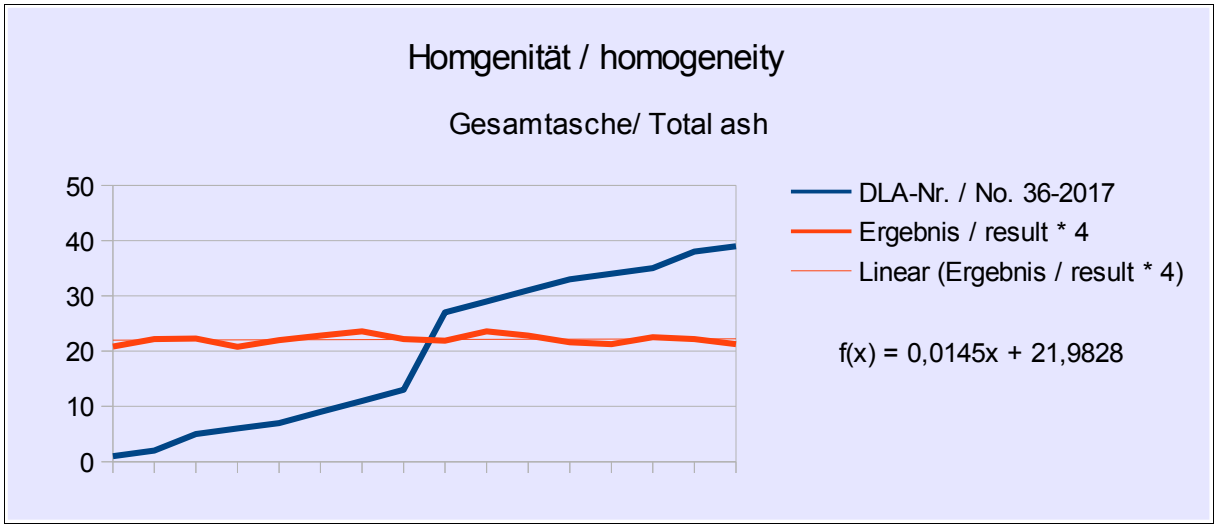

Abb./Fig. 12:
Trendfunktion Probennummern vs. Ergebnisse
trend line function sample number vs. results

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 36-2017***
PT name	***Dry Matter, total Ash, acid insoluble Ash and volatile oil in Spice***
*Sample matrix**	*Samples :* ***caraway and low portion (1,2%) of fennel seeds***
Number of samples and sample amount	*2 identical samples 100 g each.*
Storage	*Samples A + B: cooled 2 - 10°C*
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative:* ***dry matter, total ash, acid insoluble ash and volatile oil (ml/100g dry matter)***
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	*g/100g, volatile oil ml/100g DM*
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 20th October 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
		Spain
		Germany
		France
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany

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

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

7. Index of 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. HORWITZ EQUATION AS QUALITY BENCHMARK IN ISO/IEC 17025 TESTING LABORATORY, C. Rivera, R. Rodriguez, Pimentel 4104 –B; Col. Las Granjas. Chihuahua Chihuahua Mexico. C.P. 31160
17. AOAC Guidlines for Standard Method Performance Requirements (2016)
18. ASU § 64 LFGB L 53.00-10 Bestimmung des ätherischen Ölgehaltes in Gewürzen, würzenden Zutaten und Kräutern, Wasserdampfdestillationsverfahren (September 2010) (DIN EN ISO 6571/ November 2008)
19. ASU § 64 LFGB L 53.00-8 Bestimmung von Gewürzen und würzenden Zutaten, Bestimmung des Wassergehaltes (Destillationsverfahren) (Juli 2004) (DIN 10229/ August 2000)
20. ASU § 64 LFGB L 53.00-4 Untersuchung von Gewürzen und würzende Zutaten, Bestimmung der Gesamtasche und der säureunlöslichen Asche (Februar 1996) (DIN 10223/ Januar 1996)
21. ASU § 64 LFGB L 46.03-9 Bestimmung des Massenverlustes von ungemahlenem Tee bei 103 °C, (Oktober 2017) (DIN 10800, Juli 2016)
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