Proficiency Tests

DLA

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Evaluation Report

proficiency test

DLA 30/2016

Contaminated Food:
Sudan Dyes in Spice Powder

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

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EP-Nummer *PT-Number*	DLA 30/2016
EP-Koordinator *PT-Coordinator*	Dr. Gerhard Wichmann
Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report : 17/02/17
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: 17 February 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.

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Inhalt / Content

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1. Introduction

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

2. Realisation

2.1 Test material

The test material is a mixture of different spices and a microtracer pre-mix (wheat flour, microtracer iron particles (FSS red lake) for homogeneity verification. The spices contained a quantity of Sudan dyes known from previous PT´s.

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

Approximately 1 kg of the material was packaged in about 10 grams in metallized PET film bags. The portions were numbered chronologically.

The detectability of the Sudan dyes were ensured by preliminary investigations of the material.

The material was checked for homogeneity.

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2.1.1 Homogeneity

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

Before mixing dye coated iron particles of µm size are added to the sample and the number of particles is determined after homogenization in taken aliquots. The evaluation of the mixture homogeneity is based on the Poisson distribution using the chi-square test. A probability of ≥ 5 % is equivalent to a good homogeneous mixture and of ≥ 25% to an excellent mixture [14, 15]. The microtracer analysis of the present PT sample showed probability of 82%. Additionally particle number results were converted into concentrations, statistically evaluated according to normal distribution and compared to the standard deviation according to Horwitz. This gave a HorRat value of 0,8. The results of microtracer analysis are given in the documentation.

The calculation of the **variation coefficient** of the repeatability standard deviation (CV_r) was used as an indicator of homogeneity, see table 1. Compared to the previous PTs, the variation coefficients and the quotient S^* / σ_{pt} of the present PT are of the same order of magnitude, see table 2 (3.6.3).

	CV_r	**Quotient S^*/σ_{pt}**
Sudan I	14,3 %	1,4
Sudan II	7,4 %	1,6
Sudan IV	31,3 %	2,0

Table 1: Compilation of the variation coefficients CV_r and the quotient S^*/σ_{pt} of the present PT.

Furthermore, the homogeneity for Sudan I was characterized by the **trend line function of participants' results for chronological bottled single samples**. The maximum deviations from the mean value of the trend line was in the range of 30% of the target standard deviation σ_{pt} (s. 5.2 homogeneity) and is to be judged as slightly increased. The reason for this is the relatively large variability between the participants (reproducibility standard deviation) with normal repeatability standard deviation.

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].

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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 Sudan dyes 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 48th week of 2016. The testing method was optional. The tests should be finished at January 13th 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.

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.

Of the 14 participants, 3 participants did not submit any results.

The other 11 participants submitted at least one result in time.

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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.

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. For the method description, see documentation 5.1.

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].

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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].

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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.

The target standard deviation according to Horwitz was used for Sudan I, II, III and IV (see 3.6.1). Due to the increased variability, the results of Sudan III and IV were evaluated using the standard deviation with z´-Score.

For the purpose of information, the target standard deviation, calculated from the values from perception (PT´s from the years 2011 - 2014) is also given, see 3.6.3 / Table 2.

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)

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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]:

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

From the precision data of the relevant official method the target standard deviation for the corresponding parameters are calculated, if available, and used for the evaluation.

3.6.3 Value by perception

The target standard deviation for proficiency assessment can be set at a value that corresponds to the level of performance that the coordinator would wish laboratories to be able to achieve [3].

For the present evaluation the target standard deviation according to 3.6.1 were regarded suitable.

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

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Table 2: Characteristics of the present PT (on blue-grey) in comparison to previous PTs since 2011 (SD = standard deviation, CV = coefficient of variation)

Parameter	rob. Mean (µg/kg)	rob. SD (S*) (µg/kg)	rel. SD (CV_r) [%]	rel. SD (CV_R) [%]	Target-SD (σ_{pt}) (µg/kg)	Quotient S^*/σ_{pt}	DLA-report
Sudan I	27200	3430	14,3 %	33,3 %	2490	1,4	30-2016
Sudan III	539	210	7,4%	53,6 %	133	1,6	30-2016
Sudan IV	3920	2140	32,3 %	54,3 %	1070	2,0	30-2016
Sudan I	2679	1151	4,0 %	38,7 %	370	3,1	20-2014
Sudan III	328	94,3	22,0 %	31,6 %	65,1	1,5	20-2014
Sudan IV	519	132	6,4 %	20,8 %	91,7	1,4	20-2014
Sudan I	32000	5010	8,3 %	68,0 %	8610	0,58	22-2012
Sudan III	5300	1640	6,9 %	28,6 %	1870	0,88	22-2012
Sudan IV	7600	3520	4,1 %	44,5 %	2550	1,4	22-2012
Sudan I	5900	1420	8,1 %	35,4 %	2040	0,70	18-2011
Sudan III	400	110	8,7 %	44,0 %	190	0,57	18-2011
Sudan IV	1200	720	31,3 %	75,5 %	510	1,4	18-2011

From the previous PT´s, an average relative repeatability standard deviation (CV_r) of 11% and an average reproducibility standard deviation (CV_R) of 43% can be calculated.
These average characteristics were used for the calculation of the target standard deviation which is given for information additionally.

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.

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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.

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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 ($U(x_{pt})$) for this PT is calculated as follows [3]:

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

If $U(x_{pt}) \leq 0{,}3\ \sigma_{pt}$ 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.

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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 second table the individual results of the participating laboratories are listed:

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

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4.1 Sudan I (C.I. 12055) in µg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	11
Number of outliers	1
Mean	27200
Median	25600
Robust Mean (X)	**25300**
Robust standard deviation (S*)	**3430**
Number with 2 replicates	9
Repeatability SD (S_r)	4030
Repeatability (CV_r)	14,3%
Reproducibility SD (S_R)	9340
Reproducibility (CV_R)	33,3%
Target range:	
Target standard deviation σ_{pt}	**2490**
Target standard deviation (for Information)	10700
lower limit of target range	**20400**
upper limit of target range	**30300**
Quotient S^*/σ_{pt}	*1,4*
Standard uncertainty $U(X_{pt})$	*1290*
Quotient $U(X_{pt})/\sigma_{pt}$	*0,52*
Results in the target range	*9*
Percent in the target range	*82%*

Comments:

The standard target deviation was evaluated using the model of Horwitz. The target standard deviation "for information" was calculated from values by perception (previous PT´s), see 3.6.3.

The distribution of the results showed a normal variability. The quotient $S^*/\sigma pt$ was well below 2.0. The variation coefficient of the repeatability (CV_r) is comparable to those of prior PT´s (see 3.6.3). The comparability of results is given.

The quotient $U(X_{pt})/\sigma_p$ (0,52) is increased.

82% of the results were in the target area.

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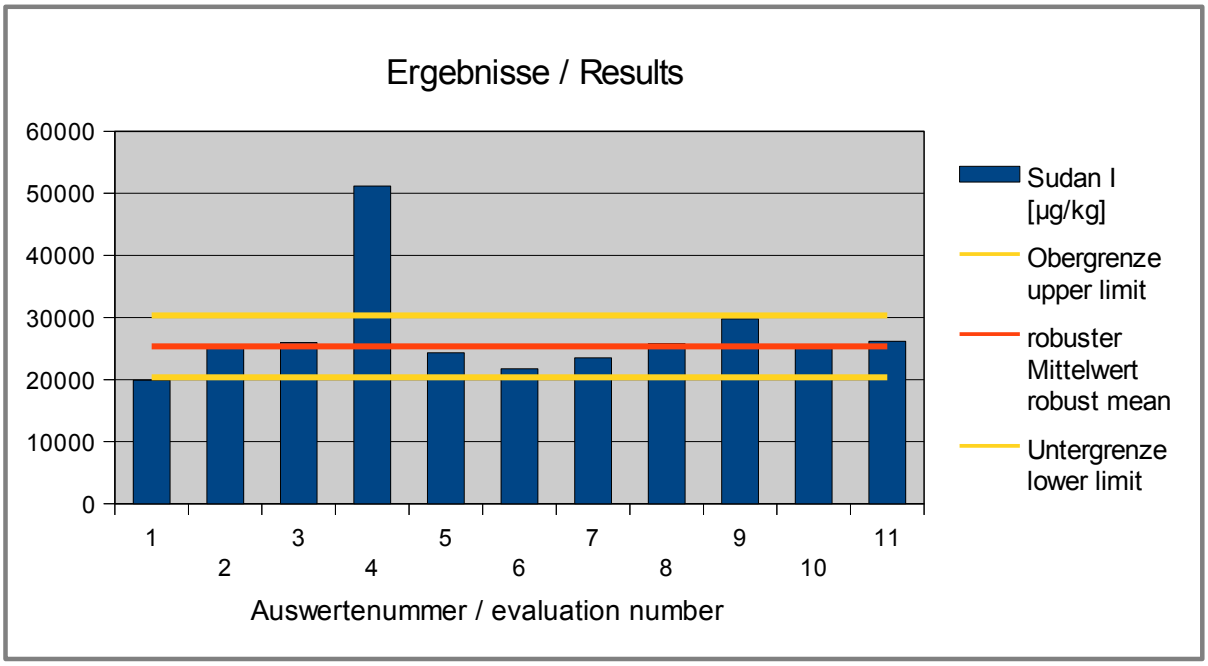

Abb. / Fig. 1: Ergebnisse Sudan I / Results Sudan I

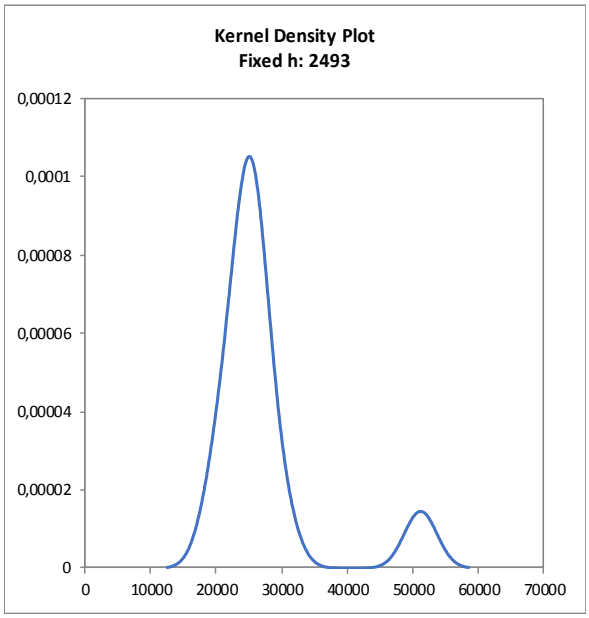

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = σ_{pt} von X_{pt} = 2493 µg/kg)

Kernel density plot of results (with h = σ_{pt} *of* X_{pt} = 2493 µg/kg)

Comment:
The kernel density shows a normal distribution of results with a clear side peak at 50000 µg/kg, due to the result of no. 4 (outlier).

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Ergebnisse der teilnehmenden Institute:
Results of Participants:

Auswerte-nummer / Evaluation number	Sudan I [µg/kg]	Abweichung [µg/kg] / Deviation [µg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis / Remark
1	19900	-5450	-2,2	-0,51	
2	25600	229	0,092	0,021	
3	26000*	601	0,24	0,056	
4	51200	25800	10,3	2,4	Ausreißer/ outlier
5	24300	-1050	-0,42	-0,10	
6	21700	-3630	-1,5	-0,34	
7	23500	-1850	-0,74	-0,17	
8	25800	407	0,16	0,038	
9	29800	4430	1,8	0,41	
10	25600	34,5	0,014	0,003	
11	26200	819	0,33	0,076	

** Mean calculated by DLA*

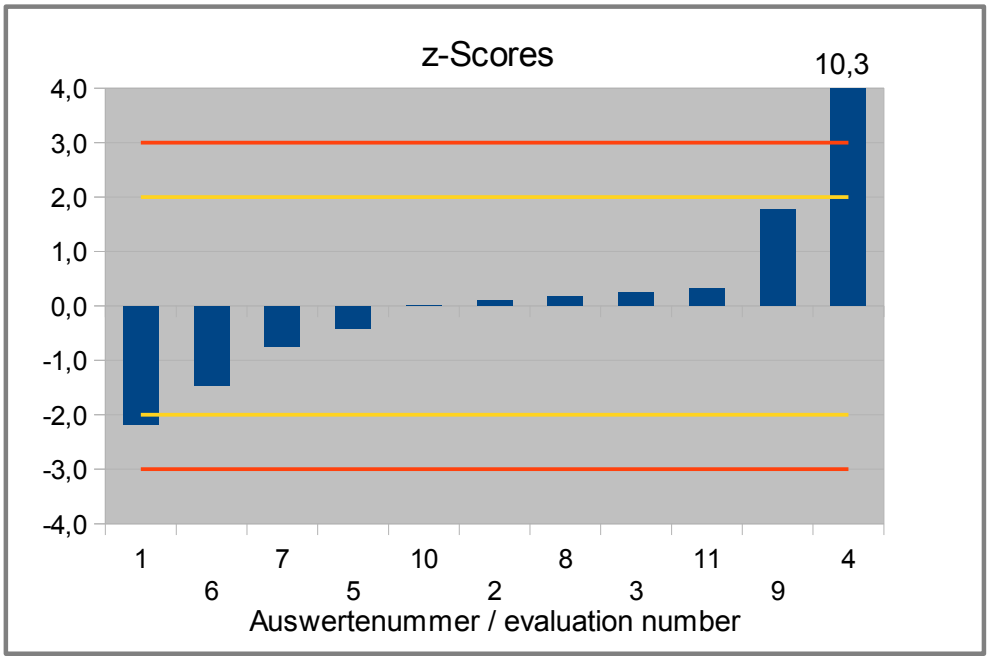

Abb. / Fig. 3: Z-Scores Sudan I

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4.2 Sudan II (C.I. 12140) in µg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	3*
Number of outliers	
Mean	12,6
Median	12,0
Robust Mean (X)	**12,6**
Robust standard deviation (S*)	**5,11**
Number with 2 replicates	
Repeatability SD (S_r)	
Repeatability (CV_r)	
Reproducibility SD (S_R)	
Reproducibility (CV_R)	
Target range:	
Target standard deviation σ_{pt}	
Target standard deviation (for Information)	
lower limit of target range	
upper limit of target range	
Quotient S^*/σ_{pt}	
Standard uncertainty $U_{(Xpt)}$	
Quotient $U_{(Xpt)}/\sigma_{pt}$	
Results in the target range	
Percent in the target range	

** Calculated without no. 2*

Comments:

The statistical evaluation is not carried out since there were no 7 results.

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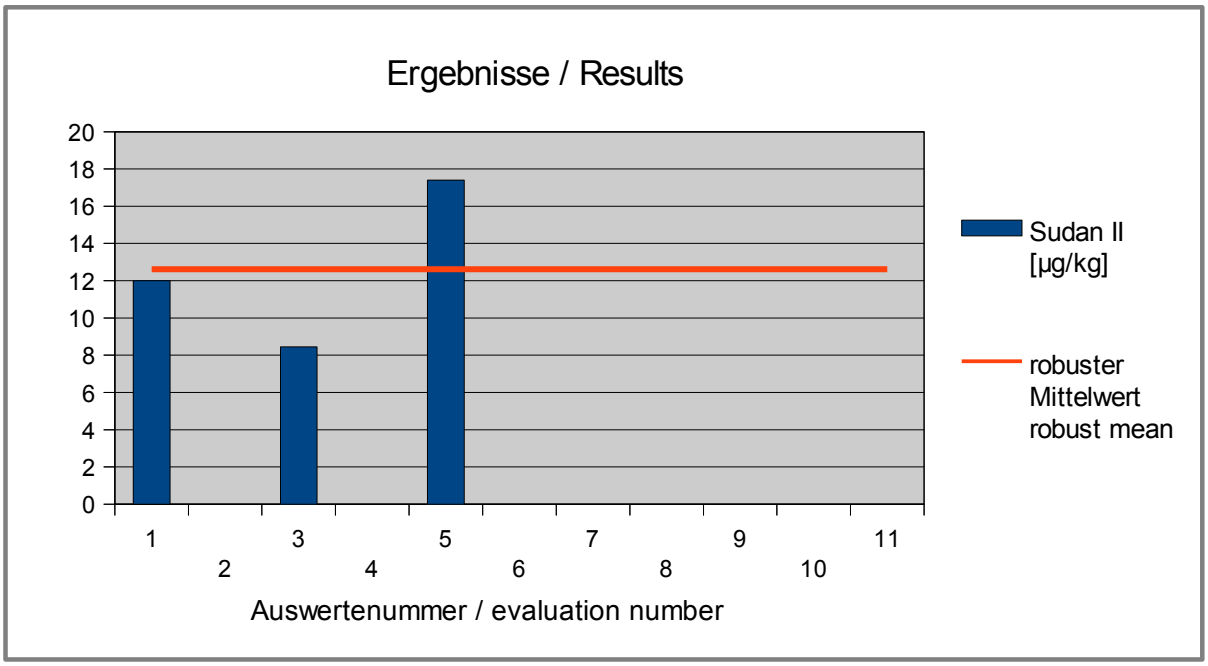

Abb. / Fig. 4: Ergebnisse Sudan II / Results Sudan II

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer / Evaluation number	Sudan II [µg/kg]	Abweichung [µg/kg] / Deviation [µg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis / Remark
1	12,0	-0,62			
2	2460	2450			
3	8,45*	-4,17			
4	< LOD				
5	17,4	4,78			
6	n.a.				
7	< 2000				
8	n.d.				
9					
10					
11					

** Mean calculated by DLA*

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4.3 Sudan III (C.I. 26100) in µg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	1
Mean	591
Median	442
Robust Mean (X)	**539**
Robust standard deviation (S*)	**210**
Number with 2 replicates	7
Repeatability SD (S_r)	46
Repeatability (CV_r)	7,4%
Reproducibility SD (S_R)	338
Reproducibility (CV_R)	53,6%
Target range:	
Target standard deviation σ_{pt}´	**133**
Target standard deviation (for Information)	228
lower limit of target range	**274**
upper limit of target range	**804**
Quotient S/σ_{pt}´*	*1,6*
Standard uncertainty $U_{(Xpt)}$	*92,8*
Quotient $U_{(Xpt)}/\sigma_{pt}$´	*0,70*
Results in the target range	7
Percent in the target range	*88%*

Anmerkungen zu den Kenndaten:

The standard target deviation was evaluated using the model of Horwitz. It was evaluated using the z'-score, taking into account the standard uncertainty. The target standard deviation "for information" was calculated from values by perception (previous PT´s), see 3.6.3.

The distribution of the results showed an increased variability. The quotient S*/σpt´ was below 2.0. The variation coefficient of the repeatability (CV_r) is comparable to those of prior PT´s (see 3.6.3). The comparability of results is given.

The quotient $U(X_{pt})/\sigma_p$´(0,70) is increased.

88% of the results were in the target area.

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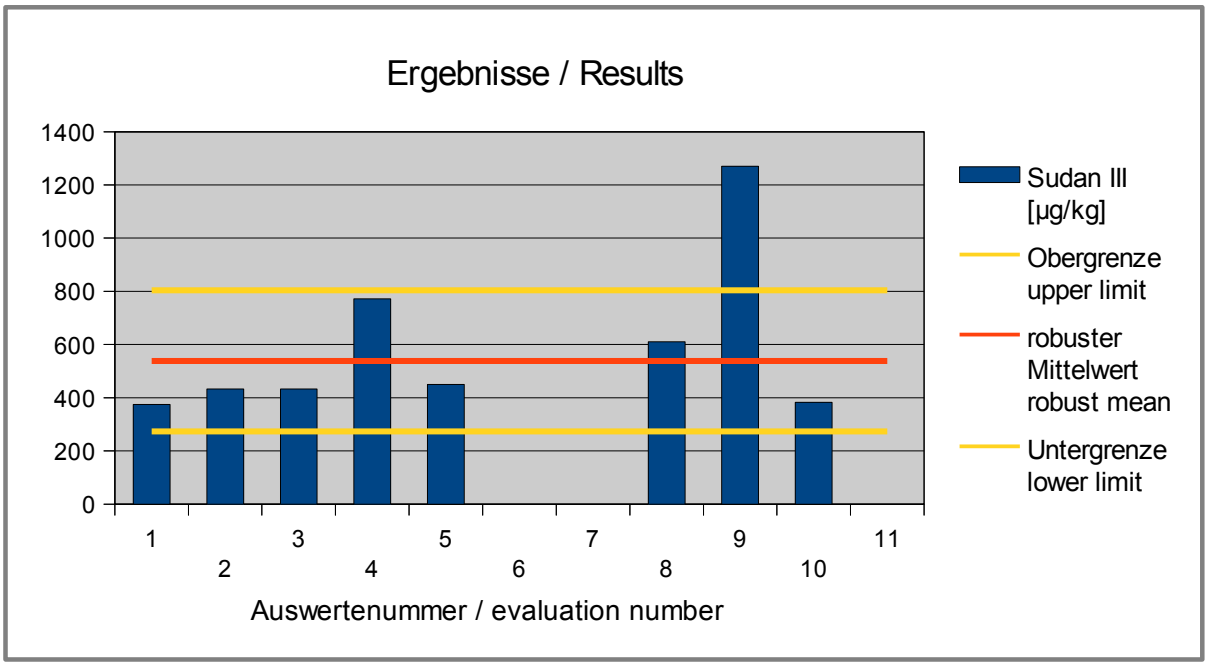

Abb. / Fig. 5: Ergebnisse Sudan III / Results Sudan III

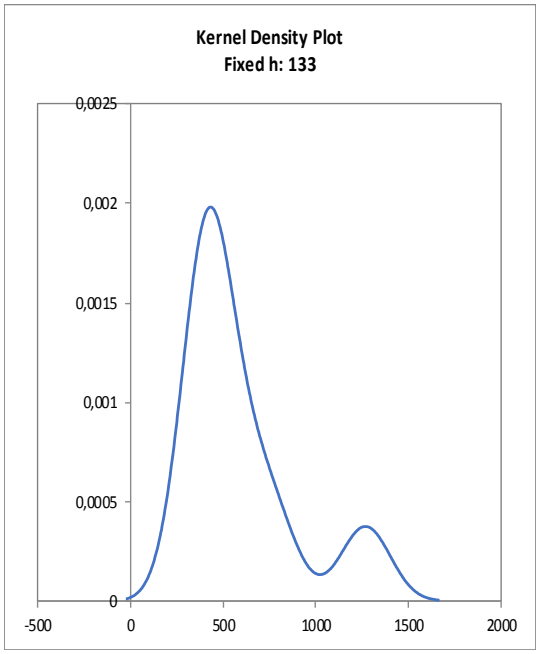

Abb. / Fig. 6:
Kerndichte-Schätzung der Ergebnisse (mit h = σ_{pt} von X_{pt} = 133 µg/kg)

Kernel density plot of results (with h = σ_{pt} of X_{pt} = 133 µg/kg)

Comment:
The kernel density shows a normal distribution of results with a side peak at 1270 µg/kg, due to the result of no. 9 (outlier).

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Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Sudan III [µg/kg]	Abweichung [µg/kg] Deviation [µg/kg]	z´-Score ($\sigma_{pt'}$)	z´-Score (Info)	Hinweis Remark
1	375	-164	-1,2	-0,72	
2	433	-106	-0,80	-0,46	
3	433*	-106	-0,80	-0,46	
4	772	233	1,8	1,0	
5	450	-88,7	-0,67	-0,39	
6	n.a.				
7	< 2000				
8	610	71,3	0,54	0,31	
9	1270	732	5,5	3,2	Ausreisser / Outlier
10	383	-156	-1,18	-0,68	
11					

** Mean calculated by DLA*

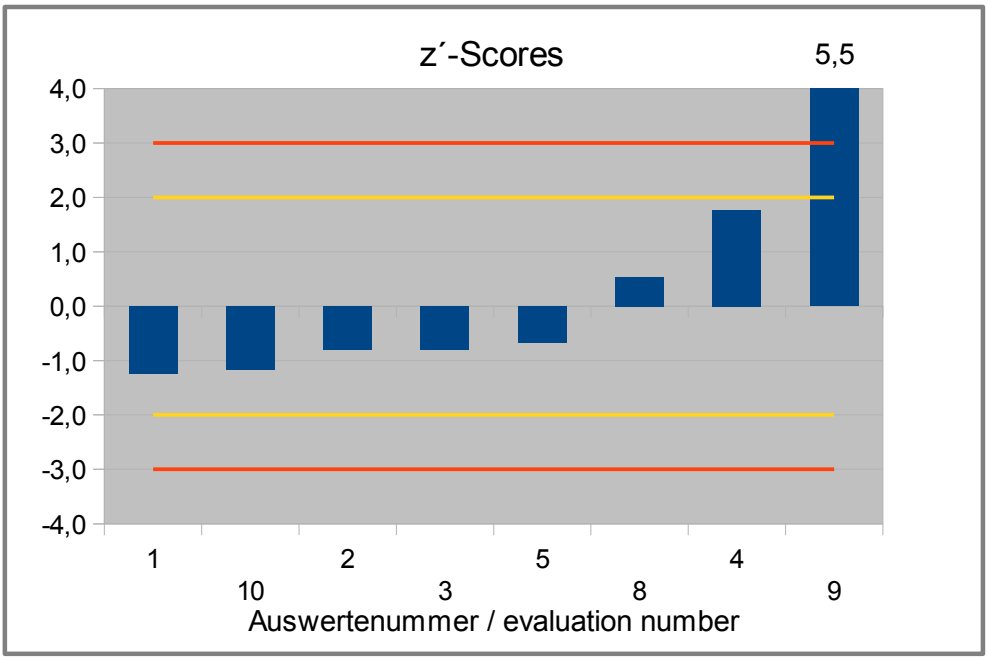

Abb. / Fig. 7: Z´-Scores Sudan III

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4.4 Sudan IV (C.I. 26105) in µg/kg

Vergleichsuntersuchung / Proficiency Test

Kenndaten	
Anzahl der Messergebnisse	8
Anzahl der Ausreißer	0
Mittelwert	3930
Median	3570
Robuster Mittelwert (X_{pt})	**3920**
Robuste Standardabweichung (S*)	**2140**
Anzahl mit 2 Wiederholmessungen	7
Wiederholstandardabweichung (S_r)	1280
Variationskoeffizient (VK_r)	31,3%
Vergleichsstandardabweichung (S_R)	2210
Variationskoeffizient (VK_R)	54,3%
Zielkenndaten:	
Zielstandardabweichung σ_{pt}´	**1070**
Zielstandardabweichung (zur Information)	1660
Untere Grenze des Zielbereichs	**1770**
Obere Grenze des Zielbereichs	**6070**
Quotient S/σ_{pt}´*	*2,0*
Standardunsicherheit $U_{(Xpt)}$	*945*
Quotient $U_{(Xpt)}/\sigma_{pt}$´	*0,88*
Ergebnisse im Zielbereich	*6*
Prozent im Zielbereich	*75%*

Anmerkungen zu den Kenndaten:

The standard target deviation was evaluated using the model of Horwitz. It was evaluated using the z'-score, taking into account the standard uncertainty. The target standard deviation "for information" was calculated from values by perception (previous PT´s), see 3.6.3.

The distribution of the results showed an increased variability. The quotient S*/σpt´ was at 2.0. The variation coefficient of the repeatability (CV_r) is comparable to those of prior PT´s (see 3.6.3). The comparability of results is given.

The quotient $U(X_{pt})/\sigma_p$´(0,88) is increased.

75% of the results were in the target area.

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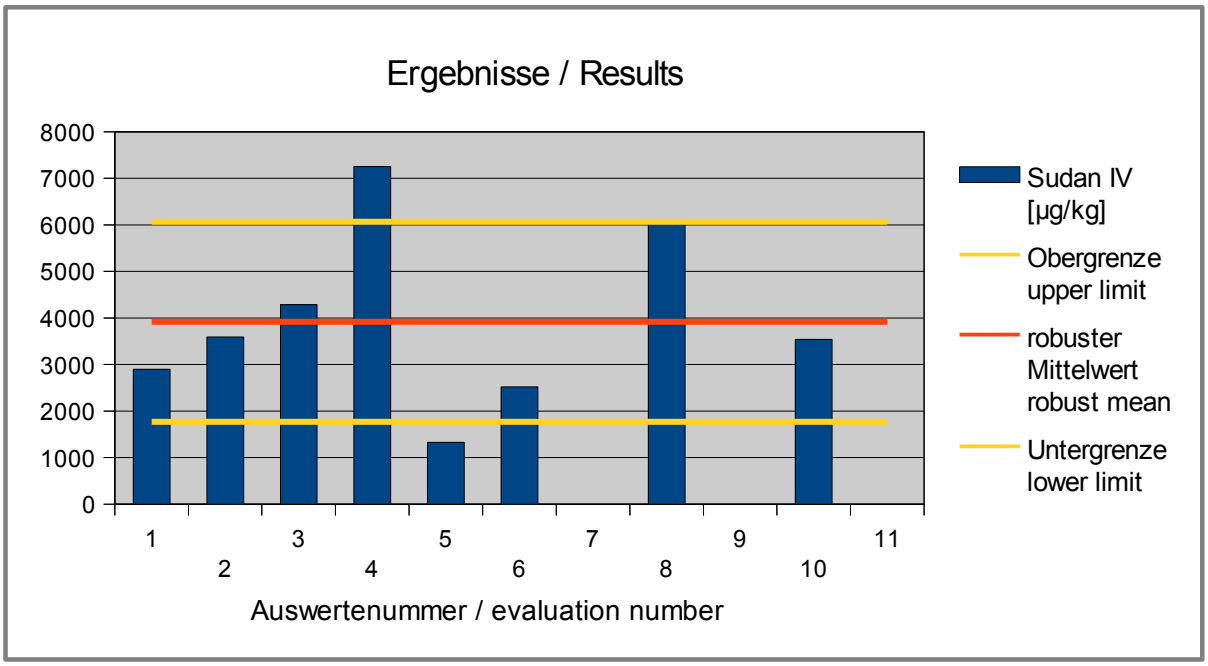

Abb. / Fig. 8: Ergebnisse Sudan IV / Results Sudan IV

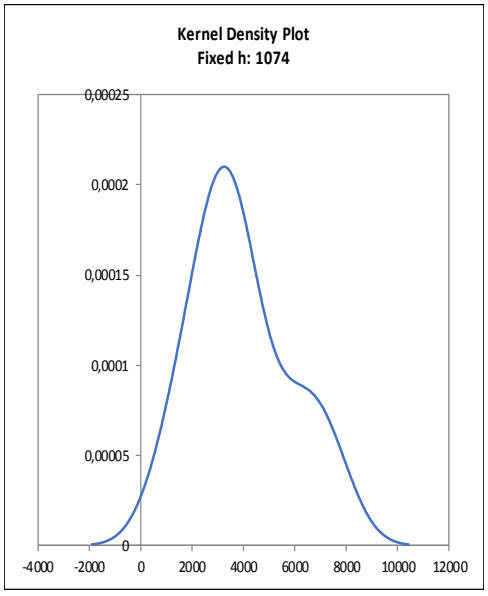

Abb. / Fig. 9:
Kerndichte-Schätzung der Ergebnisse (mit h = σ_{pt} von X_{pt} = 1074 µg/kg)

Kernel density plot of results (with h = σ_{pt} of X_{pt} = 1074 µg/kg)

Anmerkung:
The kernel density shows a normal distribution of results with a shoulder at 7000 µg/kg.

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Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer / Evaluation number	Sudan IV [µg/kg]	Abweichung [µg/kg] / Deviation [µg/kg]	z´-Score (σ_{pt}´)	z´-Score (Info)	Hinweis / Remark
1	2900	-1020	-0,95	-0,61	
2	3590	-326	-0,30	-0,20	
3	4280*	366	0,34	0,22	
4	7250	3330	3,1	2,0	
5	1330	-2590	-2,4	-1,6	
6	2520	-1400	-1,3	-0,84	
7					
8	6050	2130	2,0	1,3	
9					
10	3540*	-377	-0,35	-0,23	

** Mean calculated by DLA*

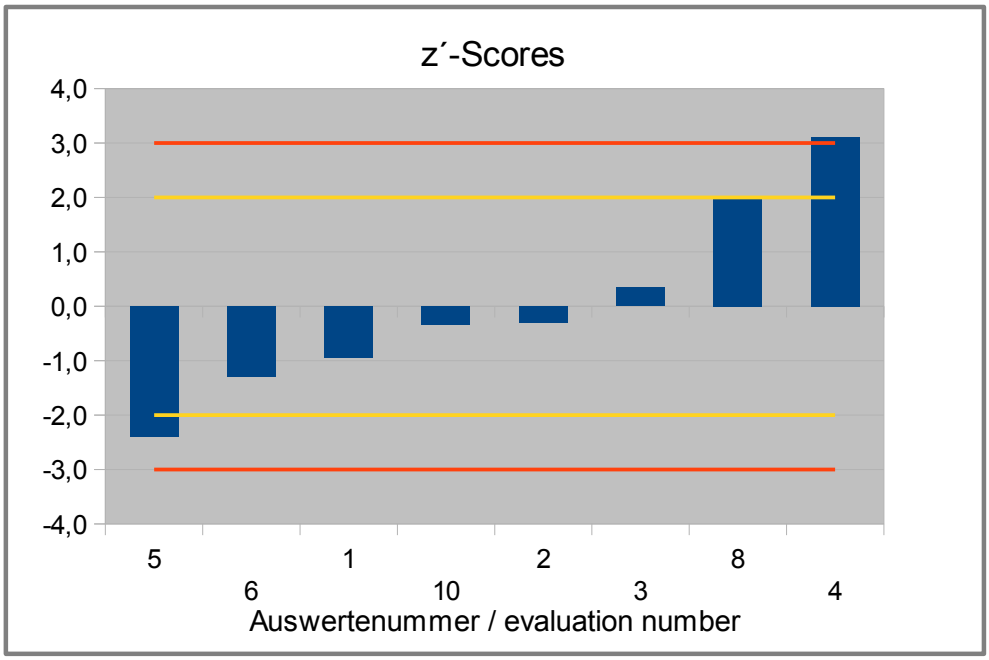

Abb. / Fig. 10: Z´-Scores Sudan IV

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5. Documentation

5.1 Details by participants

5.1.1 Primary data

5.1.1.1 Sudan I

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	In %
1		11	86	19900			
2	04.01.17	13	26	25578	25777	25378	100
3	12.01.17	28	56	25950*	26750	25150	100
4	11.01.17	16	31	51153	53288	49018	91
5	15.12.16	27	58	24300	21600	27000	80
6	11.01.17	44	53	21720	21110	22320	-
7	04.01.17	19	76	23500	23600	23400	no recovery
8	22.12.16	14	66	25756	18024,7	33497,5	
9	14.12.16	50	35	29782	28870	29800	98,5
10		1	48	25383	25805, 25315, 25294	25440, 25295, 25150	0,928
11	22.12.16	5	72	26168			

** Mean calculated by DLA*

5.1.1.2 Sudan II

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86	12			
2	04.01.17	13	26	2467	2377	2556	100
3	12.01.17	28	56	8,45*	9	7,9	100
4	11.01.17	16	31	< LOD	< LOD	< LOD	90
5	15.12.16	27	58	17,4	16,1	18,7	80
6	11.01.17	44	53	n.a.	n.a.	n.a.	-
7	04.01.17	19	76	<2000			no recovery
8	22.12.16	14	66	n.d.	n.d.	n.d.	
9	14.12.16	50	35				
10		1	48				
11		5	72				

** Mean calculated by DLA*

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5.1.1.3 Sudan III

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86	375			
2	04.01.17	13	26	433	417	449	100
3	12.01.17	28	56	433*	422	444	100
4	11.01.17	16	31	772	808	735	84
5	15.12.16	27	58	450	412	490	80
6	11.01.17	44	53	n.a.	n.a.	n.a.	-
7	04.01.17	19	76	<2000			no recovery
8	22.12.16	14	66	610	570	649,6	
9	14.12.16	50	35	1270	1277	1378	104,5
10		1	48	383	417, 375, 391	370, 369, 374	1,09
11		5	72				

** Mean calculated by DLA*

5.1.1.4 Sudan IV

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86	2900			
2	04.01.17	13	26	3591	3554	3628	100
3	12.01.17	28	56	4283*	4270	4295	100
4	11.01.17	16	31	7252	8974	5529	67
5	15.12.16	27	58	1330	1170	1486	80
6	11.01.17	44	53	2520	2660	2380	-
7	04.01.17	19	76	<2000			no recovery
8	22.12.16	14	66	6049	4406,5	7691,1	
9	14.12.16	50	35				
10		1	48	3536,33	3621, 3521, 3536	3481, 3552, 3507	0,909
11		5	72				

** Mean calculated by DLA*

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5.1.1.5 Sudan Red G

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86	<10			
2	04.01.17	13	26	<100	<100	<100	100
3	-	28	56	n.a.			
4		16	31				
5	15.12.16	27	58	<5	<5	<5	80
6		44	53	n.a.	n.a.	n.a.	n.a.
7		19	76				
8		14	66	n.a.			
9	14.12.16	50	35				
10		1	48				
11		5	72				

5.1.1.6 Sudan Red B

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86				
2	04.01.17	13	26	n.b.	n.b.	n.b.	n.b.
3	-	28	56	n.b.			
4		16	31				
5	15.12.16	27	58	1320	1181	1451	80
6		44	53	n.a.	n.a.	n.a.	n.a.
7		19	76				
8		14	66	n.a.			
9		50	35				
10		1	48				
11		5	72				

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5.1.1.7 Sudan Red 7B

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86	<10			
2	04.01.17	13	26	<100	<100	<100	100
3	12.01.17	28	56	11,5*	12,5	10,4	100
4		16	31				
5	15.12.16	27	58	10	8,7	11,4	80
6	11.01.17	44	53	n.a.	n.a.	n.a.	-
7		19	76				
8	22.12.16	14	66	n.d.	n.d.	n.d.	
9	14.12.16	50	35				
10		1	48				
11		5	72				

** Mean calculated by DLA*

5.1.1.8 Sudan Orange

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
1		11	86	<10			
2	04.01.17	13	26	<100	<100	<100	100
3	-	28	56	n.b.			
4		16	31				
5	15.12.16	27	58	<5	<5	<5	80
6	11.01.17	44	53	n.d.	n.d.	n.d.	-
7		19	76				
8		14	66	n.a.			
9	14.12.16	50	35				
10		1	48				
11		5	72				

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5.1.1.9 Other dyes: Auramin O

Teilnehmer/ participant	Datum der Analyse/ date of the analysis	DLA Nr. Probe A/ sample A	DLA Nr. Probe B/ sample B	Ergebnis/ result	Ergebnis A/ result A	Ergebnis B/ result B	Wiederfin-dungsrate/ recovery
				µg/kg	µg/kg	µg/kg	
8		14	66	n.d.	n.d.		

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5.1.2 Analytical methods

5.1.2.1 Sudan I

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan I	0.3mg/100mL	Sigma	n.d.	no	
3	In house method	Acetonitrile	No cleanup	none	LC-MS/MS	Dr.Ehrens-torfer	1,5,10,25,50,100 ng/ml	no	yes	yes	
4	Determination of Sudan Dyes with LC-MS/MS	Ethylacetate	dilution with ACN	LC	MS/MS	Fa. TCI/Fa. Sigma-Aldrich	0,5-100 ng/ml 30.12.2016	-	yes	yes	-
5	0034-LC				LCMSMS				no	no	
6	WIN-VM-003	MeOH/acetone	no	HPLC C18	MS/MS	Sigma	10-600 ppb/ 8 months	Sigma	-	yes	
7	HPLC-DAD	Acetonitrile/ water 70/30	Filtration	HPLC RP-18	DAD	Sigma	0,1-5 mg/l			yes	Recovery not taken into account!
8	Extraction with Ethylacetate	Ethylacetate	centrifugate	LC	MSMS	Sigma-Aldrich	Not longer than 6 months	no	no	no	Standard addition
9	Extraction with THF; analysed with HPLC with UV-Vis detection	THF	Filtration on 0.45 µm PTFE	HPLC	UV-Vis	Commercial STDs	50 µg/mL stock solution 12-12-2016	In house method	yes	yes	
10	The samples were homogenized, 3x elaborated and with ESI-LC-MSMS analysed.	Extracting agent: Acetonitrile	Addition of NaCl, extract freezing	HPLC, C18-column	MSMS		1-50 ng/mL	Deuterated Standards	yes	no	
11	lipophilic azodyes with HPLC		SPE	HPLC	DAD				yes	no	

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5.1.2.1 Sudan II

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan II	0.3mg/100mL	Sigma	n.d.	no	
3	In house method	Acetonitrile	No cleanup	none	LC-MS/MS	Dr.Ehrens-torfer	1,5,10,25,50,100 ng/ml	no	yes	yes	
4	Determination of Sudan Dyes with LC-MS/MS	Ethylacetate	dilution with ACN	LC	MS/MS	Fa. TCI/Fa. Sigma-Aldrich	0,5-100 ng/ml 30.12.2016	-	yes	yes	LOD = 150 µg/kg
5	0034-LC				LCMSMS				no	no	
6	WIN-VM-003	MeOH/acetone	no	HPLC C18	MS/MS	Sigma	10-600 ppb/ 8 months	Sigma	-	yes	
7	HPLC-DAD	Acetonitrile/ water 70/30	Filtration	HPLC RP-18	DAD	Sigma	0,1-5 mg/l			yes	Recovery not taken into account!
8	Extraction with Ethylacetate	Ethylacetate	centrifugate	LC	MSMS	Sigma-Aldrich	Not longer than 6 months	no	no	no	Standard addition
9											
10											
11											

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5.1.2.3 Sudan III

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan III	0.3mg/100mL	Sigma	n.d.	no	
3	In house method	Acetonitrile	No cleanup	none	LC-MS/MS	Dr.Ehrens-torfer	1,5,10,25,50,100 ng/ml	no	yes	yes	
4	Determination of Sudan Dyes with LC-MS/MS	Ethylacetate	dilution with ACN	LC	MS/MS	Fa. TCI/Fa. Sigma-Aldrich	0,5-100 ng/ml 30.12.2016	-	yes	yes	-
5	0034-LC				LCMSMS				no	no	
6	WIN-VM-003	MeOH/acetone	no	HPLC C18	MS/MS	Sigma	10-600 ppb/ 8 months	Sigma	-	yes	
7	HPLC-DAD	Acetonitrile/ water 70/30	Filtration	HPLC RP-18	DAD	Sigma	0,1-5 mg/l			yes	Recovery not taken into account!
8	Extraction with Ethylacetate	Ethylacetate	centrifugate	LC	MSMS	Sigma-Aldrich	Not longer than 6 months	no	no	no	Standard addition
9	Extraction with THF; analysed with HPLC with UV-Vis detection	THF	Filtration on 0.45 µm PTFE	HPLC	UV-Vis	Commercial STDs	50 µg/mL stock solution 12-12-2016	In house method	yes	yes	
10	The samples were homogenized, 3x elaborated and with ESI-LC-MSMS analysed.	Extracting agent: Acetonitrile	Addition of NaCl, extract freezing	HPLC, C18-column	MSMS		1-50 ng/mL	Deuterated Standards	yes	no	
11											

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5.1.2.4 Sudan IV

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreinigung/ Clean up	Trennmethode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standardlösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan IV	0.3mg/100mL	Sigma	n.d.	no	
3	In house method	Acetonitrile	No cleanup	none	LC-MS/MS	Dr.Ehrensdorfer	1,5,10,25,50,100 ng/ml	no	yes	yes	
4	Determination of Sudan Dyes with LC-MS/MS	Ethylacetate	dilution with ACN	LC	MS/MS	Fa. TCI/Fa. Sigma-Aldrich	0,5-100 ng/ml 30.12.2016	-	yes	yes	-
5	0034-LC				LCMSMS				no	no	
6	WIN-VM-003	MeOH/acetone	no	HPLC C18	MS/MS	Sigma	10-600 ppb/ 8 months	Sigma	-	yes	
7	HPLC-DAD	Acetonitrile/ water 70/30	Filtration	HPLC RP-18	DAD	Sigma	0,1-5 mg/l			yes	Recovery not taken into account!
8	Extraction with Ethylacetate	Ethylacetate	centrifugate	LC	MSMS	Sigma-Aldrich	Not longer than 6 months	no	no	no	Standard addition
9											
10	The samples were homogenized, 3x elaborated and with ESI-LC-MSMS analysed.	Extracting agent: Acetonitrile	Addition of NaCl, extract freezing	HPLC, C18-column	MSMS		1-50 ng/mL	Deuterated Standards	yes	no	
11											

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5.1.2.5 Sudan Red G

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan Red G	0.3mg/100mL	Sigma	n.d.	no	
3											
4											-
5	0034-LC				LCMSMS				no	no	
6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Sudan Red G is not in the test.
7											
8											
9											
10											
11											

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5.1.2.6 Sudan Red B

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1											
2											
3											
4											-
5	0034-LC				LCMSMS				no	no	
6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Sudan Red B is not in the test.
7											
8											
9											
10											
11											

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5.1.2.7 Sudan Red 7B

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan Red 7B	0.3mg/100mL	Sigma	n.d.	no	
3											
4											-
5	0034-LC				LCMSMS				no	no	
6	WIN-VM-003	MeOH/acetone	no	HPLC C18	MS/MS	Sigma	10-600 ppb/ 8 months	Sigma	-	yes	Sudan Red 7B ((C.I 26050)?
8	Extraction with Ethylacetate	Ethylacetate	centrifugate	LC	MSMS	Sigma-Aldrich	Not longer than 6 months	no	no	no	Standard addition
9											
10											
11											

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5.1.2.8 Sudan Orange

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
1		Quechers		LC	MSMS					no	
2	PDA Method for Sudan Dyes	Ultrasonic bath	no	HPLC C 18	UV	Sudan Orange G	0.3mg/100mL	Sigma	n.d.	no	
3											
4											-
5	0034-LC				LCMSMS				no	no	
6	WIN-VM-003	MeOH/acetone	no	HPLC C18	MS/MS	Sigma	10-600 ppb/ 8 months	Sigma	-	yes	Sudan Red 7B ((C.I 26050)?
7											
8											
9											
10											
11											

5.1.2.9 Auramin O

Teilnehmer/ participant	Methode/ Method	Extraktion/ Extraction	Probenaufreini-gung/ Clean up	Trenn-methode/ Separation method	Detektion/ Detection	Standard material/ Calibration material	Konzentration und Alter der Standard-lösungen/ Concentration and age of calibration solutions	Referenz material/ Reference material	Wiederfindung mit gleicher Matrix/ Recovery with same metrix	Methode ist akkreditiert/ Method is accredited	Sonstige Hinweise/ Further remarks
8	Extraction with Ethylacetate	Ethylacetate	centrifugate	LC	MSMS	Sigma-Aldrich	Not longer than 6 months	no	no	no	Standard addition

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5.2 Homogeneity

5.2.1 Homogeneity testing before PT

The **mixture homogeneity before bottling** was examined 10-fold by **microtracer analysis.**

Microtracer Homogeneity test DLA 30-2016		
Weight whle sample	1,000	kg
Microtracer	FSS-rot lake	
Particle size	75 – 300	µm
Weight per particle	2,0	µg
Addition of tracer	23,5	mg/kg

Results of analysis

Sample	Weight [g]	Particle number	Particles [mg/kg]
1	8,25	94	22,8
2	8,99	98	21,8
3	9,90	106	21,4
4	8,03	99	24,7
5	8,52	83	19,5
6	9,00	87	19,3
7	10,0	111	22,1
8	9,04	107	23,7
9	9,06	95	21,0
10	8,83	95	21,5

Poisson distribution		
Number of samples	10	
Degree of freedom	9	
mean	97,6	Particles
Standard deviation	7,49	Particles
χ^2 (CHI-Quadrat)	5,17	
Probablity	**82**	%
Recovery rate	93	%

Normalverteilung		
Number of samples	10	
Mean	21,8	mg/kg
Standard deviation	1,67	mg/kg
rel. Standard deviation	7,67	%
Horwitz Standard deviation	10,1	%
HorRat value	**0,8**	
Recovery rate	93	%

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5.2.2 Comparison of sample number/test results and trend line

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

Sudan I				
Target standard deviation σ_{pt}	2490			µg/kg
Sample numbers	1 – 76*			
Total numbers of samples	16			
Slope	-102			
Trend line range	24764	–	23132	µg/kg
Deviation trend line	23948	±	816	µg/kg
Percent of σ_{pt}	32,8	%		

* Without sample no. 16 + 31

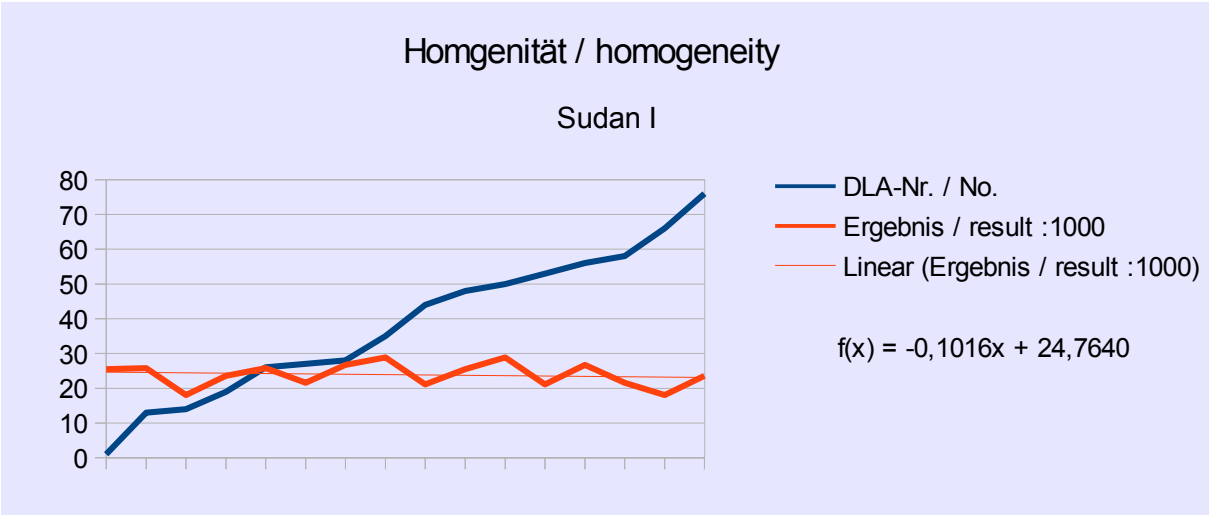

Abb./Fig. 11:
Trendfunktion Probennummern vs. Ergebnisse
trend line function sample number vs. results

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6. Index of participant laboratories

Teilnehmer/ participant	Ort/ town	Land/ country
		Deutschland
		CANADA
		Deutschland
		Deutschland
		SCHWEIZ
		Deutschland
		Deutschland
		Deutschland
		FRANKREICH
		Deutschland
		NIEDERLANDE
		INDIEN
		SÜDAFRIKA
		Deutschland

[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.]

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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
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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
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