

Proficiency Tests

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Evaluation Report
proficiency test

DLA 55/2017

Tattoo Dyes:
Determination of 13 elements
(As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Zn)
in tattoo Dyes

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

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<i>Unteraufträge</i> <i>Subcontractors</i>	<p>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.</p>
<i>Vertraulichkeit</i> <i>Confidentiality</i>	<p>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.</p>

Inhalt / Content

1. Introduction.....	4
2. Realisation.....	4
2.1 Test material.....	4
2.1.1 Homogeneity.....	5
2.1.2 Stability.....	6
2.2 Sample shipment and information to the test.....	6
2.3 Results.....	6
3. Evaluation.....	7
3.1 Consensus values from participants (Assigned value).....	7
3.2 Robust standard deviation.....	7
3.3 Repeatability standard deviation.....	7
3.4 Reproducibility standard deviation.....	8
3.5 Exclusion of results and outliers.....	8
3.6 Target standard deviation (for proficiency assessment).....	9
3.6.1 General model (Horwitz).....	9
3.6.2 Precision experiment.....	10
3.6.3 Value by perception.....	12
3.7 z-Score.....	12
3.7.1 Warning and action signals.....	12
3.8 z'-Score.....	13
3.9 Reproducibility coefficient of variation (CV).....	13
3.10 Quotient S^*/σ_{pt}	14
3.11 Standard uncertainty.....	14
4. Results.....	15
4.1 Arsenic (mg/kg).....	17
4.2 Barium in mg/kg.....	20
4.3 Cadmium in mg/kg.....	23
4.4 Cobalt in mg/kg.....	26
4.5 Chromium in mg/kg.....	29
4.6 Copper in mg/kg.....	32
4.7 Mercury in mg/kg.....	35
4.8 Nickel in mg/kg.....	38
4.9 Lead in mg/kg.....	41
4.10 Antimony in mg/kg.....	44
4.11 Selenium in mg/kg.....	46
4.12 Tin in mg/kg.....	49
4.13 Zinc in mg/kg.....	52
5. Documentation.....	55
5.1 Details by participants.....	55
5.1.1 Primary data.....	55
5.1.2 Analytical Methods.....	68
5.2 Homogeneity.....	81
5.2.1 Repeatability std. dev. of the double determinations.....	81
5.2.2 Comparison of sample number/test results and trend line.....	82
5.3 Sample cover letter: Information on the Proficiency Test (PT).....	83
6. Index of participant laboratories.....	84
7. Index of literature.....	85

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 two standard tattoo dyes from a European supplier with the same basic substance: Tattoo dye VIOLET (Ingredients: Aqua, Cl 7789, Alcohol denat., Glycerin, Rosa damascena extract, Cl 77891, Cl 51345, MEK) and Tattoo dye GREEN (Ingredients: Aqua, Cl 74265, Alcohol denat., Glycerin, CL 77891 Rosa damascena extract, MEK).

In a preliminary study, the tattoo color samples were analyzed for a basic load of elements. Copper was present in the green tattoo dye in a relatively high concentration. The other 12 elements arsenic, barium, cadmium, cobalt, chromium, mercury, nickel, lead, antimony, selenium, tin and zinc (copper was not added) were added as standard solutions (each 1000 mg/litre).

The 0,25 l batch was homogenized in the glass container with a stirrer for 3 × 60 minutes. Subsequently, the samples were filled into PE screw tubes in portions of approx. 5 g and numbered chronologically.

The content of elements calculated from the preliminary analysis and the added elements is shown in Table 1.

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

Table 1: Content of elements in the samples calculated from the preliminary analyses and the content of added elements:

Elements	Content (mg/kg)
Arsenic	2,2
Barium	22
Cadmium	2,2
Cobalt	4,3
Chromium	3,1
Copper	3800
Mercury	1,3
Nickel	2,2
Lead	1,0
Antimony	4,3
Selenium	2,2
Tin	2,2
Zinc	2,2

2.1.1 Homogeneity

The calculation of the variation coefficient (CV) of the repeatability standard deviation (CV_r) and of the reproducibility standard deviation (CV_R) was used as an indicator of homogeneity, see table 1. They are for the analytes < 4% (1.05% - 3.58%). The coefficients (CV_r and CV_R) are comparable to the precision data of the official method, see 3.6.2/ table 2 [18-21, 24-26]. The repeatability standard deviations and the reproducibility standard deviations of the participants are given at the characteristics (4.1 to 4.13).

Furthermore, the homogeneity was characterized by the **trend line function of participants' results for chronological bottled single samples**. The maximum deviations for chromium from the mean value of the trend line was in the range of 23% of the target standard deviation σ_{pt} (s. 5.2 homogeneity) and is to be judged as low.

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

2.1.2 Stability

The samples are a mixture of stable, preserved, commercially available tattoo dyes. Experience has shown that the storage stability or shelf life of the samples (microbial spoilage) and the content of elements is thus guaranteed during the investigation period.

2.2 Sample shipment and information to the test

Two portions of test material were sent to every participating laboratory in the 39th week of 2017. The testing method was optional. The tests should be finished at November 10th 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, 8 participants submitted at least one result in time. 1 participant has not submitted any results.

A registration has been cancelled before sending the samples.

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]. If there are < 12 quantitative results and an increased difference between robust mean and median, the **median** may be used as the assigned value (criterion: $\Delta \text{median} - \text{rob. mean} > 0,3 \sigma_{pt}$) [3].

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

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

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

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

3.2 Robust standard deviation

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

3.3 Repeatability standard deviation

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

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

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

from participants are available.

3.4 Reproducibility standard deviation

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

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

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

The relative reproducibility standard deviation 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 a 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 the target standard deviation from the general model of Horwitz (s. 3.6.1) was applied. In addition, the standard uncertainty for the elements arsenic, cadmium, mercury, copper, selenium and zinc was taken into account and the results were evaluated using z'-score (see 3.6.8). For information, the target standard deviation of a precision experiment was given (ASU §64 Method: [18]-[21] and [24-26]), see 3.6.2.

No statistical evaluation was carried out for the elements antimony and tin, as relatively few results were available and the distribution of the results showed increased variability.

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
$\sigma_R = 0,22c$	$c < 1,2 \times 10^{-7}$	$< 120 \mu\text{g}/\text{kg}$
$\sigma_R = 0,02c^{0,8495}$	$1,2 \times 10^{-7} \leq c \leq 0,138$	$\geq 120 \mu\text{g}/\text{kg}$
$\sigma_R = 0,01c^{0,5}$	$c > 0,138$	$> 13,8 \text{ g}/100\text{g}$

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

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]:

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

The relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviation (RSD_R) given in Table 2 were determined in ring tests using the indicated methods.

The resulting target standard deviations σ_{pt} , which were identified there, were used to evaluate the results and to provide additional information for the statistical data.

Table 2: relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviations (RSD_R) according to selected evaluations of tests for precision and the resulting target standard deviation σ_{pt} [18 - 21, 24-26].

Parameter	Matrix	Mean (mg/kg)	RSD_r (%)	RSD_R (%)	σ_{pt} (%)	Method / Literature
Arsenic	Spinach	0,215	3,3	7,4	7,02 ¹	AAS [21]
Barium	Tattoo dye	21,54	5,79	8,93	7,94 ¹	ICP-OES [25]
Cadmium	CRM Plastics	5,24	4,7	7,3	6,50 ¹	AAS [24]
Cadmium	Lipstick	0,885	3,82	11,30	11,0	ICP-OES [25]
Cadmium	Bodylotion	4,19	1,75	3,37	3,14	ICP-OES [25]
Cadmium	Bodylotion	4,12	3,37	9,47	9,17	ICP-OES [25]
Chromium	White cabbage	0,97	15,0	23	20,4 ¹	AAS [19]
Copper	Biscuit	2,432	3,61	12,1	11,8	AAS [18]
Copper	Liver	120,55	2,86	6,5	6,08 ¹	AAS [18]
Mercury	Tattoo dye	0,110	2,84	11,68	11,5	AAS [26]
Mercury	Bodylotion	1,40	3,04	24,92	24,8 ¹	AAS [26]
Nickel	Lipstick	10,42	8,52	10,40	8,48	ICP-OES [25]
Nickel	Tattoo dye	5,22	3,89	19,31	19,1 ¹	ICP-OES [25]
Lead	Bodylotion	16,71	4,35	7,18	6,49 ¹	ICP-OES [25]
Lead	Bodylotion	17,48	4,16	10,81	10,4	ICP-OES [25]
Antimony	Bodylotion	13,21	3,68	7,88	7,39 ¹	ICP-OES [25]
Antimony	Bodylotion	13,43	3,67	4,82	4,06	ICP-OES [25]
Selenium	Cloverleaf	7,233	3,26	7,23	6,85 ¹	AAS [20]
Zinc	Biscuit	13,04	2,45	7,82	7,63 ¹	AAS [18]

¹ values used in the evaluation, see section 4.

For the elements the cobalt and tin, the precision values $RSD_r = 3,80\%$, $RSD_R = 9,84\%$ used for tattoo dyes of comparable elements were used, since no such values are available.

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:

$$z_i = \frac{(x_i - x_{pt})}{\sigma_{pt}}$$

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 ($U_{x_{pt}}$) [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 ($U(X_{pt})$) 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.

4. Results

Although there were only 6 (or 5) results, an evaluation could be made, since acceptable statistic data are available, a normal distribution could be proved by means of kernel density and generally good agreement of the assigned values with the spiked level.

No statistical evaluation was carried out for the elements antimony and tin, as relatively few results were available and the distribution of the results showed increased variability.

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

In the first table the characteristics are listed:

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

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

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

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

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

4.1 Arsenic (mg/kg)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	1
Mean	2,42
Median	1,81
Robust Mean (X)	1,99
Robust standard deviation (S*)	0,773
Number with 2 replicates	5
Repeatability SD (S_r)	0,0626
Repeatability (CV_r)	3,58%
Reproducibility SD (S_R)	0,406
Reproducibility (CV_R)	23,2%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,488
Target standard deviation (for Information)	0,140
lower limit of target range	1,01
upper limit of target range	2,97
Quotient S^*/σ_{pt}	1,6
Standard uncertainty $U_{(X_{pt})}$	0,395
Quotient $U_{(X_{pt})}/\sigma_{pt}$	0,81
Results in the target range	5
Percent in the target range	83%

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. In addition, the standard uncertainty was taken into account and the results were evaluated using z'-score (see 3.6.8). For information, the target standard deviation from a precision experiment (ASU § 64 LFGB L00.00-135) was given, see 3.6.2.

The distribution of the results showed a slightly increased variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U_{(X_{pt})}/\sigma_{pt}$ is 0,8 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

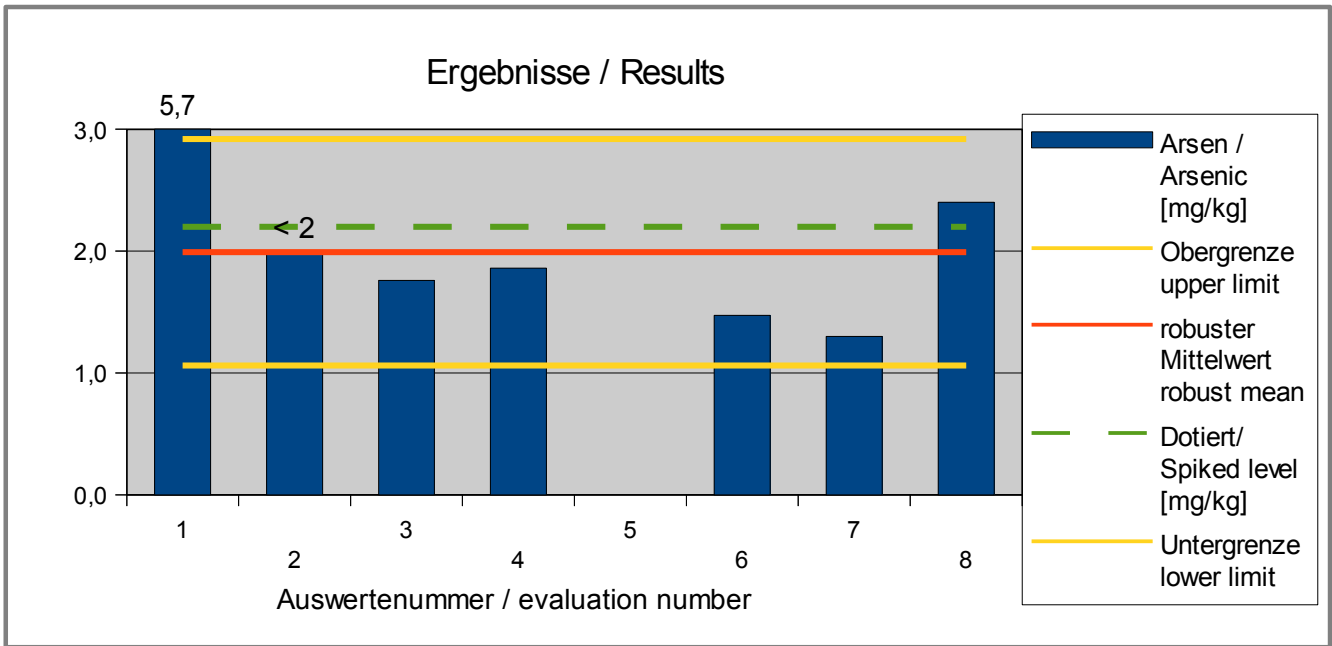


Abb. / Fig. 1: Ergebnisse Arsen / Results Arsenic

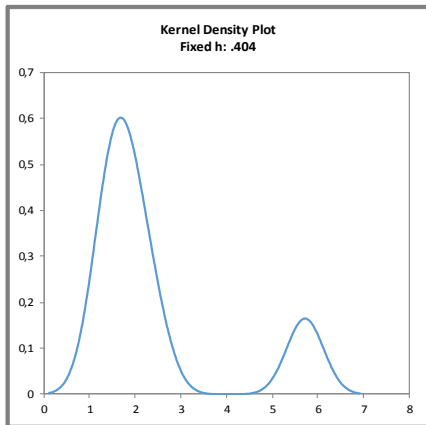


Abb. / Fig. 2:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ of X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 6 mg/kg, due to the result outside the target range (outlier).

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Arsen / Arsenic [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ _{pt'})	z-Score (Info)	Hinweis Remark
1	5,72*	3,73	7,6	27	Ausreisser / Outlier
2	< 2,0				BG im Zielbereich/ LOQ in the target area
3	1,76	-0,230	-0,47	-1,65	
4	1,86	-0,130	-0,27	-0,93	
5					
6	1,47	-0,517	-1,1	-3,7	
7	1,30	-0,690	-1,4	-4,9	
8	2,40	0,410	0,8	2,9	

* Mean calculated by DLA

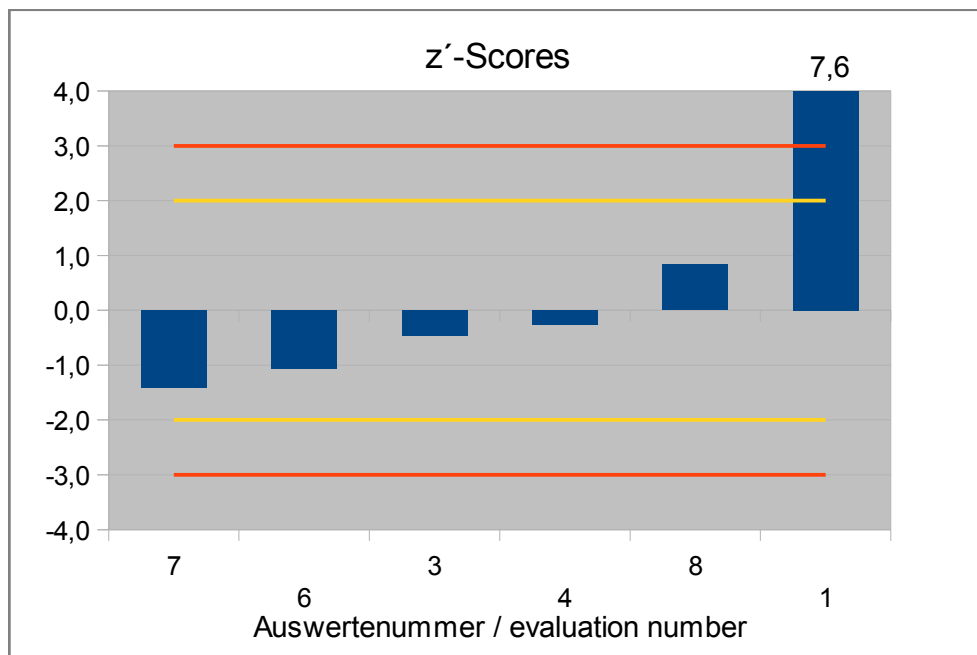


Abb. / Fig. 3: z'-Scores Arsen/ Arsenic

4.2 Barium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	0
Mean	22,2
Median	23,1
Robust Mean (X)	23,0
Robust standard deviation (S*)	4,30
Number with 2 replicates	5
Repeatability SD (S_r)	0,253
Repeatability (CV_r)	1,19%
Reproducibility SD (S_R)	5,70
Reproducibility (CV_R)	26,9%
<i>Target range:</i>	
Target standard deviation σ_{pt}	2,30
Target standard deviation (for Information)	1,83
lower limit of target range	18,4
upper limit of target range	27,6
Quotient S^*/σ_{pt}	1,9
Standard uncertainty $U_{(X_{pt})}$	2,19
Quotient $U_{(X_{pt})}/\sigma_{pt}$	1,0
Results in the target range	5
Percent in the target range	83%

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 experiment (ASU § 64 LFGB K 84.00-32) was given, see 3.6.2.

The distribution of the results showed a normal variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U_{(X_{pt})}/\sigma_{pt}$ is 1,0 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

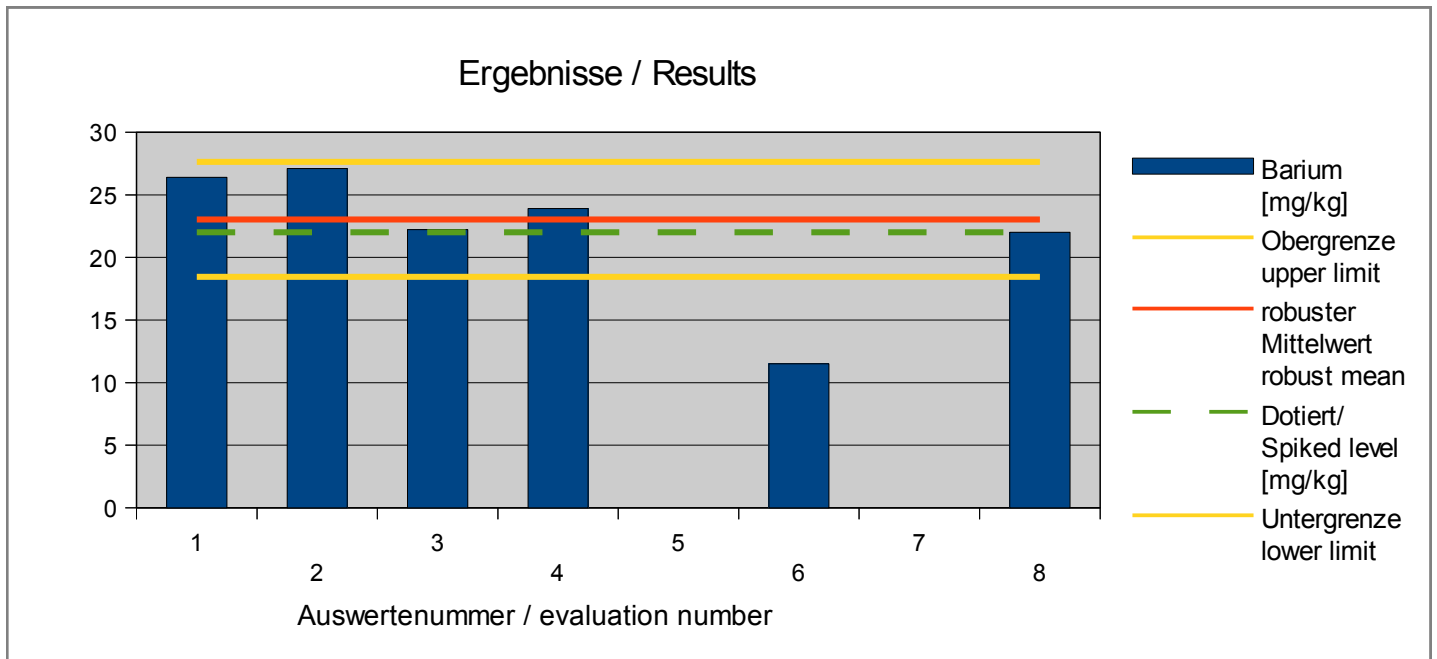


Abb. / Fig. 4: Ergebnisse/ Results Barium

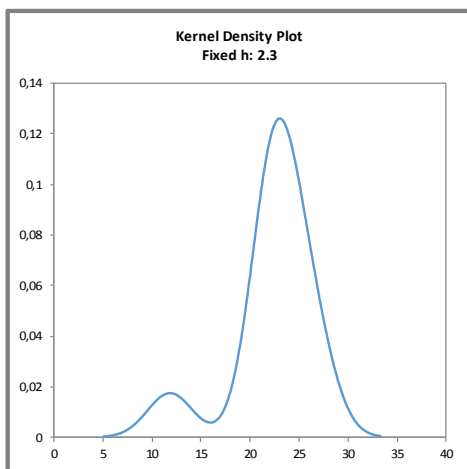


Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})
Kernel density plot of results (with $h = \sigma_{pt}$ of X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 11 mg/kg, due to the result outside the target range.

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Barium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	26,4*	3,36	1,5	1,8	
2	27,1	4,06	1,8	2,2	
3	22,2	-0,815	-0,35	-0,45	
4	23,9	0,865	0,38	0,47	
5					
6	11,5	-11,5	-5,0	-6,3	
7					
8	22,0	-1,04	-0,5	-0,6	

* Mean calculated by DLA

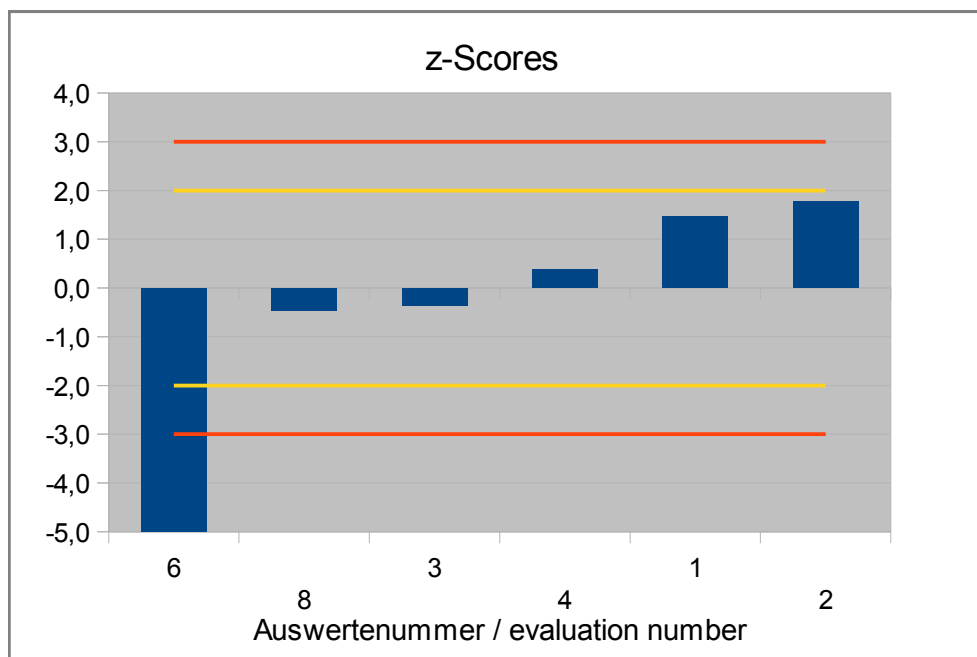


Abb. / Fig. 6: Z-Scores Barium

4.3 Cadmium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	0
Mean	2,44
Median	2,22
Robust Mean (X)	2,28
Robust standard deviation (S*)	0,676
Number with 2 replicates	6
Repeatability SD (S_x)	0,0255
Repeatability (CV_x)	1,05%
Reproducibility SD (S_R)	0,932
Reproducibility (CV_R)	38,3%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,473
Target standard deviation (for Information)	0,148
lower limit of target range	1,34
upper limit of target range	3,23
Quotient S^*/σ_{pt}	1,4
Standard uncertainty $U(X_{pt})$	0,345
Quotient $U(X_{pt})/\sigma_{pt}$	0,73
Results in the target range	5
Percent in the target range	83%

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. In addition, the standard uncertainty was taken into account and the results were evaluated using z' -score (see 3.6.8). For information, the target standard deviation from a precision experiment (ASU § 64 LFGB K84.00-29) was given, see 3.6.2.

The distribution of the results showed a slightly increased variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_x and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U(X_{pt})/\sigma_{pt}$ is 0,7 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

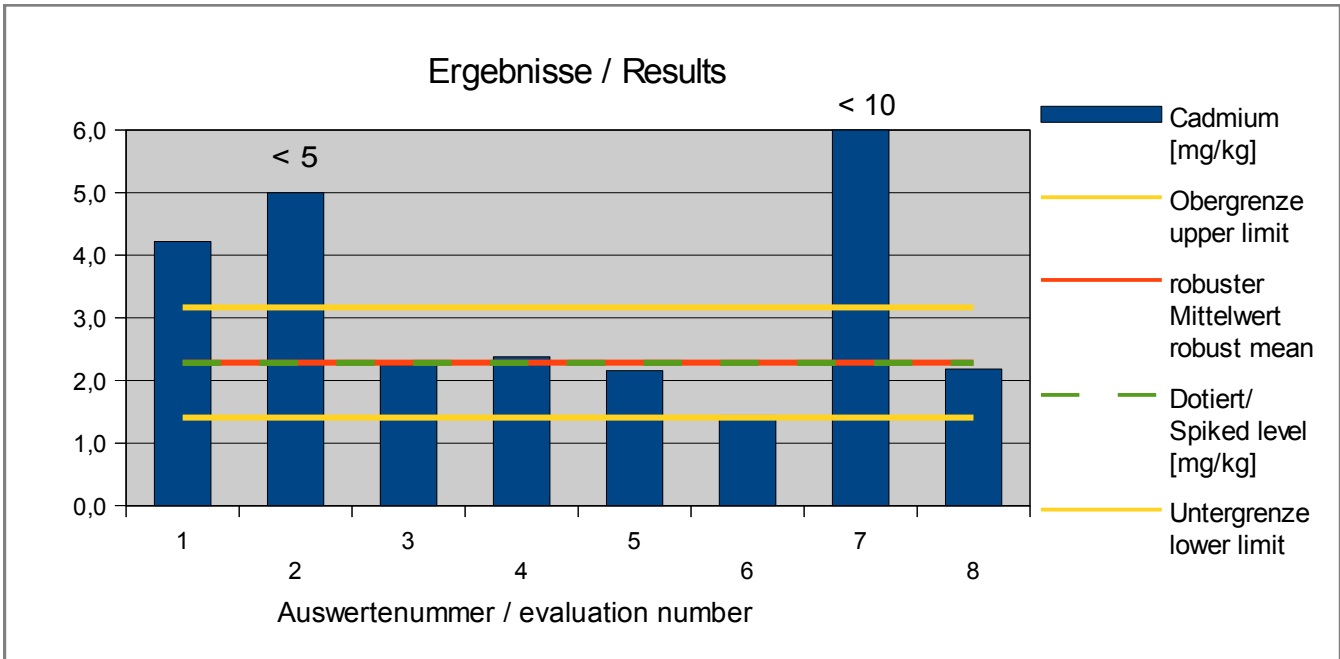


Abb. / Fig. 7: Ergebnisse/ Results Cadmium

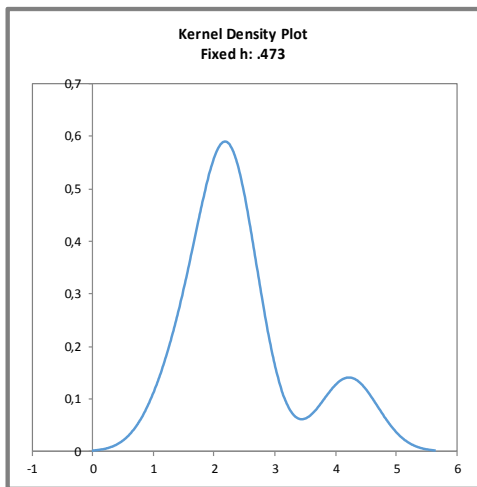


Abb. / Fig. 8:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 4 mg/kg, due to the result outside the target range.

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Cadmium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	4,22*	1,94	4,1	13	
2	< 5,0				BG über Zielbereich/ LOQ above target area
3	2,25	-0,035	-0,073	-0,23	
4	2,38	0,0954	0,20	0,64	
5	2,16	-0,126	-0,27	-0,85	
6	1,44	-0,845	-1,8	-5,7	
7	< 10				BG über Zielbereich/ LOQ above target area
8	2,18	-0,105	-0,22	-0,70	

* Mean calculated by DLA

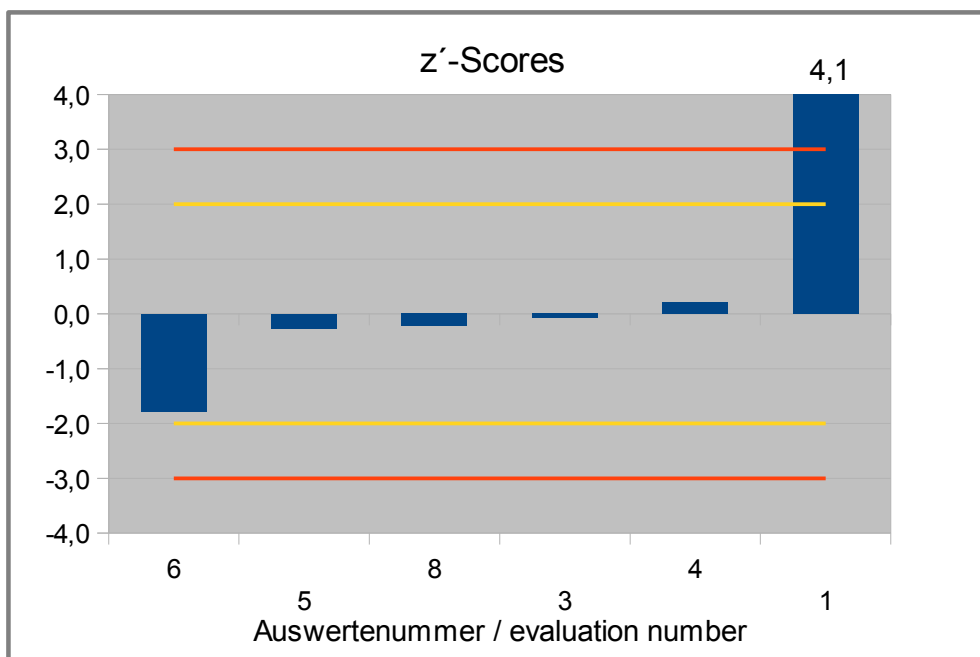


Abb. / Fig. 9: z'-Scores Cadmium

4.4 Cobalt in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	4,90
Median	4,49
Robust Mean (X)	4,76
Robust standard deviation (S*)	1,11
Number with 2 replicates	5
Repeatability SD (S_r)	0,112
Repeatability (CV_r)	2,29%
Reproducibility SD (S_R)	1,26
Reproducibility (CV_R)	25,8%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,864
Target standard deviation (for Information)	0,451
lower limit of target range	3,03
upper limit of target range	6,49
Quotient S^*/σ_{pt}	1,3
Standard uncertainty $U(X_{pt})$	0,619
Quotient $U(X_{pt})/\sigma_{pt}$	0,72
Results in the target range	4
Percent in the target range	80%

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 experiment (ASU § 64 LFGB K 84.00-32) was given, see 3.6.2.

The distribution of the results showed a normal variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U(X_{pt})/\sigma_{pt}$ is 0,7 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

80% of the results were in the target area.

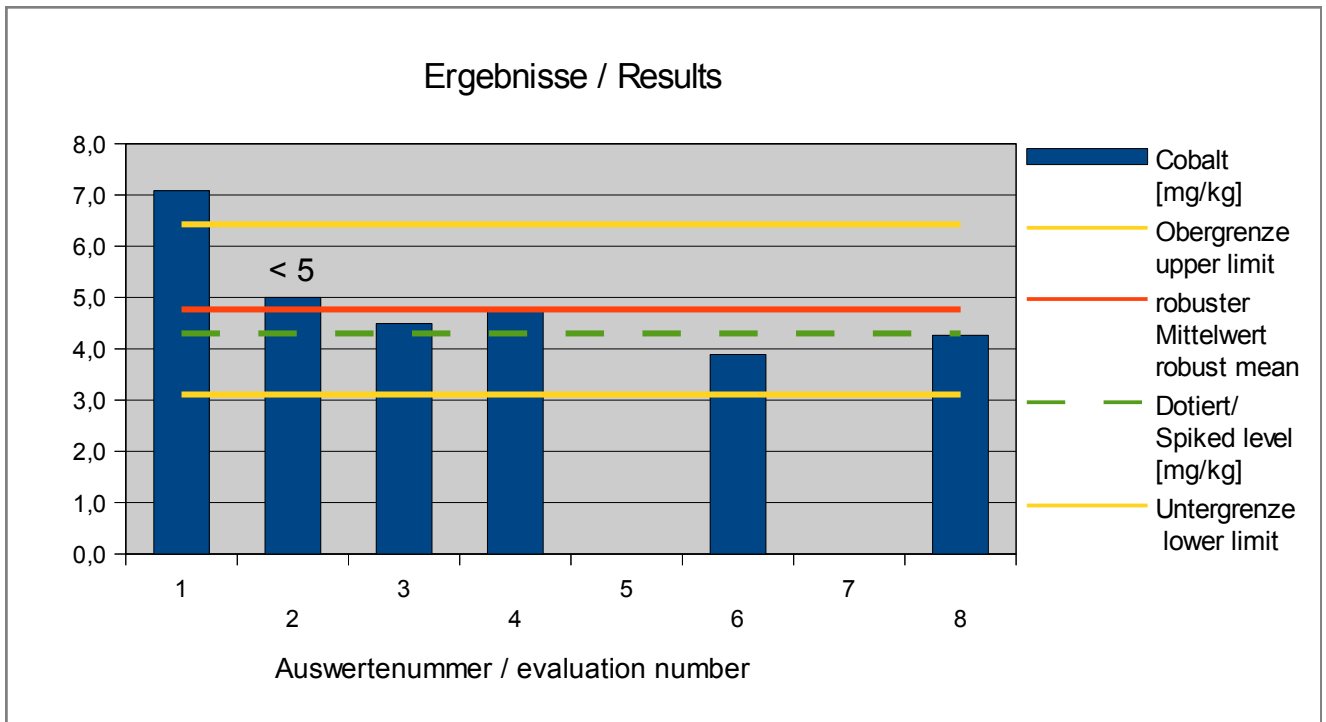


Abb. / Fig. 10: Ergebnisse/ Results Cobalt

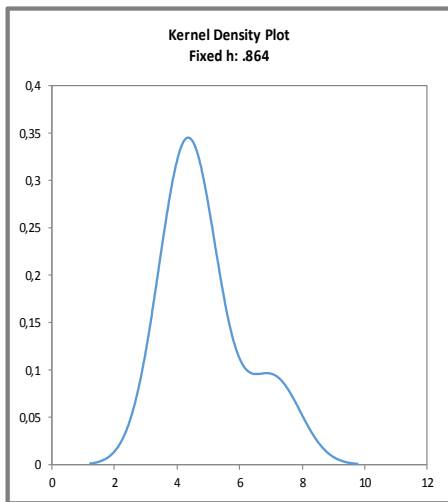


Abb. / Fig. 11:
Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 7 mg/kg, due to the result outside the target range.

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Cobalt [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	7,08*	2,32	2,7	5,1	
2	< 5,0				BG im Zielbereich/ LOQ in the target area
3	4,49	-0,273	-0,32	-0,61	
4	4,76	-0,00303	-0,0035	-0,0067	
5					
6	3,89	-0,873	-1,0	-1,9	
7					
8	4,26	-0,503	-0,58	-1,1	

* Mean calculated by DLA



Abb. / Fig. 12: Z-Scores Cobalt

4.5 Chromium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
<i>Number of results</i>	6
<i>Number of outliers</i>	1
Mean	4,26
Median	3,90
Robust Mean (X)	3,96
Robust standard deviation (S*)	0,710
<i>Number with 2 replicates</i>	5
Repeatability SD (S_r)	0,112
Repeatability (CV_r)	2,99%
Reproducibility SD (S_R)	0,407
Reproducibility (CV_R)	10,8%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,515
Target standard deviation (for Information)	0,808
lower limit of target range	2,93
upper limit of target range	4,99
<i>Quotient S^*/σ_{pt}</i>	1,4
<i>Standard uncertainty $U(x_{pt})$</i>	0,362
<i>Quotient $U(x_{pt})/\sigma_{pt}$</i>	0,70
<i>Results in the target range</i>	5
<i>Percent in the target range</i>	83%

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 experiment (ASU § 64 LFGB L00.00-19-3) was given, see 3.6.2.

The distribution of the results showed a normal variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U(x_{pt})/\sigma_{pt}$ is 0,7 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

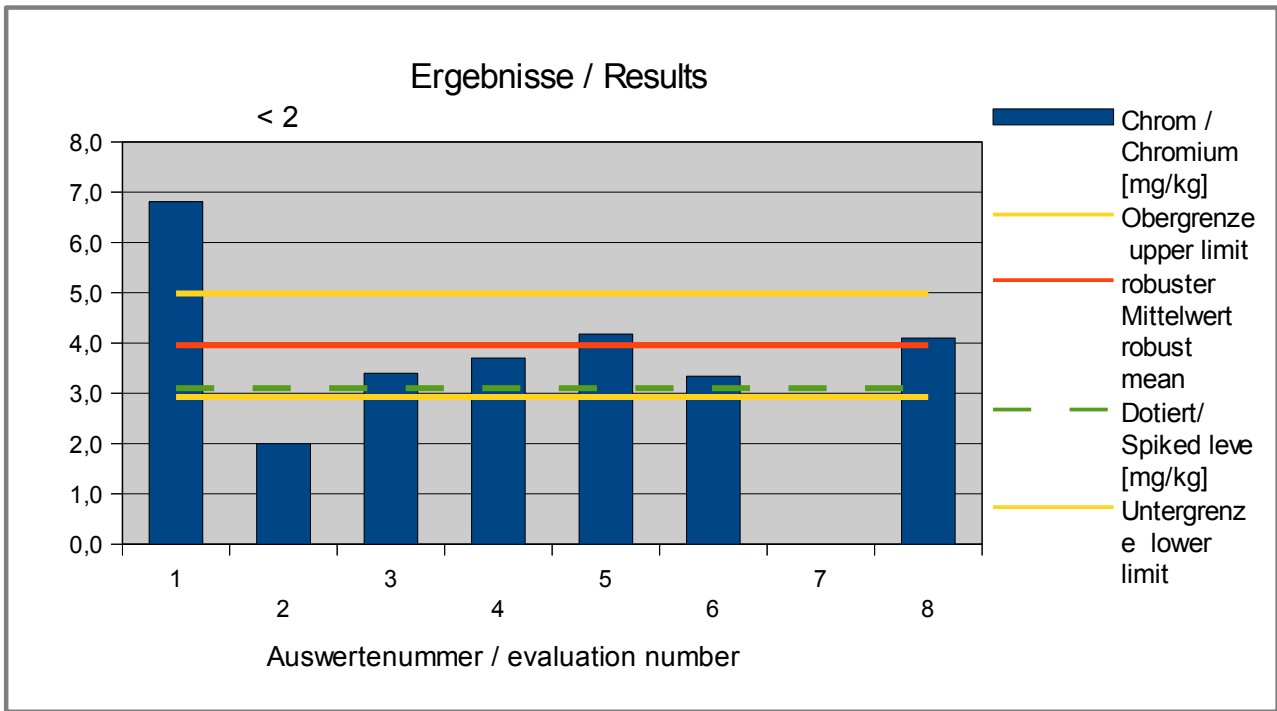


Abb. / Fig. 13: Ergebnisse Chrom / Results Chromium

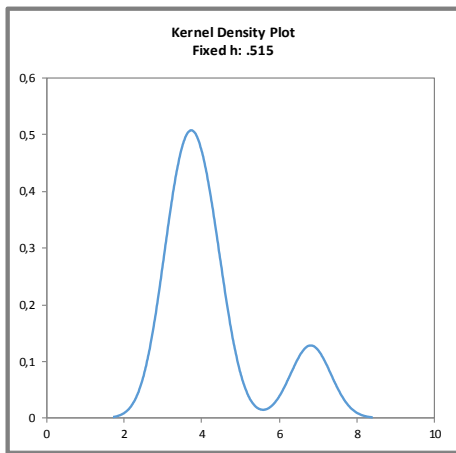


Abb. / Fig. 14:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 7 mg/kg, due to the result outside the target range (outlier).

Ergebnisse der Teilnehmer:
Results of Participants:

Auswertenummer	Chrom / Chromium [mg/kg]	Abweichung [mg/kg]	z-Score (σ _{pt})	z-Score (Info)	Hinweis
Evaluation number		Deviation [mg/kg]			Remark
1	6,81*	2,85	5,5	3,5	Ausreisser / Outlier
2	< 2,0				BG unter Zielbereich / LOQ below target area
3	3,40	-0,557	-1,1	-0,69	
4	3,70	-0,2568	-0,50	-0,32	
5	4,18	0,223	0,43	0,28	
6	3,34	-0,617	-1,2	-0,76	
7					
8	4,10	0,143	0,28	0,18	

* Mean calculated by DLA

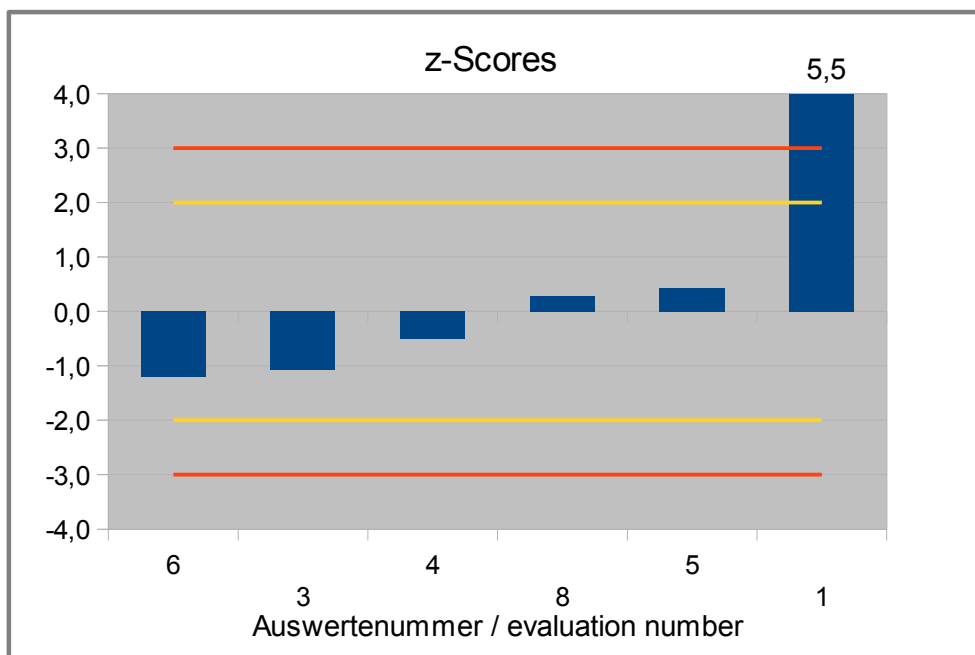


Abb. / Fig. 15: z-Scores Chrom / Chromium

4.6 Copper in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	1
Mean	4310
Median	4640
Robust Mean (X)	4730
Robust standard deviation (S*)	1390
Number with 2 replicates	5
Repeatability SD (S_r)	182
Repeatability (CV_r)	3,54%
Reproducibility SD (S_R)	768
Reproducibility (CV_R)	14,9%
<i>Target range:</i>	
Target standard deviation σ_{pt}	739
Target standard deviation (for Information)	292
lower limit of target range	3250
upper limit of target range	6210
Quotient S^*/σ_{pt}	1,9
Standard uncertainty $U(x_{pt})$	708
Quotient $U(x_{pt})/\sigma_{pt}$	1,0
Results in the target range	5
Percent in the target range	83%

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. In addition, the standard uncertainty was taken into account and the results were evaluated using z'-score (see 3.6.8). For information, the target standard deviation from a precision experiment (ASU § 64 LFGB L00.00-19-2) was given, see 3.6.2.

The distribution of the results showed a slightly increased variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U(x_{pt})/\sigma_{pt}$ is 0,8 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

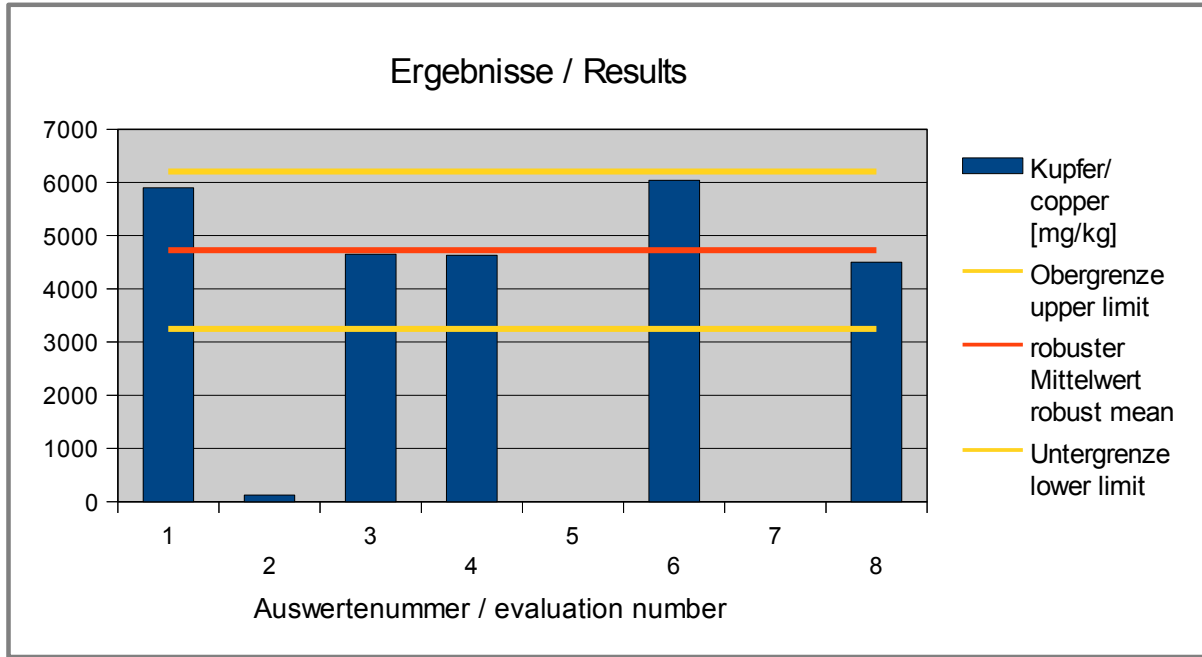


Abb. / Fig. 16: Ergebnisse Kupfer/ Results Copper

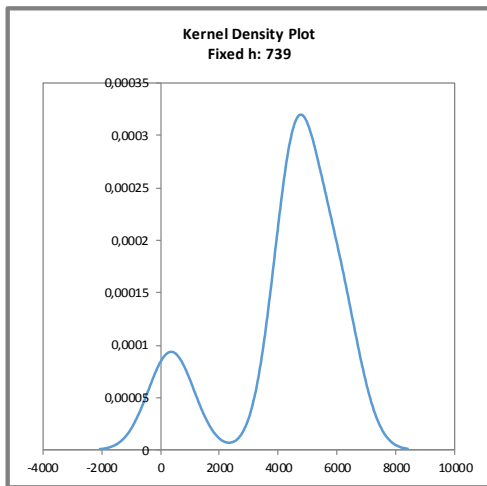


Abb. / Fig. 17:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}'$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}'$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 100 mg/kg, due to the result outside the target range (outlier).

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Kupfer/ copper [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	5900	1170	1,6	4,0	
2	125	-4600	-6,2	-16	Ausreisser / Outlier
3	4650	-76,2	-0,10	-0,26	
4	4630	-98,2	-0,13	-0,34	
5					
6	6040	1310	1,8	4,5	
7					
8	4500	-228	-0,3	-0,8	

* Mean calculated by DLA

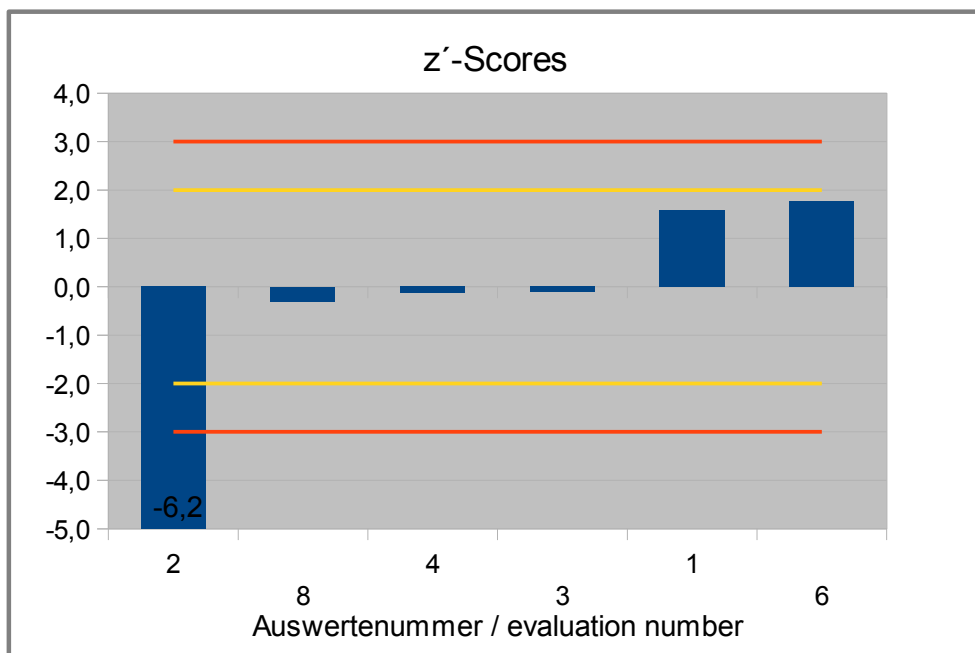


Abb. / Fig. 18: z'-Scores Kupfer/ Copper

4.7 Mercury in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	1,34
Median	1,42
Robust Mean (X)	1,23
Robust standard deviation (S*)	0,415
Number with 2 replicates	6
Repeatability SD (S_r)	0,0328
Repeatability (CV_r)	2,98%
Reproducibility SD (S_R)	0,469
Reproducibility (CV_R)	42,6%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,300
Target standard deviation (for Information)	0,304
lower limit of target range	0,625
upper limit of target range	1,83
Quotient S^*/σ_{pt}	1,4
Standard uncertainty $U_{(X_{pt})}$	0,232
Quotient $U_{(X_{pt})}/\sigma_{pt}$	0,8
Results in the target range	4
Percent in the target range	80%

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. In addition, the standard uncertainty was taken into account and the results were evaluated using z'-score (see 3.6.8). For information, the target standard deviation from a precision experiment (ASU § 64 LFGB K 84.00-33) was given, see 3.6.2.

The distribution of the results showed a slightly increased variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U_{(X_{pt})}/\sigma_{pt}$ is 0,8 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

80% of the results were in the target area.

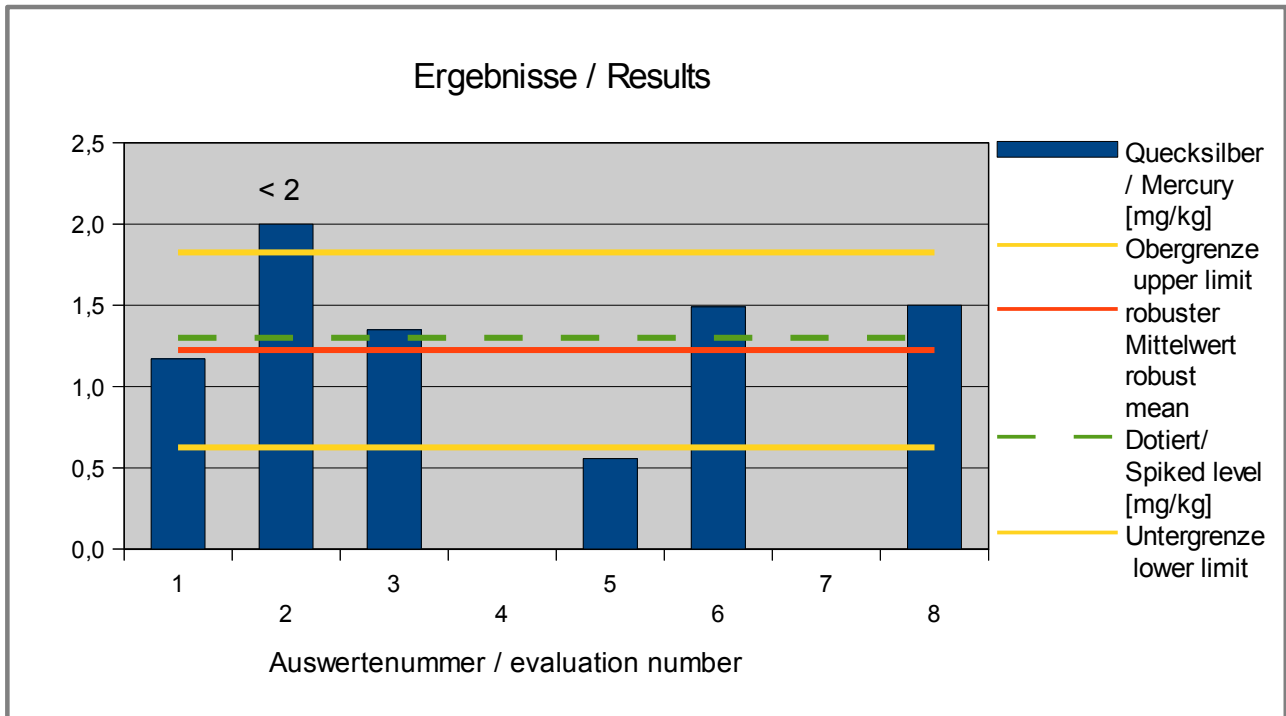


Abb. / Fig. 19: Ergebnisse Quecksilber / Results Mercury

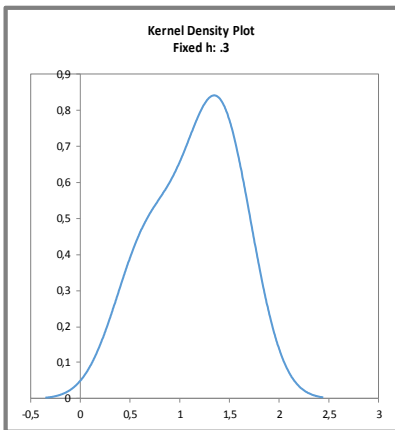


Abb. / Fig. 20:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a shoulder at 0,6 mg/kg, due to the result outside the target range.

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Quecksilber/ Mercury [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	1,17*	-0,0551	-0,18	-0,18	
2	< 2,0				BG über Zielbereich/ LOQ above target area
3	1,35	0,125	0,42	0,41	
4					
5	0,557*	-0,668	-2,2	-2,2	Für die statistische Auswertung wurde der Mittelwert von 5a und 5b verwendet/ The mean value of 5a and 5b was used for the statistical evaluation
5a	0,332*				
5b	0,791*				
6	1,49	0,265	0,88	0,87	
7					
8	1,50	0,275	0,92	0,90	

* Mean calculated by DLA

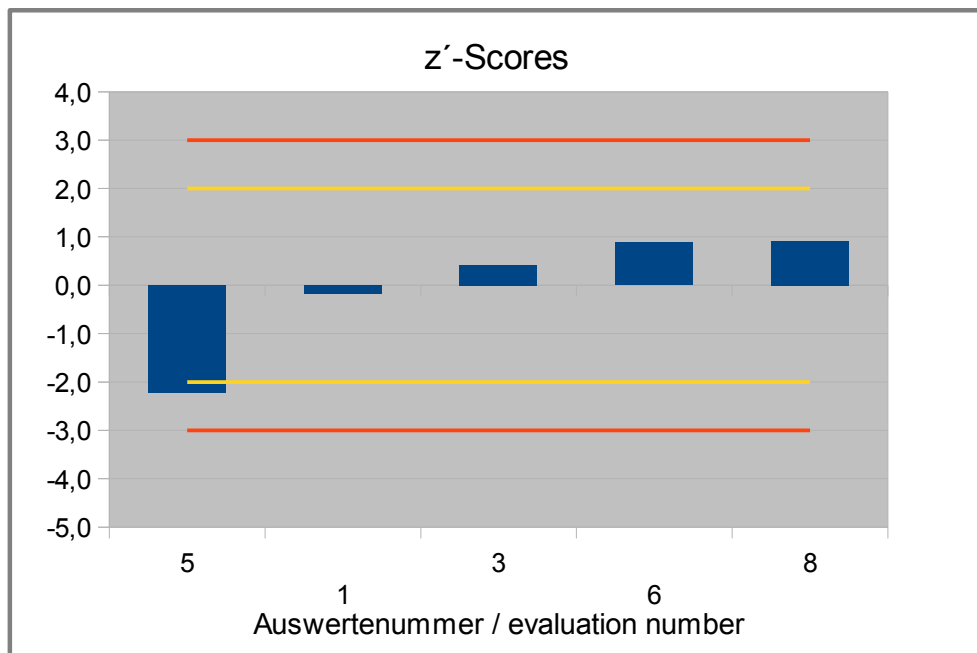


Abb. / Fig. 21: z'-Scores Quecksilber/ Mercury

4.8 Nickel in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	1
Mean	4,65
Median	3,19
Robust Mean (X)	3,21
Robust standard deviation (S*)	0,546
Number with 2 replicates	5
Repeatability SD (S_r)	0,104
Repeatability (CV_r)	3,43%
Reproducibility SD (S_R)	0,31
Reproducibility (CV_R)	10,3%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,430
Target standard deviation (for Information)	0,613
lower limit of target range	2,34
upper limit of target range	4,07
Quotient S^*/σ_{pt}	1,3
Standard uncertainty $U_{(X_{pt})}$	0,279
Quotient $U_{(X_{pt})}/\sigma_{pt}$	0,65
Results in the target range	5
Percent in the target range	83%

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 experiment (ASU § 64 LFGB K 84.00-32) was given, see 3.6.2.

The distribution of the results showed a normal variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U_{(X_{pt})}/\sigma_{pt}$ is 0,6 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

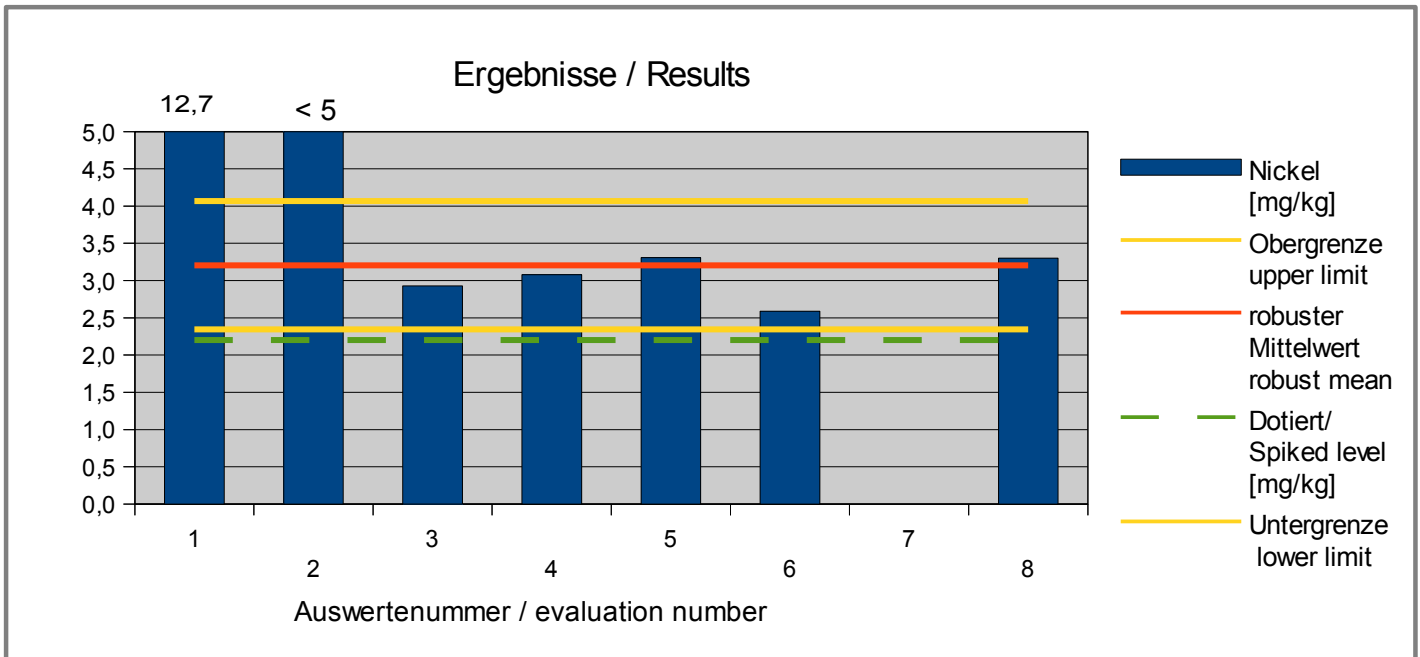


Abb. / Fig. 22: Ergebnisse/ Results Nickel

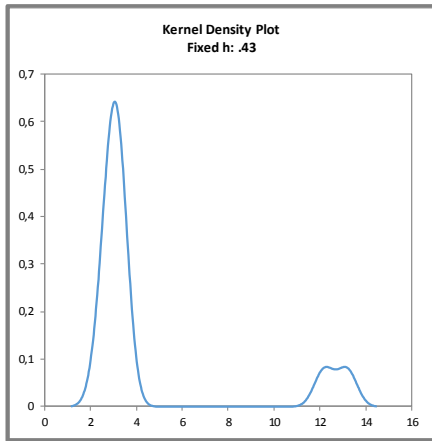


Abb. / Fig. 23:

Kerndichte-Schätzung der Ergebnisse (mit h von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 12 mg/kg, due to the result outside the target range (outlier).

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Nickel [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	12,7*	9,49	22	15	Ausreisser / Outlier
2	< 5,0				BG über Zielbereich/ LOQ above target area
3	2,93	-0,276	-0,64	-0,45	
4	3,08	-0,126	-0,29	-0,20	
5	3,31	0,104	0,24	0,17	
6	2,59	-0,616	-1,4	-1,0	
7					
8	3,30	0,0945	0,22	0,15	

* Mean calculated by DLA

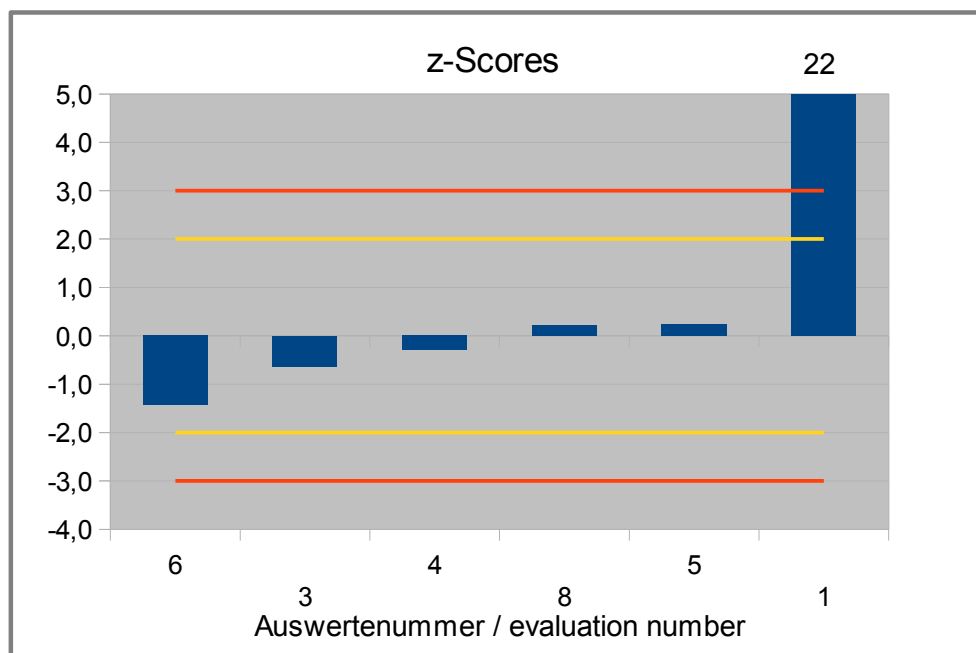


Abb. / Fig. 24: z-Scores Nickel

4.9 Lead in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	1
Mean	2,15
Median	1,27
Robust Mean (X)	1,31
Robust standard deviation (S*)	0,322
Number with 2 replicates	5
Repeatability SD (S_r)	0,0361
Repeatability (CV_r)	2,99%
Reproducibility SD (S_R)	0,177
Reproducibility (CV_R)	14,7%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,201
Target standard deviation (for Information)	0,0847
lower limit of target range	0,905
upper limit of target range	1,71
Quotient S^*/σ_{pt}	1,6
Standard uncertainty $U(x_{pt})$	0,164
Quotient $U(x_{pt})/\sigma_{pt}$	0,82
Results in the target range	5
Percent in the target range	83%

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 experiment (ASU § 64 LFGB K 84.00-32) was given, see 3.6.2.

The distribution of the results showed a normal variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r and CV_R are in the range of established values for the analytical methods used (see 3.6.2) and demonstrate an acceptable variability of the results.

The quotient $U(x_{pt})/\sigma_{pt}$ is 0,8 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

83% of the results were in the target area.

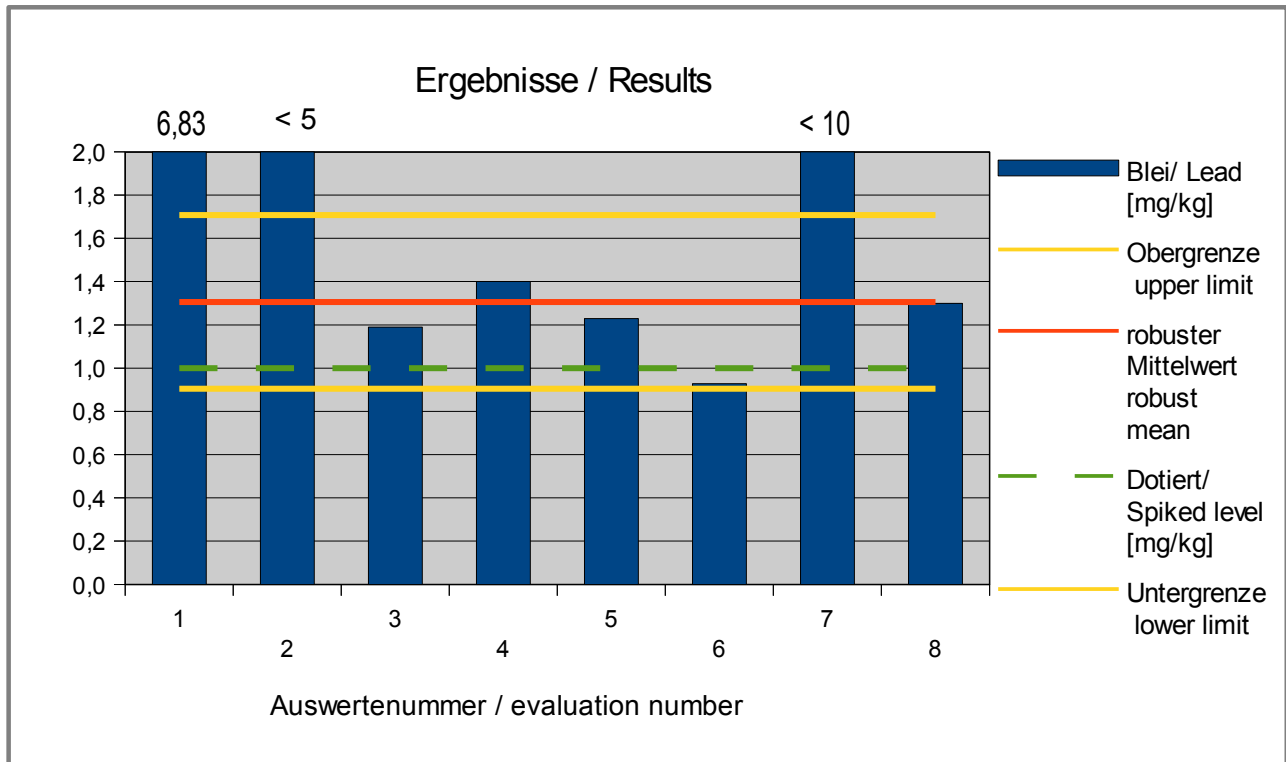


Abb. / Fig. 25: Ergebnisse Blei/ Results Lead

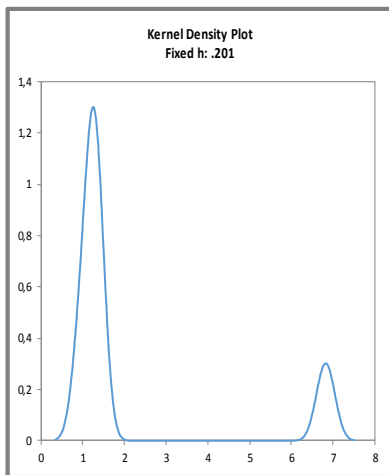


Abb. / Fig. 26:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 7 mg/kg, due to the result outside the target range (outlier).

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Blei/ Lead [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ _{pt})	z-Score (Info)	Hinweis Remark
1	6,83*	5,52	28	65	Ausreisser / Outlier
2	< 5,0				BG über Zielbereich/ Loq above target area
3	1,19	-0,116	-0,58	-1,4	
4	1,40	0,0939	0,47	1,1	
5	1,23	-0,0761	-0,38	-0,90	
6	0,928	-0,378	-1,9	-4,5	
7	< 10				BG über Zielbereich/ Loq above target area
8	1,30	-0,00609	-0,030	-0,072	

* Mean calculated by DLA

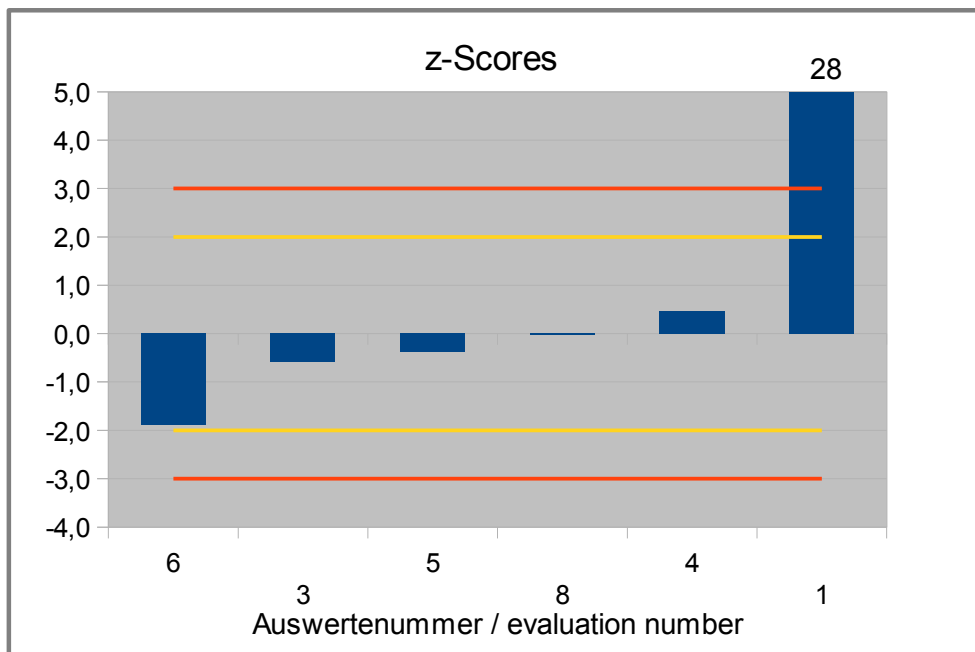


Abb. / Fig. 27: z-Scores Blei/ Lead

4.10 Antimony in mg/kg

The evaluation of the element antimony is only informative, since there were only relatively few results and the distribution of the results showed an increased variability.

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	
Mean	1,95
Median	1,76
Robust Mean (X)	1,77
Robust standard deviation (S*)	1,24
Number with 2 replicates	
Repeatability SD (S_r)	0,331
Repeatability (CV_r)	17,0%
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 $U_{(X_{pt})}$	
Quotient $U_{(X_{pt})}/\sigma_{pt}$	
Results in the target range	
Percent in the target range	

Anmerkungen zu den Kenndaten:

Statistical evaluation is not carried out because there were relatively few results and the distribution of the results showed an increased variability.

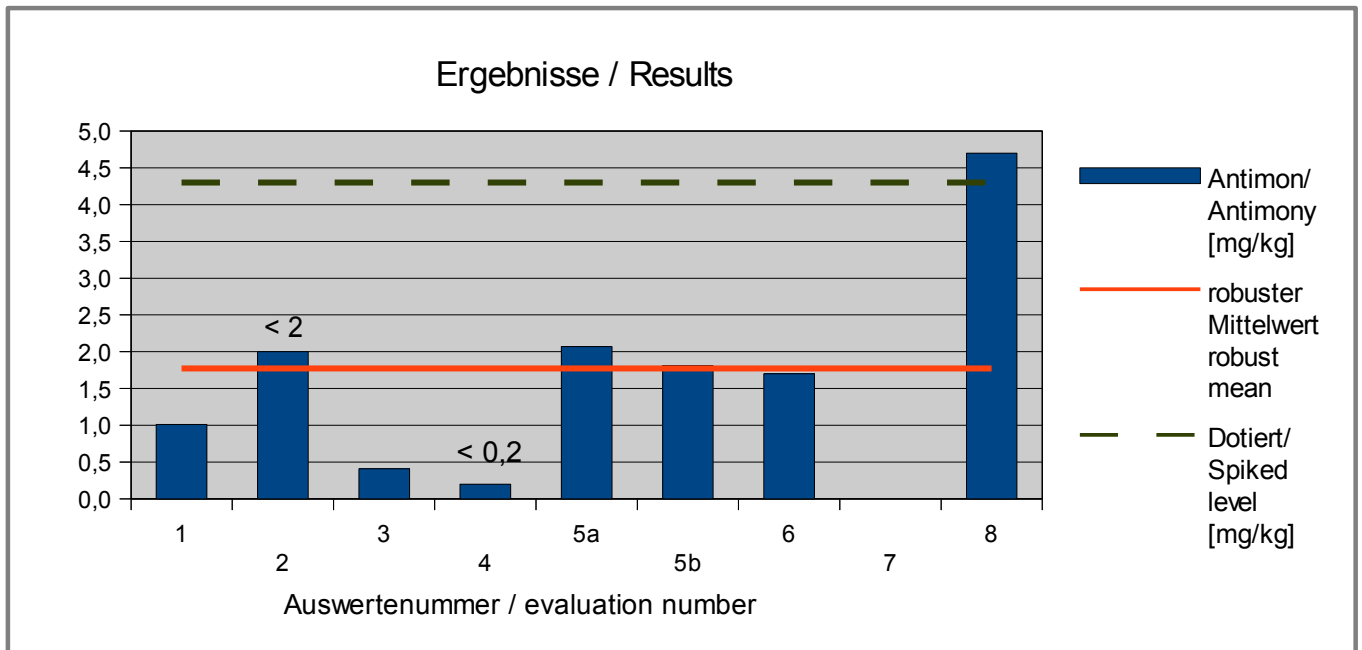


Abb. / Fig. 28: Ergebnisse Antimon/ Results Antimony

Ergebnisse der Teilnehmer:
Results of Participants:

Auswertenummer Evaluation number	Antimon/Antimony [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ _{pt})	z-Score (Info)	Hinweis Remark
1	1,01*	-0,762			
2	< 2				
3	0,410	-1,36			
4	< 0,2				
5a	2,07*	0,298			
5b	1,81*	0,0381			
6	1,70	-0,0719			
7					
8	4,70	2,93			

* Mean calculated by DLA

4.11 Selenium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	3,15
Median	3,46
Robust Mean (X)	3,15
Robust standard deviation (S*)	1,37
Number with 2 replicates	5
Repeatability SD (S_x)	0,495
Repeatability (CV_x)	15,7%
Reproducibility SD (S_R)	1,25
Reproducibility (CV_R)	39,8%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,874
Target standard deviation (for Information)	0,216
lower limit of target range	1,40
upper limit of target range	4,90
Quotient S^*/σ_{pt}	1,6
Standard uncertainty $U(X_{pt})$	0,764
Quotient $U(X_{pt})/\sigma_{pt}$	0,87
Results in the target range	5
Percent in the target range	100%

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. In addition, the standard uncertainty was taken into account and the results were evaluated using z' -score (see 3.6.8). For information, the target standard deviation from a precision experiment (ASU § 64 LFGB L00.00-19-5) was given, see 3.6.2.

The distribution of the results showed a slightly increased variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_x and CV_R are slightly higher than the established values for the analytical methods used (see 3.6.2) and indicate a slightly increased variability of the results.

The quotient $U(X_{pt})/\sigma_{pt}$ is 0,9 over 0,3 and can only be accepted to a limited extent due to the characteristics and the use of different analytical methods.

100% of the results were in the target area.

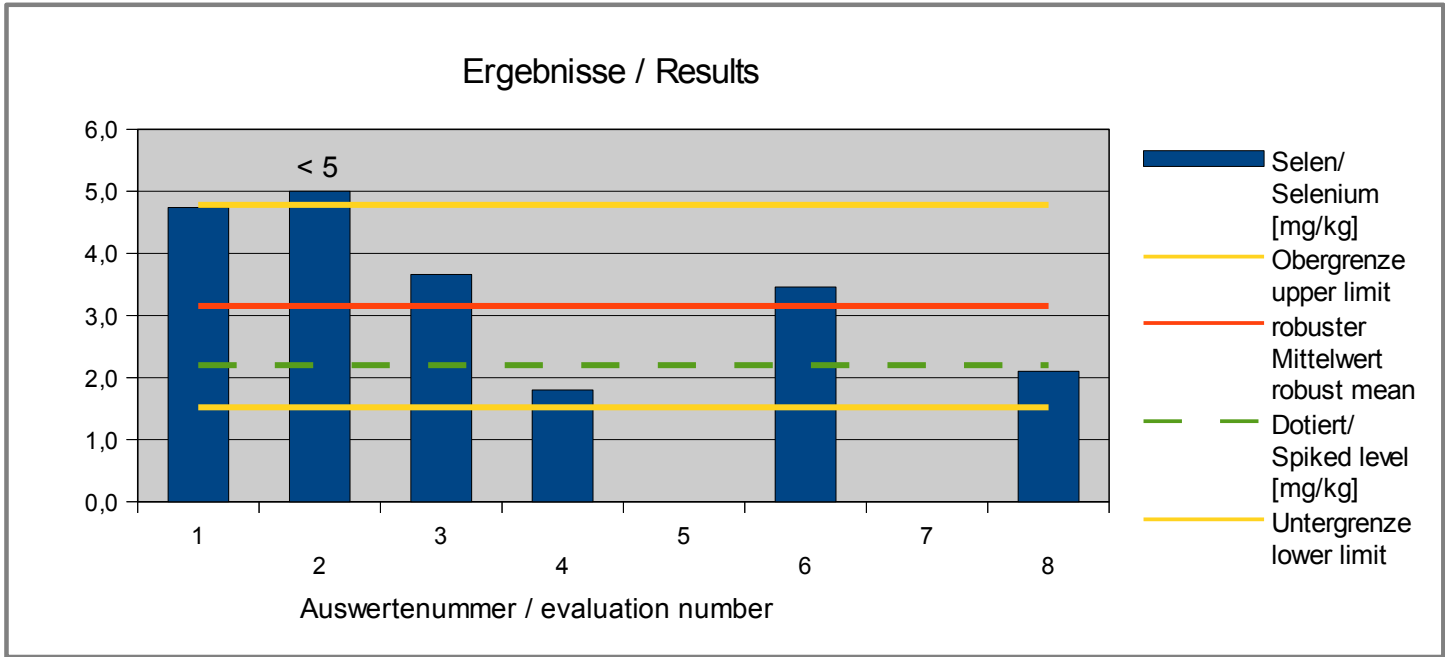


Abb. / Fig. 29: Ergebnisse Selen/ Results Selenium

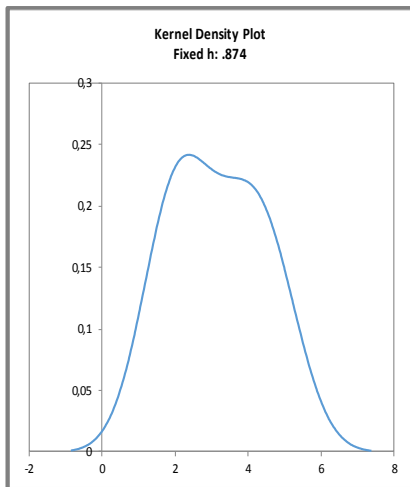


Abb. / Fig. 30:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}'$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}'$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a shoulder at 5 mg/kg.

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer Evaluation number	Selen/Selenium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ _{pt'})	z-Score (Info)	Hinweis Remark
1	4,74*	1,59	1,8	7,4	
2	< 5,0				BG über Zielbereich/ LOQ above target area
3	3,66	0,508	0,58	2,4	
4	1,80	-1,35	-1,5	-6,3	
5					
6	3,46	0,308	0,35	1,4	
7					
8	2,10	-1,05	-1,2	-4,9	

* Mean calculated by DLA

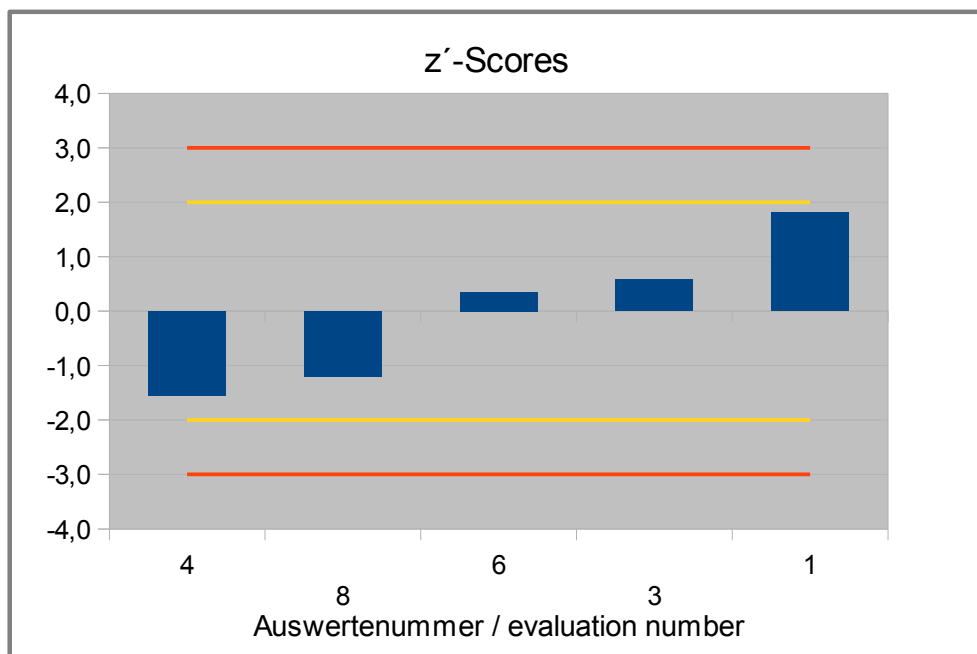


Abb. / Fig. 31: z'-Scores Selen/ Selenium

4.12 Tin in mg/kg

The statistical evaluation for the element tin is only informative, since there were relatively few results and the distribution of the results showed an increased variability.

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	1
Mean	23,5
Median (X_{PT})	2,64
Robust Mean (X)	7,18
Robust standard deviation (S*)	8,72
Number with 2 replicates	4
Repeatability SD (S _r)	0,0453
Repeatability (CV _r)	1,146%
Reproducibility SD (S _R)	3,04
Reproducibility (CV _R)	76,9%
<i>Target range:</i>	
Target standard deviation σ_{pt}	0,365
Target standard deviation (for Information)	0,250
lower limit of target range	1,91
upper limit of target range	3,37
Quotient S^*/σ_{pt}	8,3
Standard uncertainty $U(X_{pt})$	4,452
Quotient $U(X_{pt})/\sigma_{pt}$	12,2
Results in the target range	4
Percent in the target range	67%

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 experiment (ASU § 64 LFGB L00.00-19-5) was given, see 3.6.2.

The distribution of the results showed a increased variability. The quotient S^*/σ_{pt} was well below 2,0. The coefficient of variation CV_r is in the range of established values for the determination methods used (see 3.6.2) and confirms acceptable repeatability. The coefficient of variation CV_R is clearly increased and indicates a limited comparability between the participants.

The quotient $U(X_{pt})/\sigma_{pt}$ is well over 0,3 and can only be accepted to a limited extent due to the characteristics and the use of different analytical methods.

67% of the results were in the target area.

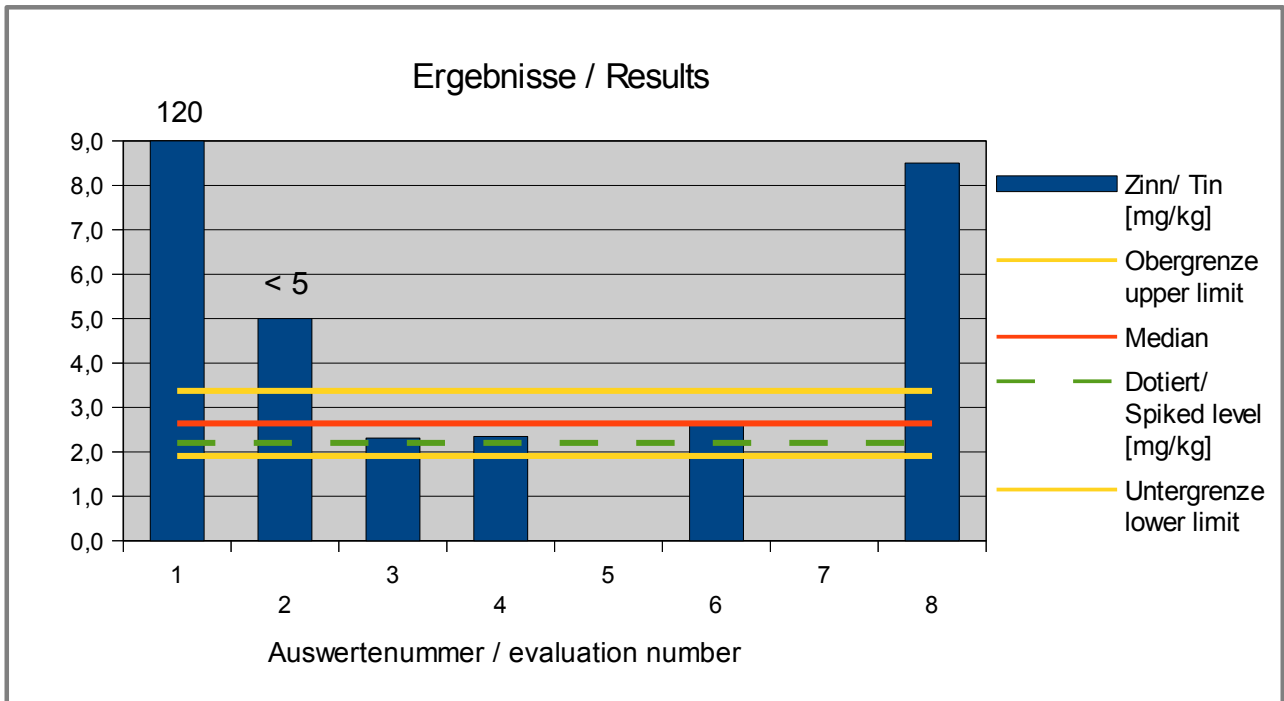


Abb. / Fig. 32: Ergebnisse Zinn/ Results Tin

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswertenummer	Zinn/ Tin [mg/kg]	Abweichung [mg/kg]	z-Score (σ _{pt})	z-Score (Info)	Hinweis
Evaluation number		Deviation [mg/kg]		(Info)	Remark
1	120*	113	322	471	Ausreisser / Outlier
2	< 5,0				BG über Zielbereich/ LOQ above target area
3	2,31	-4,87	-0,90	-1,3	
4	2,35	-4,83	-0,79	-1,2	
5					
6	2,64	-4,54	0,0	0,0	
7					
8	8,50	1,32	16	23	

* Mean calculated by DLA

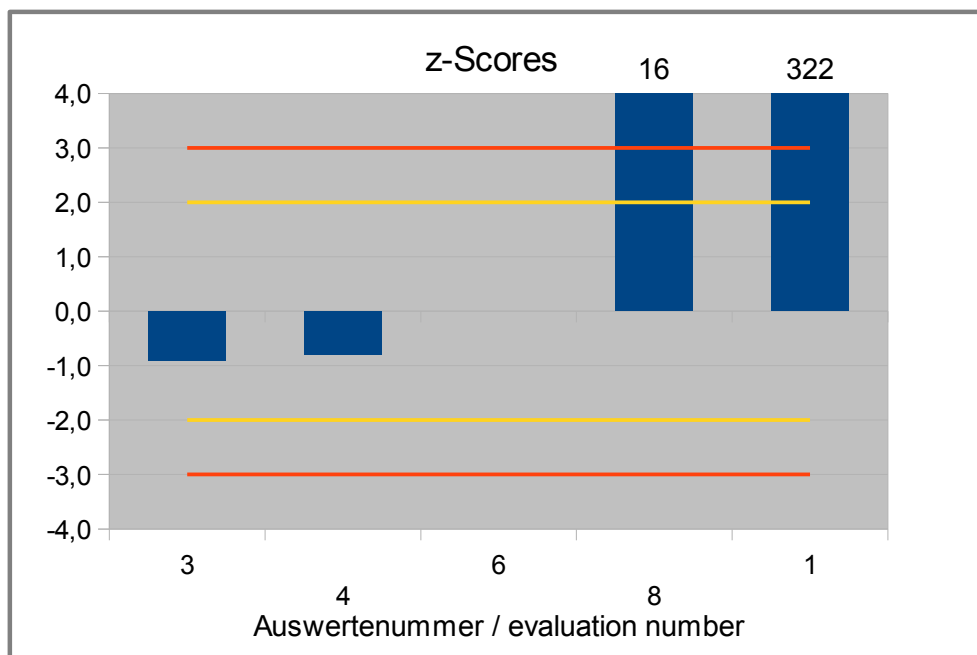


Abb. / Fig. 33: z-Scores Selen/ Selenium

4.13 Zinc in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	1
Mean	10,2
Median (X_{pt})	2,70
Robust Mean	3,14
Robust standard deviation (S^*)	1,84
Number with 2 replicates	4
Repeatability SD (S_r)	0,276
Repeatability (CV_r)	11,2%
Reproducibility SD (S_R)	0,641
Reproducibility (CV_R)	26,1%
<i>Target range:</i>	
Target standard deviation σ_{pt}	1,09
Target standard deviation (for Information)	0,206
lower limit of target range	0,513
upper limit of target range	4,89
Quotient S^*/σ_{pt}	1,7
Standard uncertainty $U(X_{pt})$	1,03
Quotient $U(X_{pt})/\sigma_{pt}$	0,94
Results in the target range	4
Percent in the target range	80%

Comments:

For the valuation the target standard deviation of the general model according to Horwitz was applied. In addition, the standard uncertainty was taken into account and the results were evaluated using z' -score (see 3.6.8). For information, the target standard deviation from a precision experiment (ASU § 64 LFGB L00.00-19-2) was given, see 3.6.2.

The distribution of the results showed a increased variability. The quotient S^*/σ_{pt} was below 2,0. The coefficient of variation CV_r and CV_R are above the range of established values for the analytical methods used (see 3.6.2) and indicate a slightly increased variability of the results.

The quotient $U(X_{pt})/\sigma_{pt}$ is 0,9 over 0,3, but is acceptable due to the other characteristics and the use of different analytical methods.

80% of the results were in the target area.

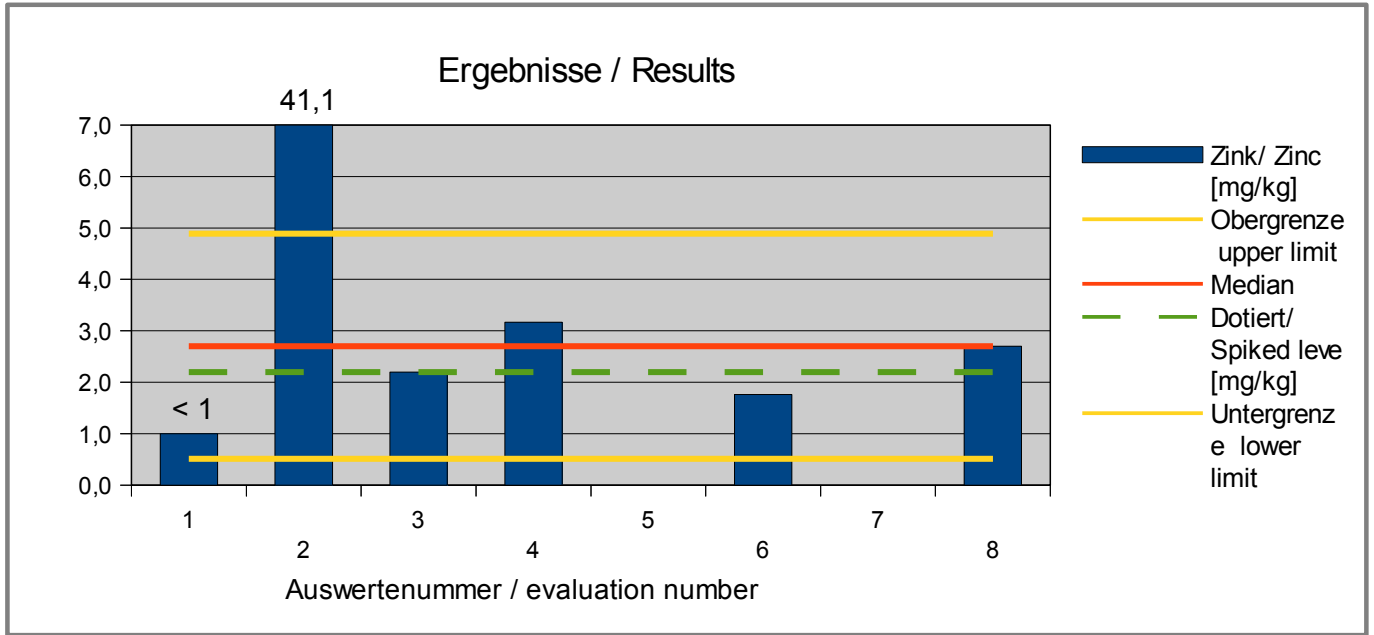


Abb. / Fig. 34: Ergebnisse Zink/ Results Zinc

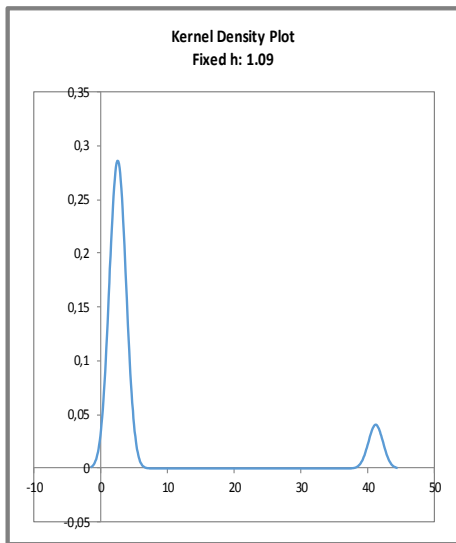


Abb. / Fig. 35:

Kerndichte-Schätzung der Ergebnisse (mit $h = \sigma_{pt}'$ von X_{pt})

Kernel density plot of results (with $h = \sigma_{pt}'$ von X_{pt})

Comment:

The kernel density shows a normal distribution of results with a side peak at 40 mg/kg, due to the result outside the target range (outlier).

**Ergebnisse der Teilnehmer:
Results of Participants:**

Auswerte- nummer	Zink/ Zinc [mg/kg]	Abweichung [mg/kg]	z'-Score (σ _{pt'})	z-Score (Info)	Hinweis
Evaluation number		Deviation [mg/kg]			Remark
1	< 1,0				BG im Zielbereich/ LOQ in the target area
2	41,1	38,0	35	180	Ausreisser / Outlier
3	2,20	-0,943	-0,86	-4,6	
4	3,17	0,0266	0,024	0,13	
5					
6	1,76	-1,38	-1,3	-6,7	
7					
8	2,70	-0,443	-0,41	-2,2	

* Mean calculated by DLA



Abb. / Fig. 36: z'-Scores Zink/ Zinc

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 Arsenic

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	5,72*	5,71	5,72	1	no	
2	3	27	31.10.17	<2	--	--	<2	no	--
3	7	23	08.11.	1,76	1,77	1,76	0,4	no	97
4	14	16	25/10 - 3/11	1,86	1,83	1,88	0,05	no	-
5	21	12							
6	1	29	10.10.17	1,4735	1,555	1,392	0,06		
7	02	28	19.10.17	1,3	1,3	1,3	0,5	no	
8	11	19	19.10.17	2,4	2,3	2,4	0,1		

* Mean calculated by DLA

5.1.1.2 Barium

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	26,4*	26,25	26,51	1	no	
2	3	27	31.10.17	27,1	--	--	<5	no	--
3	7	23	08.11.	22,22	22,24	22,2	5	no	95
4	14	16	25/10 - 3/11	23,9	23,7	24,1	0,05	no	-
5	21	12							
6	1	29	10.10.17	11,505	11,81	11,2	0,0076		
7	02	28							
8	11	19	19.10.17	22	2,1,9	22,1	0,1		

* Mean calculated by DLA

5.1.1.3 Cadmium

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	4,22*	4,22	4,21	1	no	
2	3	27	31.10.17	<5	--	--	<5	no	--
3	7	23	08.11.	2,25	2,24	2,25	0,02	no	98
4	14	16	25/10 - 3/11	2,38	2,37	2,38	0,01	no	-
5	21	12	26.10.+06 .11.17	2,159	2,183	2,135	0,05	no	99
6	1	29	10.10.17	1,44	1,47	1,41	0,0004		
7	02	28	19.10.17	<10	<10	<10	10	no	
8	11	19	19.10.17	2,18	2,16	2,2	0,1		

* Mean calculated by DLA

5.1.1.4 Cobalt

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	7,08*	6,95	7,21	1	no	
2	3	27	31.10.17	<5	--	--	<5	no	--
3	7	23	08.11.	4,49	4,52	4,45	0,1	no	100
4	14	16	25/10 - 3/11	4,76	4,73	4,79	0,05	no	-
5	21	12							
6	1	29	10.10.17	3,89	3,99	3,79	0,002		
7	02	28							
8	11	19	19.10.17	4,26	4,21	4,31	0,1		

* Mean calculated by DLA

5.1.1.5 Chromium

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	6,81*	6,75	6,86	1	no	
2	3	27	31.10.17	<2	--	--	<2	no	--
3	7	23	08.11.	3,40	3,42	3,37	0,3	no	98
4	14	16	25/10 - 3/11	3,70	3,62	3,78	0,05	no	-
5	21	12	03.11.17	4,18	4,3	4,05	0,5	no	103
6	1	29	10.10.17	3,34	3,42	3,26	0,0016		
7	02	28							
8	11	19	19.10.17	4,1	4,2	4,1	0,1		

* Mean calculated by DLA

5.1.1.6 Copper

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	5899,48*	5895,35	5903,6	1	no	
2	3	27	31.10.17	124,9	--	--	<5	no	--
3	7	23	08.11.	4652	4652	4651	1	no	99
4	14	16	25/10 - 3/11	4630	4400	4850	0,05	no	-
5	21	12							
6	1	29	10.10.17	6040,5	6211	5870	0,0008		
7	02	28							
8	11	19	19.10.17	4500	4450	4560	0,1		

* Mean calculated by DLA

5.1.1.7 Mercury

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	1,17*	1,19	1,15	1	no	
2	3	27	31.10.17	<2	--	--	<2	no	--
3	7	23	06.11.18	1,35	1,35	1,36	0,03	no	98
4	14	16	-		-	-		-	-
5	21	12	06.+19.10.17	See single values	see further remarks	see further remarks	0,05	no	119
5a	21			0,322*	0,302/ 0,337/ 0,326				
5b		12		0,791*		0,774/ 0,777/ 0,823			
6	1	29	10.10.17	1,49	1,54	1,44	0,0008		
7	02	28							
8	11	19	19.10.17	1,5	1,5	1,5	0,1		

* Mean calculated by DLA

5.1.1.8 Nickel

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	12,7*	12,19	13,19	1	no	
2	3	27	31.10.17	<5	--	--	<5	no	--
3	7	23	08.11.	2,93	2,88	2,9	0,3	no	98
4	14	16	25/10 - 3/11	3,08	3,04	3,12	0,05	no	-
5	21	12	02.11.17	3,31	3,34	3,28	0,5	no	100
6	1	29	10.10.17	2,59	2,73	2,45	0,0008		
7	02	28							
8	11	19	19.10.17	3,3	3,24	3,38	0,1		

* Mean calculated by DLA

5.1.1.9 Lead

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	6,83*	6,74	6,91	1	no	
2	3	27	31.10.17	<5	--	--	<5	no	--
3	7	23	08.11.	1,19	1,185	1,189	0,04	no	98
4	14	16	25/10 - 3/11	1,40	1,38	1,41	0,05	no	-
5	21	12	25.10.+06 .11.17	1,23	1,29	1,18	0,5	no	100
6	1	29	10.10.17	0,928	0,93	0,926	0,0008		
7	02	28	19.10.17	<10	<10	<10	10	no	
8	11	19	19.10.17	1,3	1,3	1,3	0,1		

* Mean calculated by DLA

5.1.1.10 Antimony

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	1,01*	0,94	1,07	1	no	
2	3	27	31.10.17	<2	--	--	<2	no	--
3	7	23	08.11.	0,41	0,61	0,35	0,5	no	100
4	14	16	25/10 - 3/11	< 0,2	< BG	< BG	0,2	no	-
5	21	12	30.10.17	See single values	see further remarks	see further remarks	0,5	no	92 and 82
5a	21			2,07*	1,48/ 2,52/ 2,22				
5b		12		1,81*		1,76/1,75 /1,85/1,86			
6	1	29	10.10.17	1,7	1,86	1,54	0,0004		
7	02	28							
8	11	19	19.10.17	4,7	4,8	4,6	0,1		

* Mean calculated by DLA

5.1.1.11 Selenium

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	4,74*	4,73	4,75	1	no	
2	3	27	31.10.17	<5	--	--	<5	no	--
3	7	23	08.11.	3,66	3,72	3,6	0,4	no	100
4	14	16	25/10 - 3/11	1,80	1,78	1,82	0,05	no	-
5	21	12							
6	1	29	10.10.17	3,46	2,68	4,24	0,0012		
7	02	28							
8	11	19	19.10.17	2,1	2,1	2,1	0,1		

* Mean calculated by DLA

5.1.1.12 Tin

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	120,31*	119,99	120,63	1	no	
2	3	27	31.10.17	<5	--	--	<5	no	--
3	7	23	08.11.	2,31	2,3	2,32	1,3	no	
4	14	16	25/10 - 3/11	2,35	2,33	2,37	0,5	no	-
5	21	12							
6	1	29	10.10.17	2,64	2,7	2,58	0,0004		
7	02	28							
8	11	19	19.10.17	8,5	8,5	8,5	0,1		

* Mean calculated by DLA

5.1.1.13 Zinc

Teilnehmer	Proben-Nr. A	Proben-Nr. B	Datum d. Analyse	Ergebnis (Mittel)	Ergebnis A	Ergebnis B	Bestimmungsgrenze	Inkl. WF	Wiederfindungsrate [%]
Participant	Sample No. A	Sample No. B	Date of analysis	Result (Mean)	Result A	Result B	Limit of quantification	Incl. RR	Recovery rate [%]
			day/month	mg/kg	mg/kg	mg/kg	mg/kg	yes/no	in %
1	10	20	06.11.	<1*	<1	<1	1	no	
2	3	27	31.10.17	41,1	--	--	<5	no	--
3	7	23	08.11.	2,20	1,89	2,51	2	no	84
4	14	16	25/10 - 3/11	3,17	3,37	2,97	0,5	no	-
5	21	12							
6	1	29	10.10.17	1,76	1,84	1,68	0,0004		
7	02	28							
8	11	19	19.10.17	2,7	2,6	2,8	0,1		

* Mean calculated by DLA

5.1.2 Analytical Methods

5.1.2.1 Arsenic

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3	§64 LFGB K 84.00-31, 07.2016	§64 LFGB K 84.00-29, 07.2016		Calibration with external standards; as reference material, a water (NIST1640a, for Hg: NIST 1641e) was used	no	yes	White, milky solution after digestion. Over night a white precipitate had settled. The clear supernatant was decanted and analysed.
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7	ACM THA 05	Microwave	ICP-MS		no	yes	
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.2 Barium

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3	§64 LFGB K 84.00-31, 07.2016	§64 LFGB K 84.00-29, 07.2016			no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.3 Cadmium

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3	§64 LFGB K 84.00-31, 07.2016	§64 LFGB K 84.00-29, 07.2016			no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5	Graphite tube AAS after pressure digestion according to ASU K 84.00-29	Homogenization in an ultrasonic bath, Digestion according to ASU K 84.00-29: 30 min at 200°C	Graphite tube AAS	external Calibration	yes	yes	general hint: Homogenization in ultrasonic bath unsuitable: Sample material changes (demixture and possibly polymerisation)
6							
7	ACM THA 05	Microwave	AAS		no	yes	
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.4 Cobalt

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		§64 LFGB K 84.00-29, 07.2016	According to §64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.5 Chromium

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		§64 LFGB K 84.00-29, 07.2016	According to §64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5	Graphite tube AAS after pressure digestion according to ASU K 84.00-29	Homogenization in an ultrasonic bath, Digestion according to ASU K 84.00-29: 30 min at 200°C	Graphite tube AAS	external Calibration	yes	yes	
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.6 Copper

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	\$64 KB84.00-32	\$64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		\$64 LFGB K 84.00-29, 07.2016	According to \$64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.7 Mercury

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	\$64 KB84.00-32	\$64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3	\$64 LFGB K 84.00-33, 07.2016	\$64 LFGB K 84.00-29, 07.2016			no	yes	
4	-	-	-				
5	ASU K 84.00-33 after pressure digestion according to ASU K 84.00-29	Homogenization in an ultrasonic bath, Digestion according to ASU K 84.00-29: 30 min at 200°C	cold vapour AAS according to ASU K 84.00-33	external calibration	yes	yes	Sample material inhomogeneous => no averaging possible! Single data A: 0,302 / 0,337 / 0,326 Single data B: 0,774 / 0,777 / 0,908 / 0,823
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.8 Nickel

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3	§64 LFGB K 84.00-31, 07.2016	§64 LFGB K 84.00-29, 07.2016			no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5	Graphite tube AAS after pressure digestion according to ASU K 84.00-29	Homogenization in an ultrasonic bath, Digestion according to ASU K 84.00-29: 30 min at 200°C	Graphite tube AAS	external Calibration	yes	yes	
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.9 Lead

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	\$64 KB84.00-32	\$64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3	\$64 LFGB K 84.00-31, 07.2016	\$64 LFGB K 84.00-29, 07.2016			no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5	Graphite tube AAS after pressure digestion according to ASU K 84.00-29	Homogenization in an ultrasonic bath, Digestion according to ASU K 84.00-29: 30 min at 200°C	Graphite tube AAS	external Calibration	yes	yes	
6							
7	ACM THA 05	Microwave	AAS		no	yes	
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.10 Antimony

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibrations reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		§64 LFGB K 84.00-29, 07.2016	According to §64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5	Graphite tube AAS after pressure digestion according to ASU K 84.00-29	Homogenization in an ultrasonic bath, Digestion according to ASU K 84.00-29: 30 min at 200°C	Graphite tube AAS	external Calibration	yes	yes	Sample material inhomogeneous => no averaging possible! Single data A: 1,48 / 2,52 / 2,22 Single data B: 1,76 / 1,75 / 1,85 / 1,86
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.11 Selenium

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		§64 LFGB K 84.00-29, 07.2016	According to §64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.12 Tin

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference Material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		§64 LFGB K 84.00-29, 07.2016	According to §64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.1.2.13 Zinc

Teilnehmer	Methodenbeschreibung	Probenvorbereitung	Messmethode	Kalibrierung und Referenzmaterial	Wiederfindung mit gleicher Matrix	Methode akkreditiert	Sonstige Hinweise
Participant	Method description	Sample preparation	Measuring method	Calibration and reference material	Recovery with same matrix	Method accredited	Further remarks
					yes/no	yes/no	
1	§64 KB84.00-32	§64	ICP_OES	Multi-element standard	no	no	
2	ASTM F963-17	Sample was dewaxed before analysis	Clause 8.3.5.7 sample with oil must be dewaxed		no	yes	
3		§64 LFGB K 84.00-29, 07.2016	According to §64 LFGB K 84.00-31, 07.2016		no	yes	
4	ASU K84.00-31	ASU K84.00-29	ICP-MS			no	
5							
6							
7							
8	EN 16711-1 / 17294	* see note				yes	* Note: The samples were digested with nitric acid and hydrofluoric acid. Without hydrofluoric acid, some elements are expected to be underestimation

5.2 Homogeneity

5.2.1 Repeatability std. dev. of the double determinations

The calculation of the repeatability standard deviation S_r of the double determinations of the participants was used as a homogeneity criterion for this PT.

Element	Coefficient of variation CV_r
Arsenic	3,58%
Barium	1,19%
Cadmium	1,05%
Cobalt	2,29%
Chromium	2,99%
Copper	3,54%
Mercury	2,98%
Nickel	3,43%
Lead	2,99%
Tin	1,15%

5.2.2 Comparison of sample number/test results and trend line

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

Chromium			
Target standard deviation σ_{pt}	0,515		mg/kg
Sample numbers	1 - 29		
Total numbers of samples	12		
Slope	-0,0201		
Trend line range	4,391	-	4,150 mg/kg
Deviation trend line	4,271	±	0,121 mg/kg
Percent of σ_{pt}	23,4		%

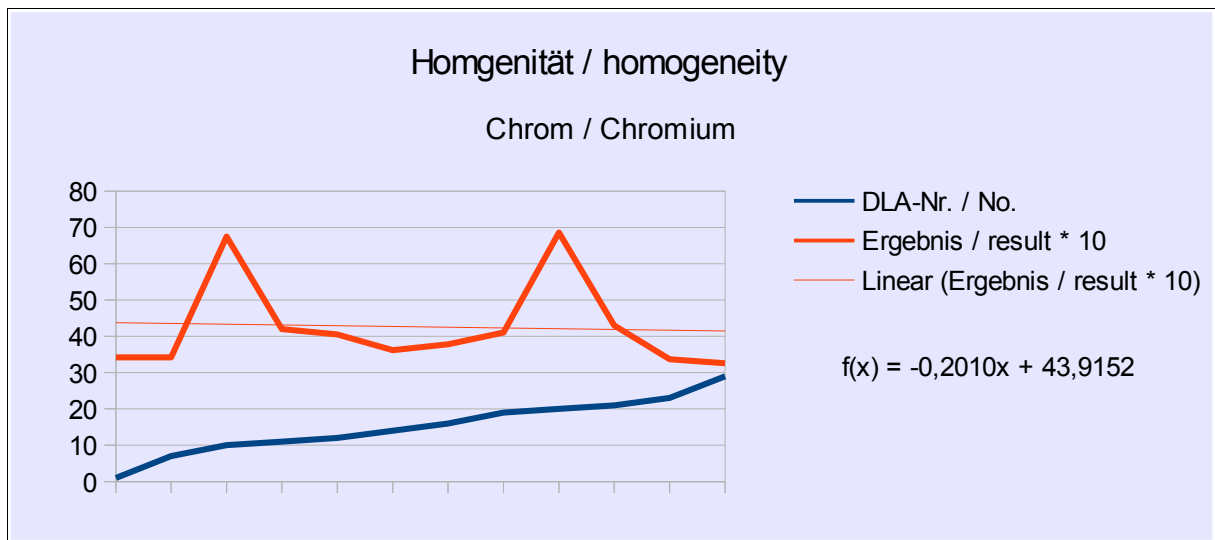


Abb./Fig. 37:

Trendfunktion Probennummern vs. Ergebnisse (*10 dargestellt)
 trend line function sample number vs. results (*10 shown)

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)

<i>PT number</i>	DLA 55-2017
<i>PT name</i>	Tattoo Product: Analysis of 13 Elements in Tattoo Dyes (As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Zn)
<i>Sample matrix*</i>	Samples A + B: Tattoo Dyes (Dye Mixture violet/green)
<i>Number of samples and sample amount</i>	2 identical samples A + B, 5 g each.
<i>Storage</i>	Samples A + B: cooled 2 - 10°C
<i>Intentional use</i>	Laboratory use only (quality control samples)
<i>Parameter</i>	quantitative: As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn and Zn
<i>Methods of analysis</i>	Analytical methods are optional
<i>Notes to analysis</i>	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.
<i>Result sheet</i>	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.
<i>Units</i>	mg/kg
<i>Number of significant digits</i>	at least 2
<i>Further information</i>	For information please specify: <ul style="list-style-type: none"> - 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
<i>Result submission</i>	The result submission file should be sent by e-mail to: pt@dla-lvu.de
<i>Deadline</i>	the latest 10th November 2017
<i>Evaluation report</i>	The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.
<i>Coordinator and contact person of PT</i>	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

[Die Adressdaten der Teilnehmer wurden für die allgemeine Veröffentlichung des Auswertebereichs 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 Methodvalidierung / 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 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 Analytical 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
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