Evaluation Report
proficiency test

DLA ptSU08 (2020)

Heavy Metals and Trace Elements:

in High-Fat Food

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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 ptSU08 (2020)
EP-Koordinator *PT-Coordinator*	Dr. Matthias Besler-Scharf
Status des EP-Bericht *Status of PT-Report*	Abschlussbericht / Final report (29 January 2021) Gültig ist die jeweils letzte Version/Korrektur des Berichts. Sie ersetzt alle vorangegangenen Versionen. Only the latest version/correction of the report is valid. It replaces all preceding versions.
EP-Bericht Freigabe *PT-Report Authorization*	Dr. Matthias Besler-Scharf (Technischer Leiter / Technical Manager) *- gezeichnet / signed M. Besler-Scharf* Alexandra Scharf MSc. (QM-Beauftragte / Quality Manager) *- gezeichnet / signed A. Scharf* Datum / Date: 29 January 2021
Unteraufträge *Subcontractors*	Im Rahmen dieser Eignungsprüfung wurden nachstehende Leistungen im Unterauftrag vergeben: Homogenitätsprüfung der EP-Parameter, As part of the present proficency test the following services were subcontracted: Homogeneity tests of PT-parameter(s),
Vertraulichkeit *Confidentiality*	Die Teilnehmerergebnisse sind im EP-Bericht in anonymisierter Form mit Auswertenummern benannt. Daten einzelner Teilnehmer werden ausschließlich nach vorheriger Zustimmung des Teilnehmers an Dritte weitergegeben. Participant result are named anonymously with evaluation numbers in the PT report. Data of individual participants will be passed on to third parties only with prior consent of the participant.

Contents

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 a milk product with sports nutrition made from cream and casein powders from European suppliers. With the exception of the elements arsenic, cadmium, chromium, mercury, lead and selenium, which were added to the material, the contents of the parameters are of natural origin.

After sieving and homogenization of the raw materials cream and casein powder (<500 mesh), the above-mentioned elements were spiked by adding standard solutions to an aliquot of the basic mixture. The mixture was dried at 40°C overnight, homogenized and sieved (mesh <600 µm). Subsequently, basic mixture was added and homogenized again in 3 further steps until the total amount was reached.

Afterwards the samples were portioned to approximately 8 g into metallised PET film bags and chronologically numbered.

The composition of the PT samples is given in Table 1.

Table 1: Composition of DLA-Samples

Ingredients	**Content**
Cream Powder Ingredients: 100% spray-dried cream Nutrients per 100 g: Fat 75 g, carbohydrates 12,5 g, protein 9,4 g	78,2 g/100 g
Casein Powder, Organic Ingredients: 100% milk casein concentrate Nutrients per 100 g: Fat 78 g, carbohydrates 5 g, protein 2 g	21,8 g/100 g
As - Arsenic (standard solution)	0,21 mg/kg
Cd - Cadmium (standard solution)	0,081 mg/kg
Cr - Chromium (standard solution)	1,0 mg/kg
Hg - Mercury (standard solution)	0,080 mg/kg
Pb - Lead (standard solution)	0,21 mg/kg
Se - Selenium (standard solution)	0,40 mg/kg

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

2.1.1 Homogeneity

The **mixture homogeneity before bottling** was examined 8-fold by determination of copper and lead by ICP/MS (DIN EN ISO 17294-2). The repeatability standard deviation was 1,5% and 11% and thus within the range of repeatability standard deviations of comparable methods (e.g. ASU §64 L 00.00-144, s. 3.6.1). The results of homogeneity analysis are given in the documentation.

The calculation of the **repeatability standard deviations S_r of the participants** was also used as an indicator of homogeneity. For all parameters with more than 7 results they are in the range of 1,1% – 8,6%. Thus they were similar to the repeatability standard deviations of the corresponding official methods (e.g. ASU §64 L 00.00-144, s. 3.6.2) (see Tab. 3) [18-28]. The repeatability standard deviations of the participants' results are given in the documentation in the statistic data (see 4.1 and 4.20).

Furthermore, the homogeneity was graphically characterized for information by the **trend line function of participants' results for chronological bottled single samples** (s. 5.2.1).

In case the criterion for sufficient homogeneity of the test items is not fulfilled the impact on the target standard deviation will be verified. If necessary the evaluation of results will be done considering the standard uncertainty of the assigned value by z'-scores (s. 3.8 and 3.11) [3].

2.1.2 Stability

A water activity (a_W) of < 0,5 is an important factor to ensure the stability of dry or dried products during storage. Optimum conditions for storage is the a_W value range of 0,15 - 0,3. In this range the lowest possible degradation rate is to be expected [16].

The experience with various DLA test materials showed good storage stability with respect to the durability of the sample (spoilage) and the content of the PT parameters for comparable food matrices and water activity (a_W value <0,5).
The a_W value of the EP samples was approx. 0,55 (15°C). The stability of the sample material was thus ensured during the investigation period under the specified storage conditions.

2.2 Sample shipment and information to the test

Two portions of test material were sent to every participating laboratory in the 40th week of 2020. The testing method was optional. The tests should be finished at 11th December 2020 the latest.

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

Heavy Metals and Trace Elements in high-fat Food (with Dairy Product and Caseinate Powder), approx. 20 Elements incl. As, Cd, Hg and Pb

The two portions contain identical samples with the parameters As, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, P, Pb, S, Se, Sn and Zn in the matrix of sports nutrition (drink powder) with dairy product and caseinate (fat content >50%). The analysis method is optional.

Please note the attached information on the proficiency test.
(see documentation, section 5.4 Information on the PT)

2.3 Submission of results

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

The finally calculated concentrations of the parameter as average of duplicate determinations of both numbered samples were 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 methods. In case participants submitted several results for the same parameter obtained by different methods these results were evaluated with the same evaluation number with a letter as a suffix and indication of the related method.

All 9 participants submitted their results in time.

3. Evaluation

3.1 Consensus value from participants (assigned value)

The robust mean of the submitted results was used as assigned value (X_{pt}) („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: Δ median - rob. mean > 0,3 σ_{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 mg/kg or < 2,5 mg/kg) or the indicating "0" will not be considered for the statistic evaluation [3].

3.2 Robust standard deviation

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

3.3 Repeatability standard deviation

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

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

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

3.4 Reproducibility standard deviation

The reproducibility standard deviation S_R represents a inter-laboratory estimate of the standard deviation for the determination of each parameter on the bases of (outlier free) individual participant results. It takes into account both the repeatability standard deviation S_r and the within-laboratory standard deviation S_S. Reproducibility standard deviations of PT´s may differ from reproducibility standard deviations of ring trials, because the participating laboratories of a PT generally use different internal conditions and methods for determining the measured values.
In the present evaluation, the specification of the reproducibility standard deviation, therefore, does not refer to a specific method, but characterizes approximately the comparability of results between the laboratories, assumed the effect of homogeneity and stability of the sample are negligible.

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

The relative reproducibility standard deviation CV_R in percent of the mean is given as variation coefficient in the statistical data of participant for each parameter. The significance of CV_R is further explained in section 3.9.

3.5 Exclusion of results and outliers

Before statistical evaluation obvious blunders, such as those with incorrect units, decimal point errors, too few significant digits (valid digits) or results for another proficiency test item can be removed from the data set [2]. Even if a result e.g. with a factor >10 deviates significantly from the mean and has an influence on the robust statistics, a result of the statistical evaluation can be excluded [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 tested for outliers by the use of robust statistics (algorithm A): If a value deviates from the robust mean by more than 3 times the robust standard deviation, it can be classified as an outlier (see above) [3]. Due to the use of robust statistics outliers are not excluded, provided that no other reasons are present [3]. Detected outliers are only mentioned in the results section, if they have been excluded from the statistical evaluation.

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.

For valuation of all elements except Ca and P in the present PT the target standard deviation according to the general model of Horwitz or Horwitz/Thompson was applied (see 3.6.1). For Ca and P the target standard deviation was calculated using data from a precision experiment (s. 3.6.2, ASU §64 method L 00.00-144).

Additionally for B the standard uncertainty was considered by evaluating with z'-scores (see 3.8).

Due to the number of < 5 the results for S and Sn were not evaluated with z-scores.

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)

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} [21, 25-28]

Para-meter	Matrix	Mean [mg/kg]	RSD_r	RSD_R	σ_{pt}	Method / Literature
Al	Cocoa powder	205	3,25%	5,83%	5,36%[1]	ICP-MS [16]
	Cocoa powder	210	1,91%	8,71%	8,61%	ICP-OES [17]
As	Fish homogenate	1,6	4,6%	8,8%	8,18%	ICP-MS [18]
	Mussels	9,3	4,5%	13%	12,6%	ICP-MS [18]
Ca	Lobster	183	4,90%	6,31%	5,27%	ICP-OES [22]
	Children´s food soy	6191	3,41%	7,97%	7,60%[1]	ICP-OES [22]
Cd	Fish homogenate	0,87	7,3%	11%	9,71%[1]	ICP-MS [18]
	Mussels	1,7	3,9%	9,5%	9,09%	ICP-MS [18]
Cr	Baby food	0,17	7,3%	19%	18,3%	GF-AAS [20]
	Rice powder	0,11	19,2%	35%	32,3%[1]	GF-AAS [20]
Cu	Lobster	16,40	5,72%	6,82%	5,49%	ICP-OES [22]
	Children´s food soy	4,51	4,30%	11,06%	10,6%[1]	ICP-OES [22]
Fe	Lobster	12,1	6,45%	8,59%	7,28%	ICP-OES [22]
	Children´s food soy	77	2,75%	6,98%	6,70%[1]	ICP-OES [22]
I	Codfish muscles	4,15	0,7%	8,9%	8,89%	ICP-MS (16)
	Soy food	1,26	3,7%	6,7%	6,17%	ICP-MS (16)
K	Lobster	871	3,63%	6,27%	5,71%	ICP-OES [22]
	Children´s food soy	6733	4,08%	5,49%	4,67%[1]	ICP-OES [22]
Mn	Lobster	1,20	4,74%	7,95%	7,21%	ICP-OES [22]
	Children´s food soy	2,19	4,67%	13,7%	13,3%[1]	ICP-OES [22]
Mg	Lobster	85	3,73%	8,63%	8,21%	ICP-OES [22]
	Children´s food soy	599	4,30%	7,64%	7,01%[1]	ICP-OES [22]
Mo	Baby food	0,50	6,6%	21%	20,5%	GF-AAS [20]
	Rice powder	0,56	8,7%	20%	19,0%[1]	GF-AAS [20]
Na	Lobster	186	3,31%	6,60%	6,17%	ICP-OES [22]
	Children´s food soy	2220	3,67%	4,89%	4,15%[1]	ICP-OES [22]
P	Lobster	973	3,16%	7,13%	6,78%	ICP-OES [22]
	Children´s food soy	4129	3,45%	7,87%	7,48%[1]	ICP-OES [22]
Pb	Fish homogenate	2,1	5,0%	8%	7,18%	ICP-MS [18]
	Mussels	2,5	13%	16%	13,1%	ICP-MS [18]
S	Lobster	876	3,13%	7,54%	7,21%	ICP-OES [22]
	Children´s food soy	1234	3,86%	10,71%	10,4%	ICP-OES [22]
Se	Katfish	1,797	9,85%	10,1%	7,31%	AAS [21]
	Rice	0,374	2,41%	11,8%	11,7%	AAS [21]
Zn	Lobster	13,9	4,63%	7,90%	7,19%	ICP-OES (22)
	Children´s food soy	43,5	2,60%	6,89%	6,64%	ICP-OES (22)

[1] *used in evaluation (s. chapter 4)*

3.6.2 Value by precision experiment

Using the reproducibility standard deviation σ_R and the repeatability standard deviation σ_r of a precision experiment (collaborative trial or proficiency test) the target standard deviation σ_{pt} can be derived considering the number of replicate measurements m of participants in the present PT [3]:

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

The relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviation (RSD_R) given in Table 2 were determined in ring tests using the indicated methods.
The resulting target standard deviations σ_{pt}, which were identified there, were used to evaluate the results and to provide additional information for the statistical data.

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 was regarded suitable.

Table 3 shows selected statistic data of participants results of present PT compared to PT results of previous years.

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 valid z-Score for each parameter is indicated as z-Score (σ_{pt}).

Table 3: Characteristics of the present PT (on grey) in comparison to previous PTs since 2017 (SD = standard deviation, CV = coefficient of variation)

Para-meter	**Matrix (Powder)**	**robust Mean** [mg/kg]	**rob. SD (S*)** [mg/kg]	**rel. SD (VK_{S*}) [%]**	**Quotient S^*/σ_{pt}**	**DLA-report**
As	Cream/Casein	0,230	0,0212	9,21%	0,46	ptSU08 (2020)
B	Potatoes	3,88	0,689	17,8%	1,4	DLA 46/2017
B	Moringa leafs	31,5	2,89	9,19%	0,97	DLA 49/2019
B	Cream/Casein	0,681	0,294	43,3%	1,6[1]	ptSU08 (2020)
Ba	Potatoes	0,220	-	-	-	DLA 46/2017
Ba	Food Supplement	0,708	0,0791	11,2%	0,66	DLA 49/2018
Ba	Moringa leafs	71,3	2,00	2,80%	0,33	DLA 49/2019
Ba	Cream/Casein	0,949	0,0708	7,46%	0,46	ptSU08 (2020)
Ca	Potatoes	238	12,0	5,04%	0,72	DLA 46/2017
Ca	Food Supplement	6540	259	3,97%	0,93	DLA 49/2018
Ca	Moringa leafs	19588	1727	8,81%	1,2	DLA 49/2019
Ca	Cream/Casein	10300	1110	10,7%	1,4	ptSU08 (2020)
Cd	Potatoes	0,0399	0,0029	7,30%	0,28	DLA 46/2017
Cd	Food Supplement	0,0116	0,00263	22,7%	0,73	DLA 49/2018
Cd	Cream/Casein	0,0757	0,00994	13,2%	0,60	ptSU08 (2020)
Cr	Food Supplement	0,218	0,0594	27,2%	1,4	DLA 49/2018
Cr	Cream/Casein	1,09	0,0797	7,31%	0,46	ptSU08 (2020)
Cu	Potatoes	1,98	0,117	5,90%	0,41	DLA 46/2017
Cu	Food Supplement	4,28	0,611	14,3%	1,1	DLA 49/2018
Cu	Moringa leafs	4,86	0,291	5,98%	0,47	DLA 49/2019
Cu	Cream/Casein	0,444	0,0499	11,2%	0,62	ptSU08 (2020)
Fe	Potatoes	15,0	1,22	8,10%	0,76	DLA 46/2017
Fe	Food Supplement	60,3	4,41	7,31%	0,85	DLA 49/2018
Fe	Moringa leafs	108	6,65	6,14%	0,78	DLA 49/2019
Fe	Cream/Casein	2,16	0,537	24,9%	1,7	ptSU08 (2020)
Hg	Cream/Casein	0,0701	0,0136	19,4%	0,88	ptSU08 (2020)
K	Potatoes	13162	604	4,59%	1,2	DLA 46/2017
K	Food Supplement	3931	347	8,83%	1,9	DLA 49/2018
K	Moringa leafs	12420	1223	9,85%	1,7[1]	DLA 49/2019
K	Cream/Casein	8800	528	6,01%	1,5	ptSU08 (2020)
Mg	Potatoes	736	27,1	3,68%	0,62	DLA 46/2017
Mg	Food Supplement	1149	36,3	3,16%	0,57	DLA 49/2018
Mg	Moringa leafs	4704	261	5,56%	1,2	DLA 49/2019
Mg	Cream/Casein	735	51,1	6,95%	1,2	ptSU08 (2020)
Mn	Potatoes	3,66	0,327	8,9%	0,68	DLA 46/2017
Mn	Food Supplement	3,58	0,326	9,10%	0,69	DLA 49/2018
Mn	Moringa leafs	61,9	4,93	7,96%	0,93	DLA 49/2019
Mn	Cream/Casein	0,321	0,0313	9,73%	0,51	ptSU08 (2020)

[1] *with target standard deviation σpt'*

Continuation next page

Continuation Tab. 3:

Para-meter	**Matrix (Powder)**	**robust Mean** [mg/kg]	**rob. SD (S*)** [mg/kg]	**rel. SD (VK_{S*}) [%]**	**Quotient S^*/σ_{pt}**	**DLA-report**
Mo	Potatoes	0,197	0,0161	8,2%	0,40	DLA 46/2017
Mo	Food Supplement	0,830	0,130	15,7%	0,95	DLA 49/2018
Mo	Moringa leafs	0,449	0,0385	8,59%	0,48	DLA 49/2019
Mo	Cream/Casein	0,297	0,0542	18,2%	0,95	ptSU08 (2020)
Na	Potatoes	195	13,7	7,03%	1,0	DLA 46/2017
Na	Food Supplement	2944	154	5,23%	1,1	DLA 49/2018
Na	Moringa leafs	2478	92,0	4,08%	0,75	DLA 49/2019
Na	Cream/Casein	2040	188	9,20%	1,8	ptSU08 (2020)
P	Potatoes	1451	49,1	3,38%	0,63	DLA 46/2017
P	Food Supplement	4870	386	7,92%	1,8	DLA 49/2018
P	Moringa leafs	2310	167	7,24%	1,0	DLA 49/2019
P	Cream/Casein	7980	995	12,5%	1,7	ptSU08 (2020)
Pb	Moringa leafs	0,258	0,0288	11,2%	0,57	DLA 49/2019
Pb	Cream/Casein	0,194	0,0191	9,84%	0,48	ptSU08 (2020)
Se	Food Supplement	0,219	0,0461	21,1%	1,0	DLA 49/2018
Se	Moringa leafs	0,578	0,0961	16,6%	0,96	DLA 49/2019
Se	Cream/Casein	0,761	0,180	23,7%	1,4	ptSU08 (2020)
Sn	Moringa leafs	1,52	0,0731	4,80%	0,32	DLA 49/2019
Zn	Potatoes	7,83	0,726	9,3%	0,79	DLA 46/2017
Zn	Food Supplement	109	15,2	14,0%	1,8	DLA 49/2018
Zn	Moringa leafs	14,5	2,19	15,2%	1,4	DLA 49/2019
Zn	Cream/Casein	36,9	4,70	12,7%	1,4	ptSU08 (2020)

[1] *with target standard deviation σpt'*

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.
An error or cause analysis can be carried out by checking the analysis process including understanding and implementation of the measurement by the staff, details of the measurement procedure, calibration of equipment and composition of reagents, transmission error or an error in the calculation, in the trueness and precision and use of reference material. If necessary, the problems must be addressed through appropriate corrective action [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. 3.11). 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 (σ_{pt}) and the standard uncertainty (Ux_{pt}) [3].

The calculation is performed by:

$$z'_i = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u_{(x_{pt})}^2}}$$

If carried out an evaluation of the results by means of z 'score, we have defined below the expression in the denominator as a target standard deviation σ_{pt}'.

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

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

For warning and action signals see 3.7.1.

3.9 Reproducibility cofficient of variation (CV_R)

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 of the assigned value

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

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

If $U_{(Xpt)} \leq 0{,}3\ \sigma_{pt}$ the standard uncertainty of the assigned value needs not to be included in the interpretation of the results of the PT [3]. Values exceeding 0,3 imply, that the target standard deviation could be too low with respect to the standard uncertainty of the assigned value.

The traceability of the assigned value is ensured on the basis of the consensus value as a robust mean of the participant results.

4. Results

Comments to the distribution of the results:

The kernel density plots showed for all elements nearly a normal distribution of results (figures see documentation 5.3). Partly slight shoulders and separate smaller peaks can be seen, which are due to individual values and outliers.

Comments to the statistic data:

For the parameters S and Sn there were < 5 results, therefore no statistical evaluation could be done.

For B and P there were < 7 results, thus the significance of the statistical evaluation could be limited due to the low number of results. However, the statistical characteristics allow an evaluation of the results.

The target standard deviation was calculated with the exception of Ca and P for all other parameters according to the model of Horwitz or Horwitz / Thompson (Cd and Hg). For Ca and P the target standard deviation calculated from statistical data obtained from precision experiments (ASU §64 method) was used.

For information the target standard deviation using statistical data obtained from precision experiments (ASU §64 method) was additionally given, when available. For Ca and P the standard deviation according to the model of Horwitz was given for information.

For B the distribution of results showed an increased variability. The quotient S^*/σ_{pt} was clearly > 2,0. Thus the parameter was evaluated considering the standard uncertainty by z'-scores. The quotient S^*/σ_{pt}' was then < 2,0 (s. Tab. 3).

For the other parameters the distribution of results showed a low to normal variability. The quotients S^*/σ_{pt} were all in the range of 0,46 to 1,8 (s. Tab. 3).

The robust standard deviation as well as the repeatability and reproducibility standard deviations were in the range of established values for the applied methods (see 3.6.2) as well as in the range of previous PTs (s. Tab. 3). Exceptions were B and Fe, which showed slightly increased values. However the comparability of results is given.

75% to 100% of results were in the regarding target range.

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 m replicate measurements
Repeatability standard deviation (S_r)
Coefficient of Variation (CV_r)in %
Reproducibility standard deviation (S_R)
Coefficient of Variation (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})
Number of results in the target range
Percent in the target range

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

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

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

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

4.1 As – Arsenic in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	–
Mean	0,240
Median	0,223
Robust Mean (X_{pt})	**0,230**
Robust standard deviation (S*)	**0,0212**
Number with 2 replicates	7
Repeatability SD (S_r)	0,0171
Repeatability (CV_r)	7,54%
Reproducibility SD (S_R)	0,0200
Reproducibility (CV_R)	8,81%
Target range:	
Target standard deviation σ_{pt}	**0,0460**
Target standard deviation (for Information)	0,0188
lower limit of target range	**0,138**
upper limit of target range	**0,322**
Quotient S/σ_{pt}*	*0,46*
Standard uncertainty $U_{(Xpt)}$	*0,00937*
Results in the target range	7
Percent in the target range	*88%*

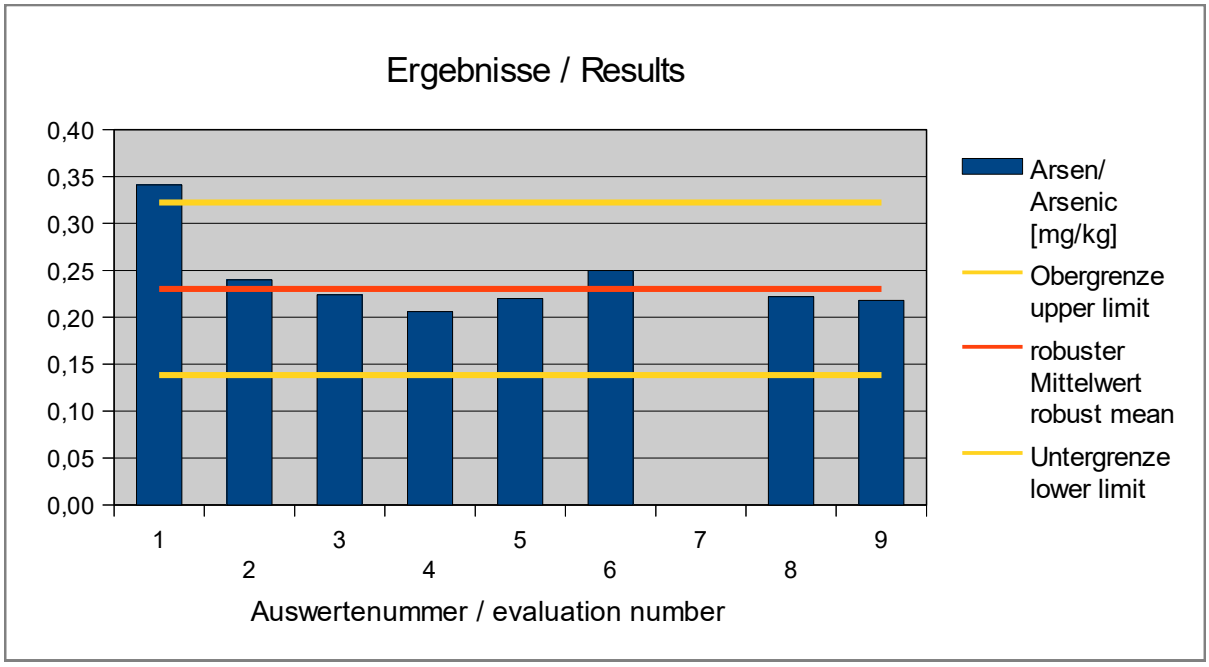


Abb. / Fig. 1: Ergebnisse Arsen / Results arsenic

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Arsen/ Arsenic [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,341	0,1107	2,4	5,9	
2	0,240	0,0097	0,21	0,52	
3	0,224	-0,0063	-0,14	-0,33	
4	0,206	-0,0243	-0,53	-1,3	
5	0,220	-0,0103	-0,22	-0,54	
6	0,250	0,0197	0,43	1,0	
7					
8	0,222	-0,0083	-0,18	-0,44	
9	0,218	-0,0123	-0,27	-0,65	

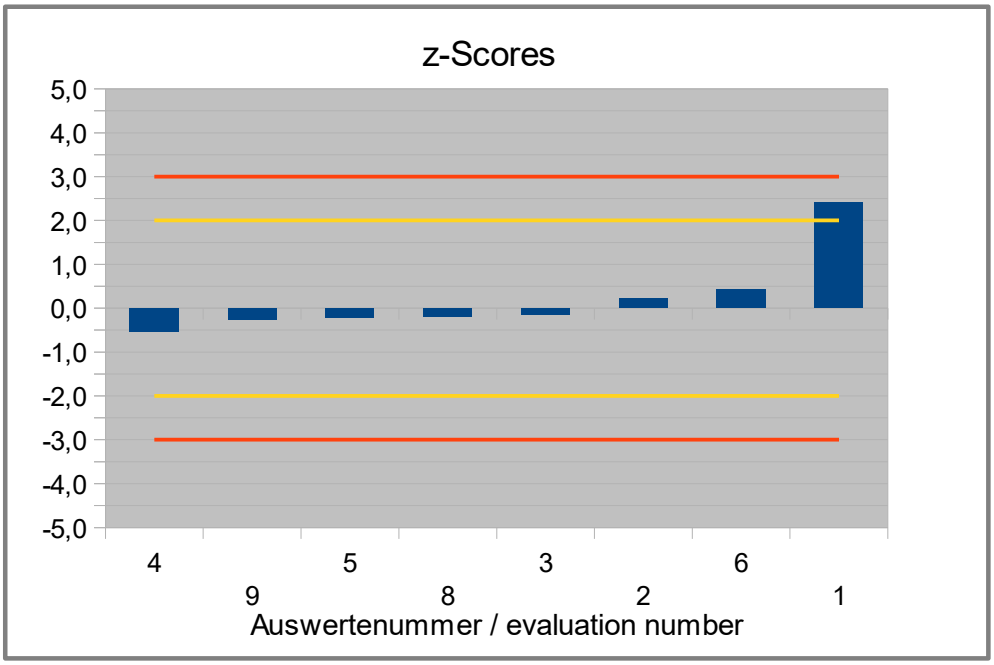


Abb. / Fig. 2: z-Scores Arsen / arsenic

4.2 B – Boron in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	6
Number of outliers	0
Mean	0,678
Median	0,813
Robust Mean (x_{pt})	**0,681**
Robust standard deviation (S*)	**0,294**
Number with 2 replicates	6
Repeatability SD (S_r)	0,0671
Repeatability (CV_r)	9,96%
Reproducibility SD (S_R)	0,265
Reproducibility (CV_R)	39,4%
Target range:	
Target standard deviation σ_{pt}'	**0,189**
lower limit of target range	**0,302**
upper limit of target range	**1,06**
Quotient S/σ_{pt}'*	*1,6*
Standard uncertainty $U_{(xpt)}$	*0,150*
Results in the target range	*5*
Percent in the target range	*83%*

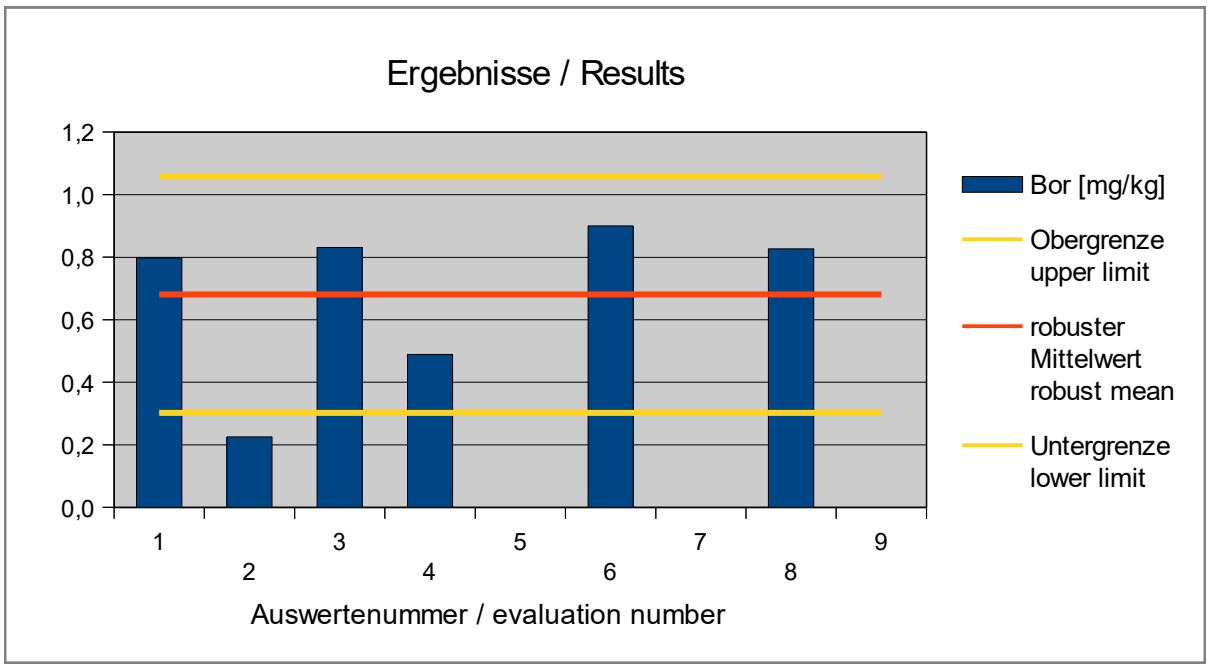


Abb. / Fig. 3: Ergebnisse Bor / Results boron

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Boron [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ_{pt})	Hinweis Remark
1	0,798	0,117	0,62	
2	0,225	-0,456	-2,4	
3	0,831	0,150	0,79	
4	0,489	-0,192	-1,0	
5				
6	0,900	0,219	1,2	
7				
8	0,827	0,146	0,77	
9				

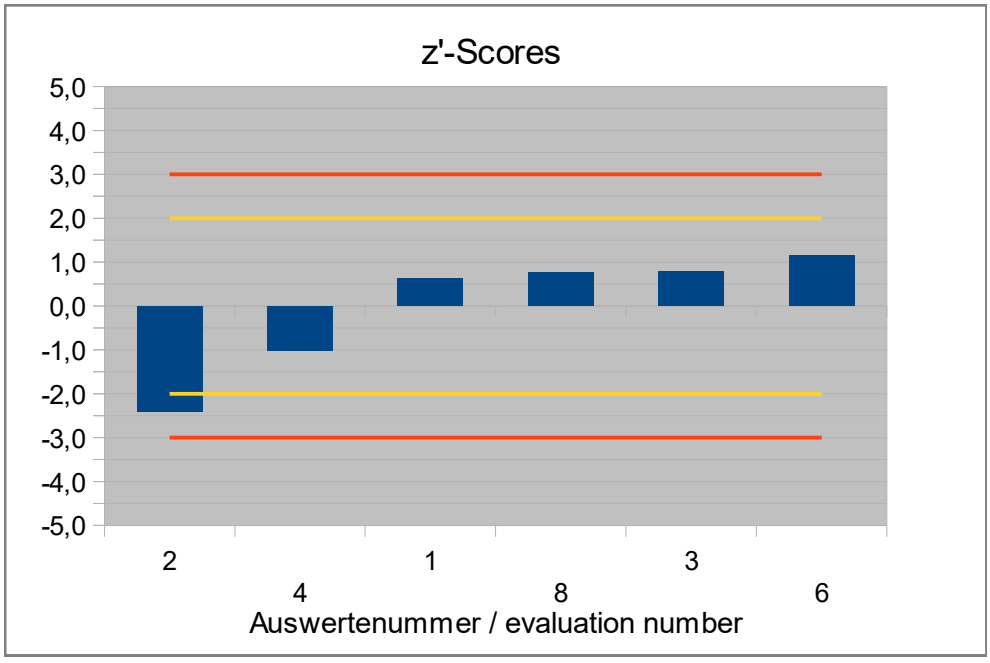


Abb. / Fig. 4: z'-Scores Boron

4.3 Ba – Barium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	–
Mean	1,16
Median	0,943
Robust Mean (x_{pt})	**0,949**
Robust standard deviation (S*)	**0,0708**
Number with 2 replicates	7
Repeatability SD (S_r)	0,0103
Repeatability (CV_r)	1,10%
Reproducibility SD (S_R)	0,048
Reproducibility (CV_R)	5,18%
Target range:	
Target standard deviation σ_{pt}	**0,153**
lower limit of target range	**0,643**
upper limit of target range	**1,26**
Quotient S/σ_{pt}*	*0,46*
Standard uncertainty $U_{(Xpt)}$	*0,0313*
Results in the target range	7
Percent in the target range	*88%*

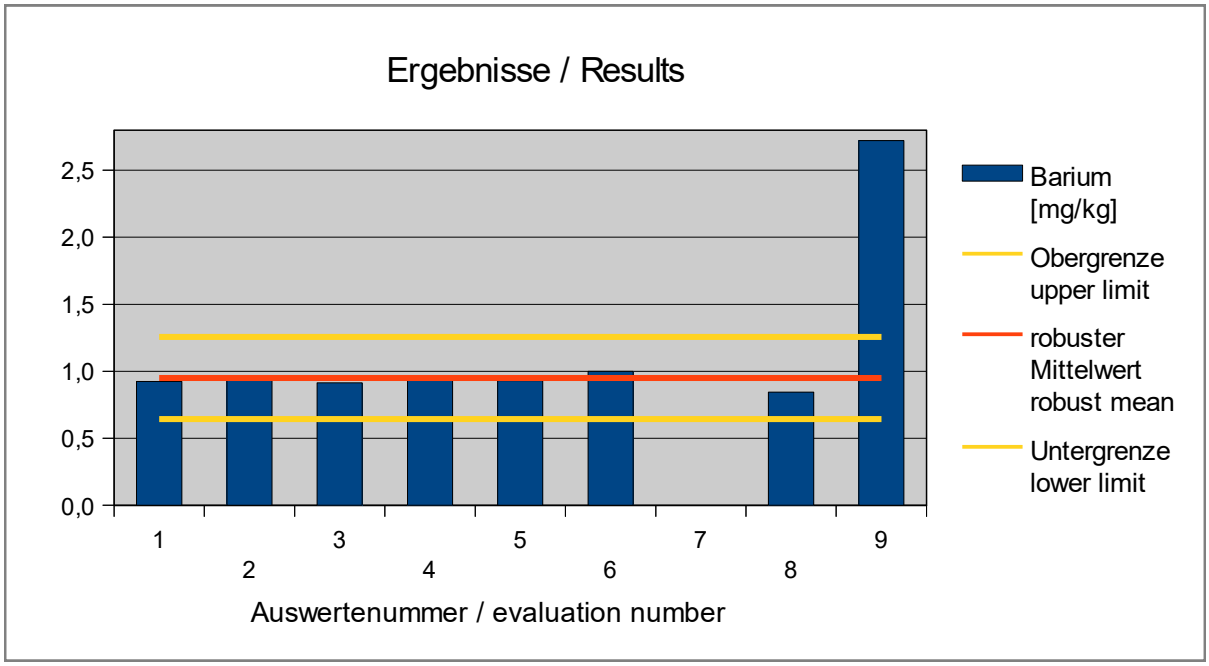


Abb. / Fig. 5: Ergebnisse Barium / Results barium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Barium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	Hinweis Remark
1	0,924	-0,0252	-0,16	
2	0,968	0,0188	0,12	
3	0,915	-0,0342	-0,22	
4	0,956	0,0068	0,04	
5	0,930	-0,0192	-0,13	
6	1,00	0,0508	0,33	
7				
8	0,845	-0,1042	-0,68	
9	2,72	1,7708	12	

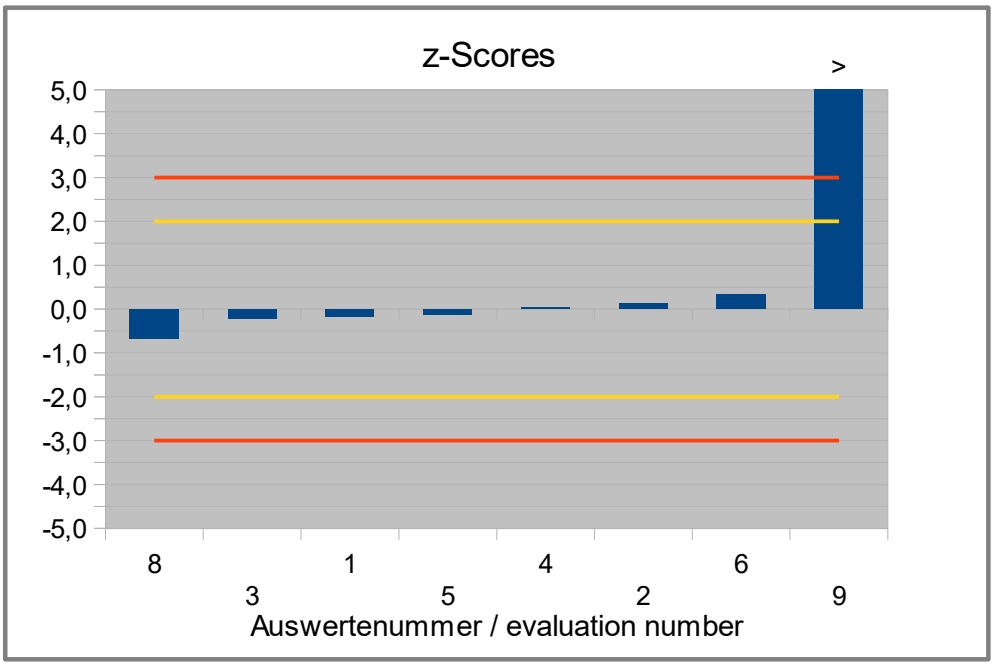


Abb. / Fig. 6: z-Scores Barium

4.4 Ca – Calcium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	10300
Median	10000
Robust Mean (X_{pt})	**10300**
Robust standard deviation (S*)	**1110**
Number with 2 replicates	8
Repeatability SD (S_r)	152
Repeatability (CV_r)	1,48%
Reproducibility SD (S_R)	973
Reproducibility (CV_R)	9,46%
Target range:	
Target standard deviation σ_{pt}	**782**
Target standard deviation (for Information)	410
lower limit of target range	**8740**
upper limit of target range	**11900**
Quotient S/σ_{pt}*	*1,4*
Standard uncertainty $U_{(Xpt)}$	*489*
Results in the target range	*8*
Percent in the target range	*100%*

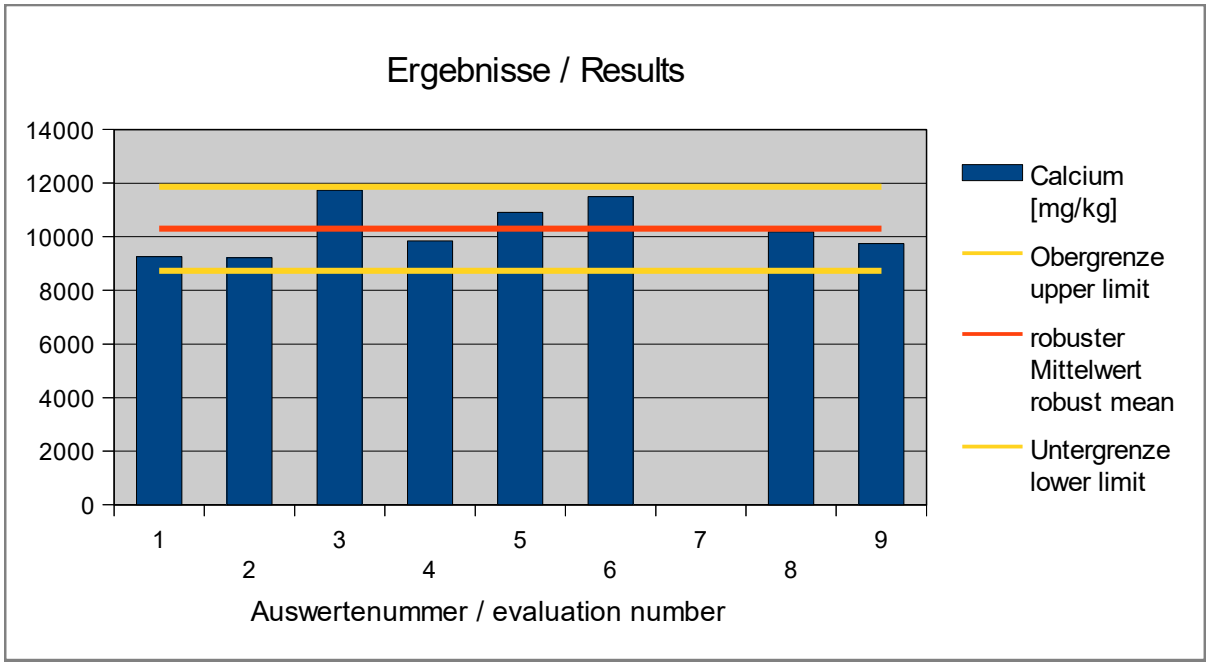


Abb. / Fig. 7: Ergebnisse Calcium / Results calcium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Calcium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	9250	-1050	-1,3	-2,6	
2	9220	-1080	-1,4	-2,6	
3	11700	1440	1,8	3,5	
4	9850	-450	-0,58	-1,1	
5	10900	606	0,77	1,5	
6	11500	1200	1,5	2,9	
7					
8	10200	-115	-0,15	-0,28	
9	9750	-550	-0,70	-1,3	

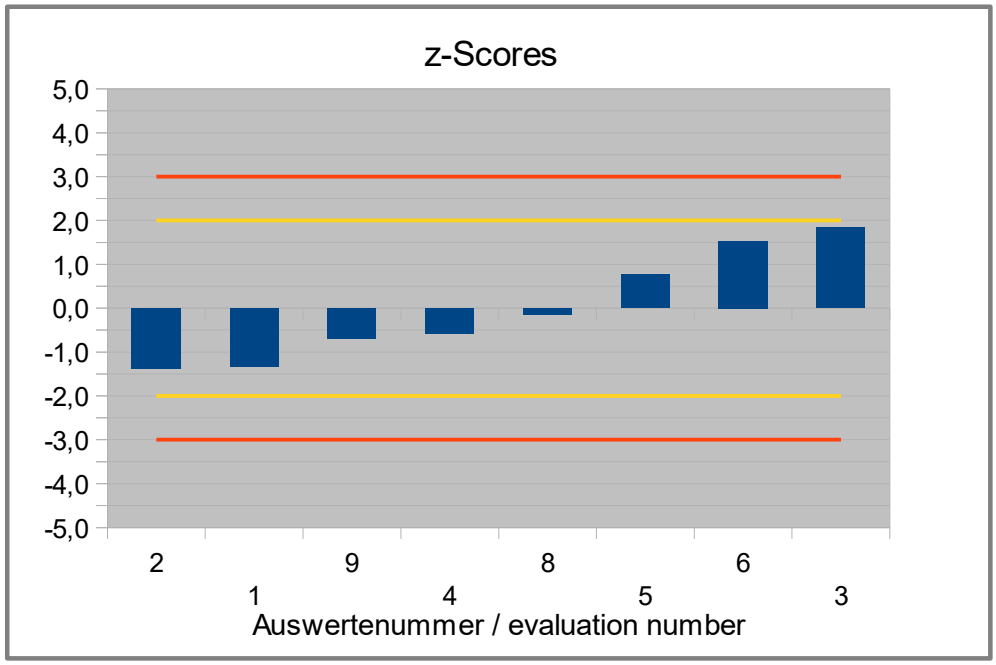


Abb. / Fig. 8: z-Scores Calcium

4.5 Cd – Cadmium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results°	7
Number of outliers	1
Mean	0,0757
Median	0,0705
Robust Mean (X_{pt})	**0,0757**
Robust standard deviation (S*)	**0,00994**
Number with 2 replicates	7
Repeatability SD (S_r)	0,00619
Repeatability (CV_r)	8,26%
Reproducibility SD (S_R)	0,00980
Reproducibility (CV_R)	13,1%
Target range:	
Target standard deviation σ_{pt}	**0,0166**
Target standard deviation (for Information)	0,00735
lower limit of target range	**0,0424**
upper limit of target range	**0,109**
Quotient S/σ_{pt}*	*0,60*
Standard uncertainty $U_{(Xpt)}$	*0,00470*
Results in the target range	7
Percent in the target range	*100%*

° *number without outlier (result no. 6)*

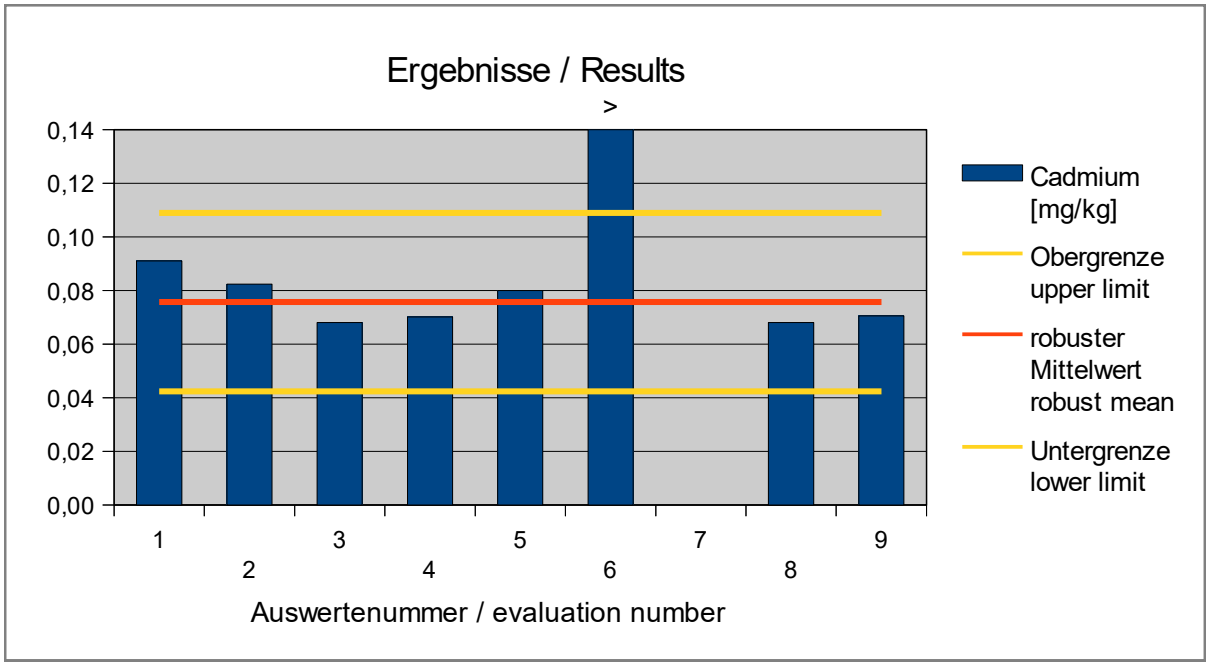


Abb. / Fig. 9: Ergebnisse Cadmium / Results cadmium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Cadmium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,0910	0,0153	0,92	2,1	
2	0,0824	0,0067	0,41	0,92	
3	0,0680	-0,0077	-0,46	-1,0	
4	0,0701	-0,0056	-0,33	-0,8	
5	0,0800	0,0043	0,26	0,59	
6	0,870				Ergebnis ausgeschlossen / Result excluded
7					
8	0,0680	-0,0077	-0,46	-1,0	
9	0,0705	-0,0052	-0,31	-0,7	

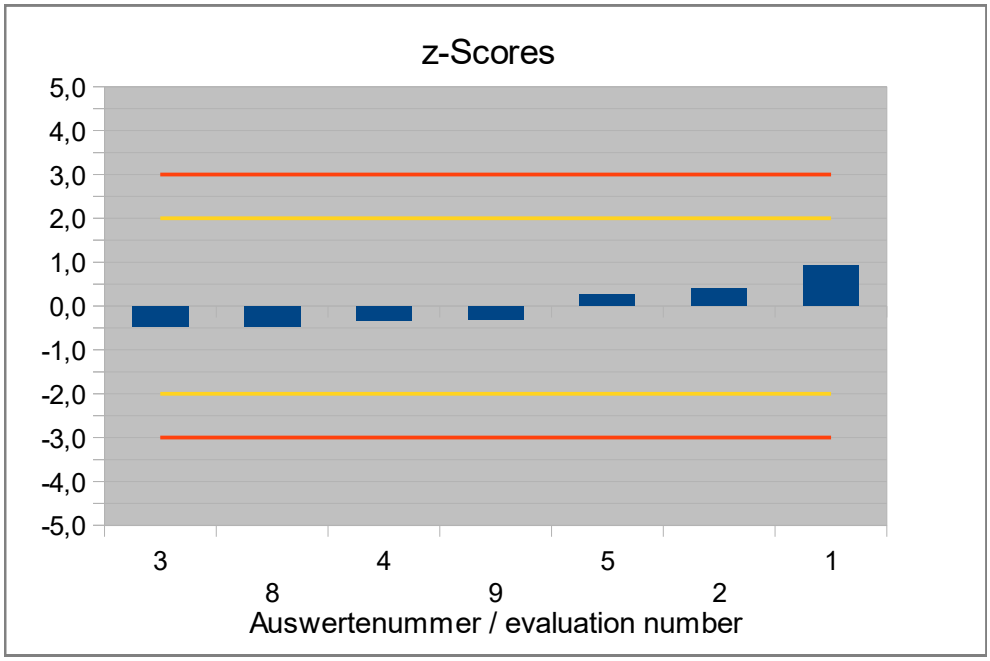


Abb. / Fig. 10: z-Scores Cadmium

4.6 Cr – Chromium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	1,09
Median	1,10
Robust Mean (x_{pt})	**1,09**
Robust standard deviation (S*)	**0,0797**
Number with 2 replicates	8
Repeatability SD (S_r)	0,0937
Repeatability (CV_r)	8,60%
Reproducibility SD (S_R)	0,0943
Reproducibility (CV_R)	8,66%
Target range:	
Target standard deviation σ_{pt}	**0,172**
Target standard deviation (for Information)	0,352
lower limit of target range	**0,746**
upper limit of target range	**1,44**
Quotient S/σ_{pt}*	*0,46*
Standard uncertainty $U_{(Xpt)}$	*0,0352*
Results in the target range	*8*
Percent in the target range	*100%*

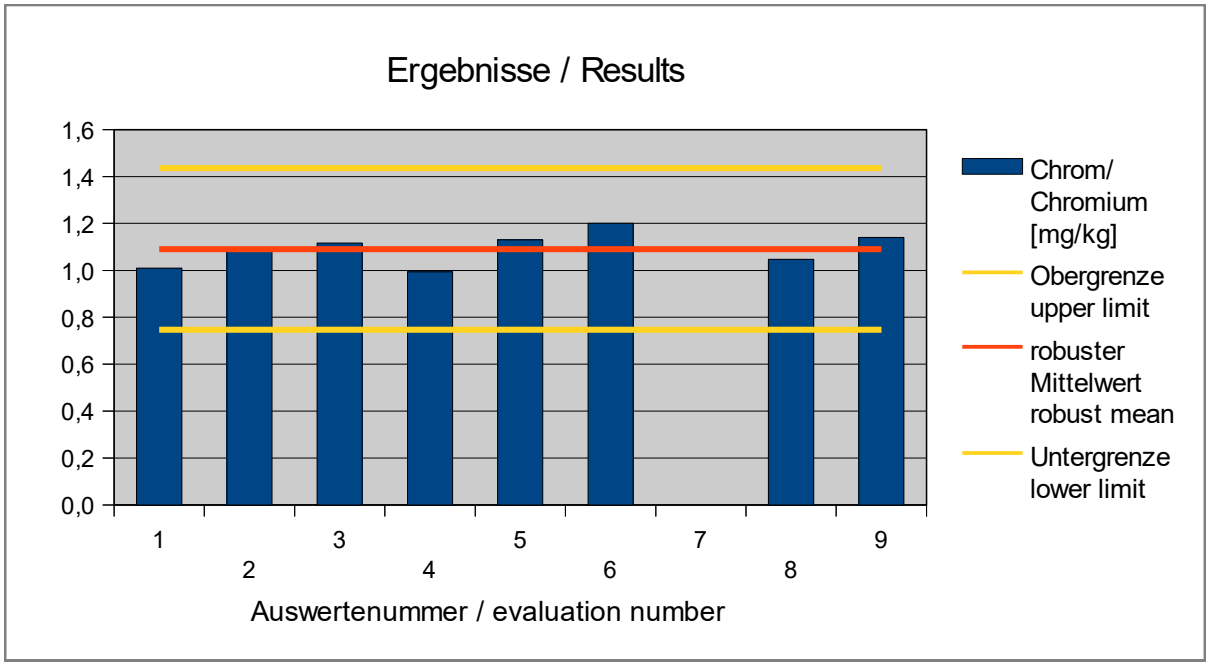


Abb. / Fig. 11: Ergebnisse Chrom / Results chromium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Chrom/ Chromium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	1,01	-0,0809	-0,47	-0,23	
2	1,09	-0,0009	-0,01	0,00	
3	1,12	0,0261	0,15	0,07	
4	0,993	-0,0979	-0,57	-0,28	
5	1,13	0,0391	0,23	0,11	
6	1,20	0,1091	0,63	0,31	
7					
8	1,05	-0,0439	-0,25	-0,12	
9	1,14	0,0491	0,29	0,14	

Abb. / Fig. 12: z-Scores Chrom / chromium

4.7 Cu – Copper in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	7
Number of outliers	0
Mean	0,444
Median	0,463
Robust Mean (X_{pt})	**0,444**
Robust standard deviation (S*)	**0,0499**
Number with 2 replicates	7
Repeatability SD (S_r)	0,0161
Repeatability (CV_r)	3,64%
Reproducibility SD (S_R)	0,0441
Reproducibility (CV_R)	9,95%
Target range:	
Target standard deviation σ_{pt}	**0,0803**
Target standard deviation (for Information)	0,0472
lower limit of target range	**0,283**
upper limit of target range	**0,604**
Quotient S/σ_{pt}*	*0,62*
Standard uncertainty $U_{(Xpt)}$	*0,0236*
Results in the target range	7
Percent in the target range	*100%*

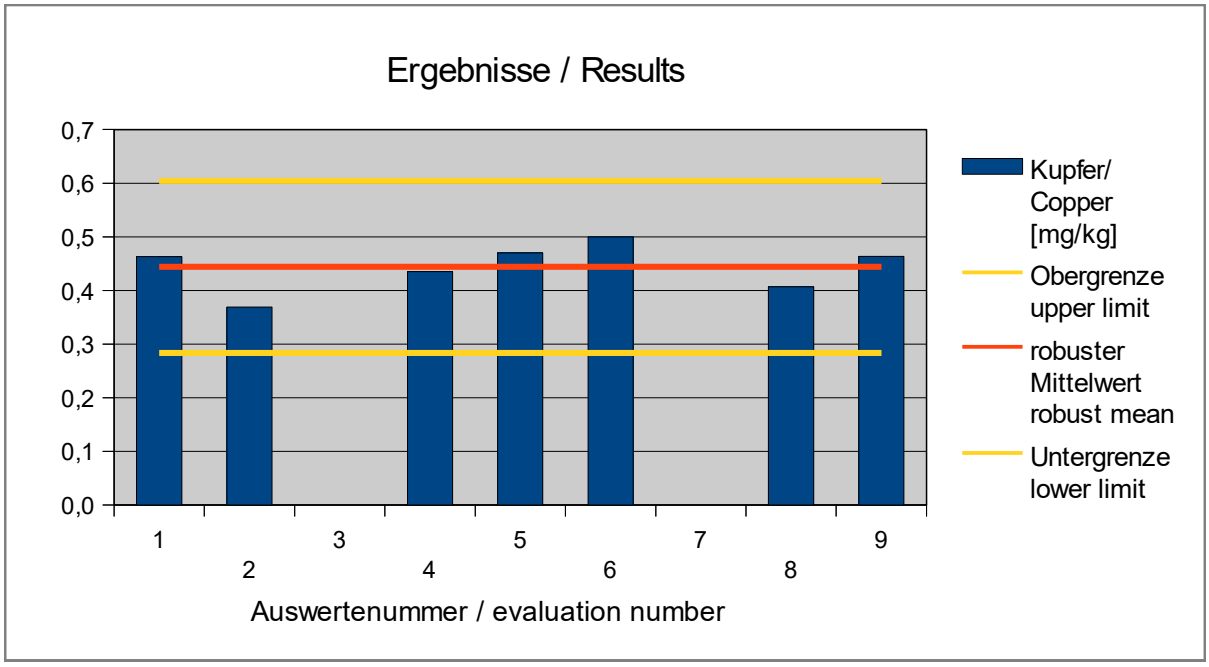


Abb. / Fig. 13: Ergebnisse Kupfer / Results copper

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Kupfer/ Copper [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,463	0,0191	0,24	0,40	
2	0,369	-0,0749	-0,93	-1,6	
3	<0,5				
4	0,435	-0,0089	-0,11	-0,19	
5	0,470	0,0261	0,32	0,55	
6	0,500	0,0561	0,70	1,2	
7					
8	0,407	-0,0369	-0,46	-0,78	
9	0,464	0,0196	0,24	0,41	

Abb. / Fig. 14: z-Scores Kupfer / copper

4.8 Fe – Iron in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	7
Number of outliers	0
Mean	2,19
Median	1,92
Robust Mean (X_{pt})	**2,16**
Robust standard deviation (S*)	**0,537**
Number with 2 replicates	7
Repeatability SD (S_r)	0,0755
Repeatability (CV_r)	3,46%
Reproducibility SD (S_R)	0,531
Reproducibility (CV_R)	24,3%
Target range:	
Target standard deviation σ_{pt}	**0,308**
Target standard deviation (for Information)	0,145
lower limit of target range	**1,54**
upper limit of target range	**2,77**
Quotient S/σ_{pt}*	*1,7*
Standard uncertainty $U_{(Xpt)}$	*0,254*
Results in the target range	*6*
Percent in the target range	*86%*

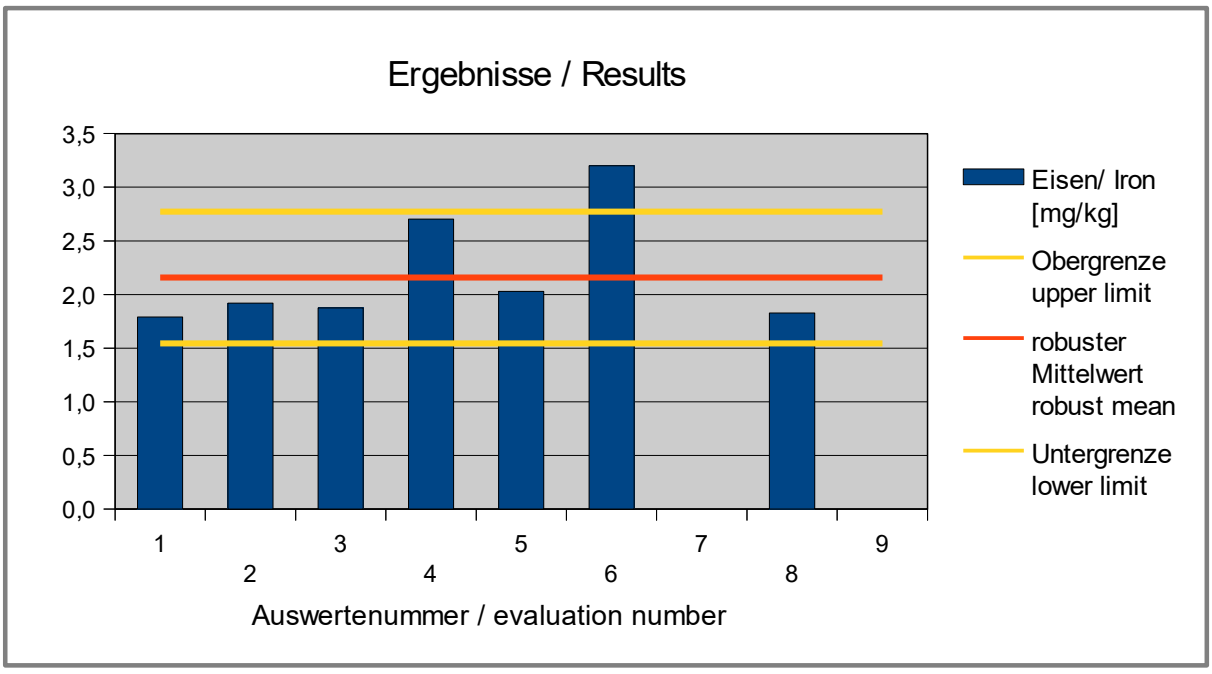


Abb. / Fig. 15: Ergebnisse Eisen / Results iron

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Eisen/ Iron [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	1,79	-0,369	-1,2	-2,5	
2	1,92	-0,239	-0,78	-1,6	
3	1,88	-0,284	-0,92	-2,0	
4	2,70	0,545	1,8	3,8	
5	2,03	-0,129	-0,42	-0,89	
6	3,20	1,041	3,4	7,2	
7					
8	1,83	-0,330	-1,1	-2,3	
9					

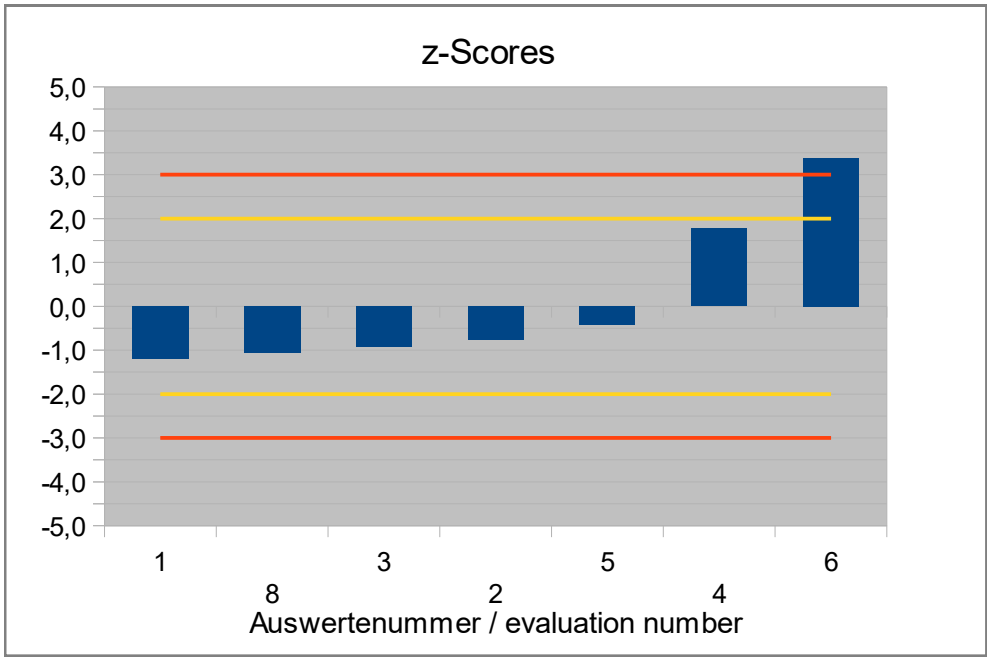


Abb. / Fig. 16: z-Scores Eisen/ iron

4.9 Hg – Mercury in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	-
Mean	0,0674
Median	0,0741
Robust Mean (X_{pt})	**0,0701**
Robust standard deviation (S*)	**0,0136**
Number with 2 replicates	7
Repeatability SD (S_r)	0,00420
Repeatability (CV_r)	5,74%
Reproducibility SD (S_R)	0,00983
Reproducibility (CV_R)	13,5%
Target range:	
Target standard deviation σ_{pt}	**0,0154**
lower limit of target range	**0,0393**
upper limit of target range	**0,101**
Quotient S/σ_{pt}*	*0,88*
Standard uncertainty $U_{(Xpt)}$	*0,00600*
Results in the target range	7
Percent in the target range	*88%*

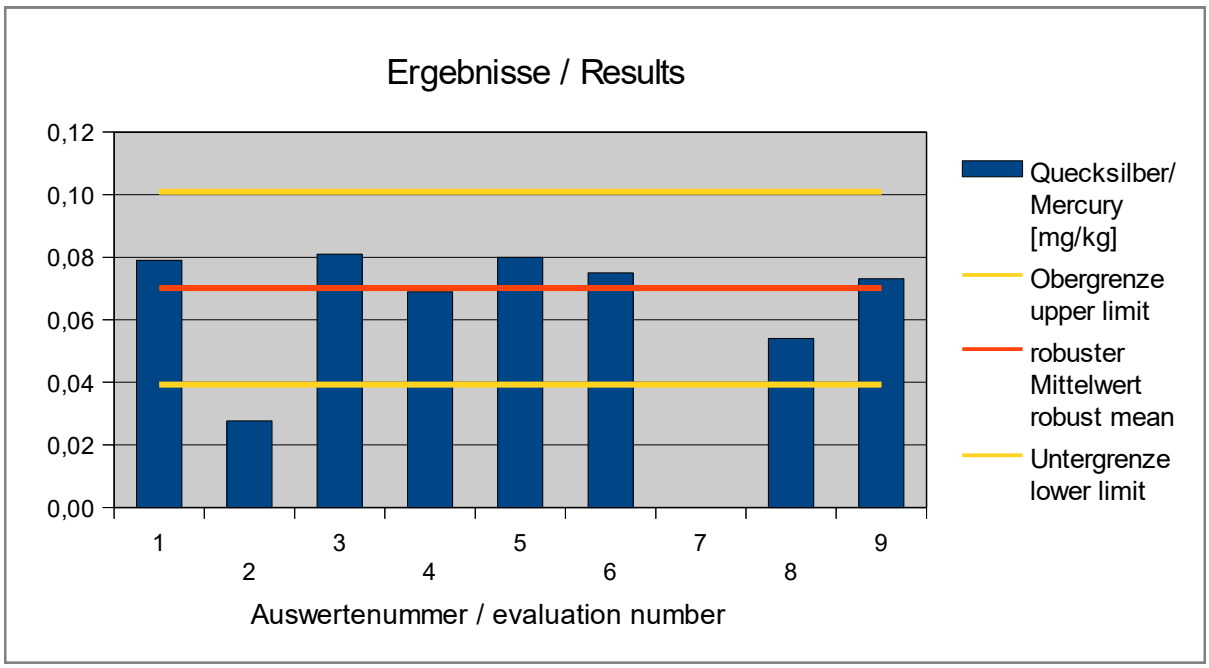


Abb. / Fig. 17: Ergebnisse Quecksilber / Results mercury

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Quecksilber/ Mercury [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,0790	0,0089	0,58	0,54	
2	0,0277	-0,0424	-2,7	-2,6	
3	0,0810	0,0109	0,71	0,66	
4	0,0690	-0,0011	-0,07	-0,07	
5	0,0800	0,0099	0,64	0,60	
6	0,0750	0,0049	0,32	0,30	
7					
8	0,0540	-0,0161	-1,0	-0,97	
9	0,0731	0,0030	0,19	0,18	

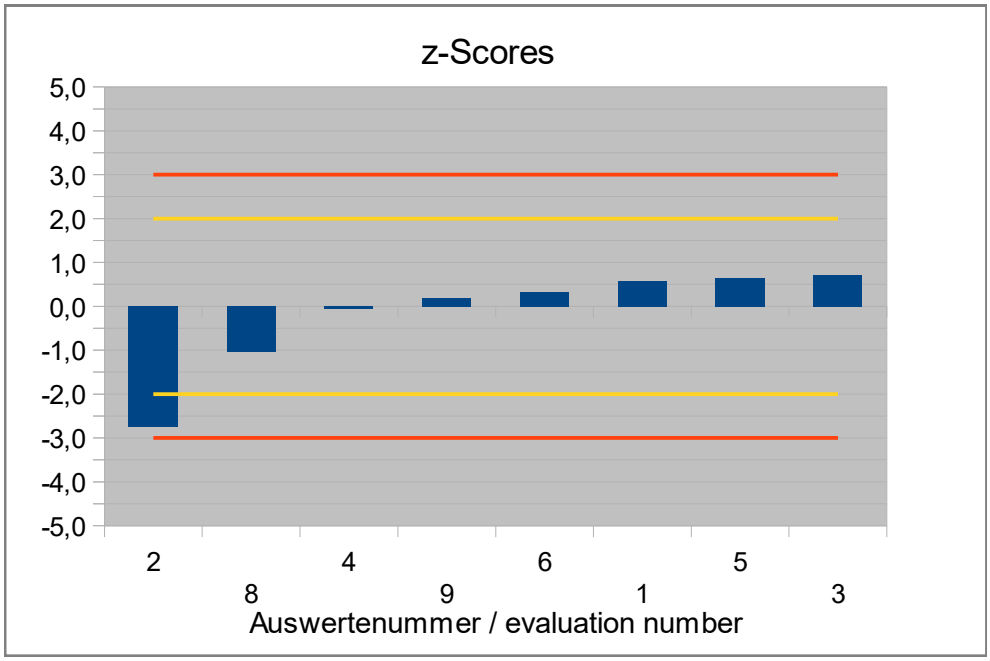


Abb. / Fig. 18: z-Scores Quecksilber / mercury

4.10 K – Potassium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results°	7
Number of outliers	1
Mean	8800
Median	8930
Robust Mean (x_{pt})	**8800**
Robust standard deviation (S*)	**528**
Number with 2 replicates	7
Repeatability SD (S_r)	171
Repeatability (CV_r)	1,94%
Reproducibility SD (S_R)	471
Reproducibility (CV_R)	5,36%
Target range:	
Target standard deviation σ_{pt}	**359**
Target standard deviation (for Information)	411
lower limit of target range	**8080**
upper limit of target range	**9510**
Quotient S/σ_{pt}*	*1,5*
Standard uncertainty $U_{(Xpt)}$	*250*
Results in the target range	7
Percent in the target range	*100%*

° *number without outlier (result no. 2)*

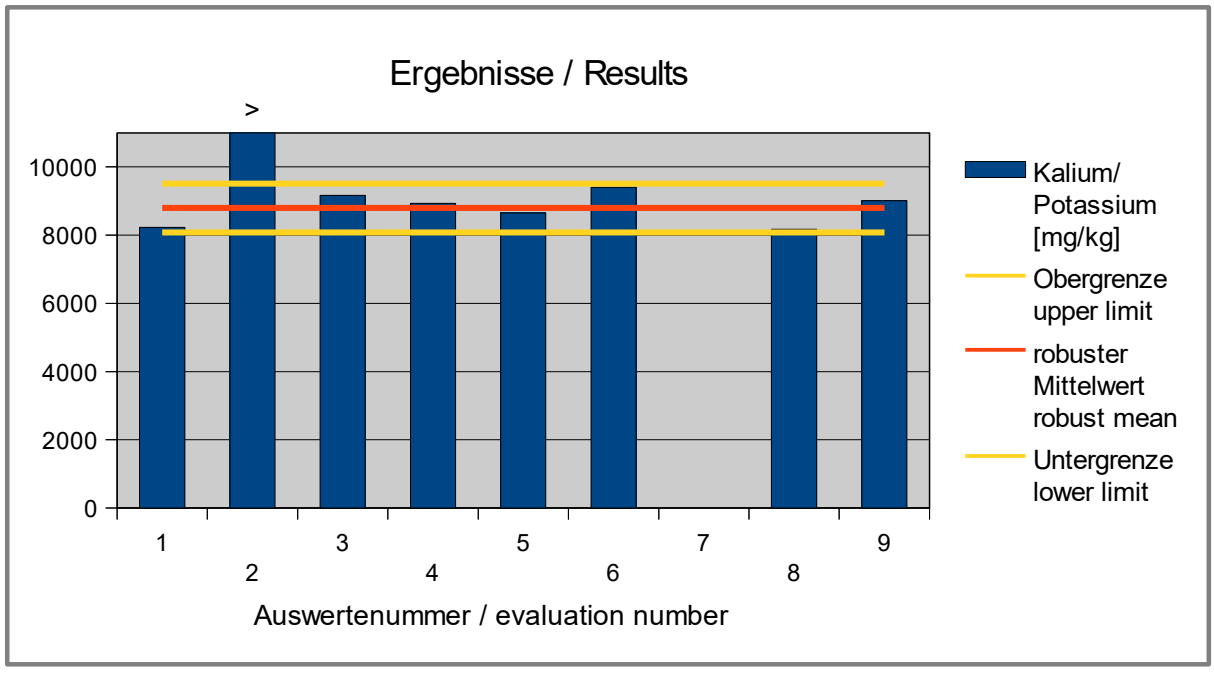


Abb. / Fig. 19: Ergebnisse Kalium / Results potassium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Kalium/ Potassium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	8230	-566	-1,6	-1,4	
2	92800				Ergebnis ausgeschlossen / Result excluded
3	9170	374	1,0	0,91	
4	8930	137	0,38	0,33	
5	8650	-141	-0,39	-0,34	
6	9400	605	1,7	1,5	
7					
8	8170	-625	-1,7	-1,5	
9	9010	215	0,60	0,52	

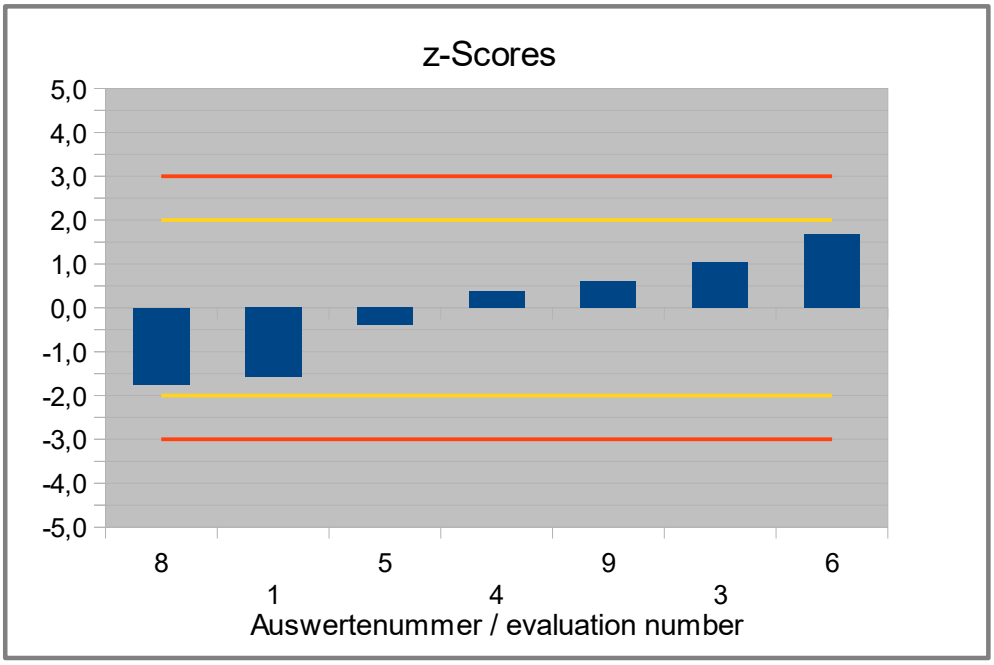


Abb. / Fig. 20: z-Scores Kalium / potassium

4.11 Mg – Magnesium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	735
Median	746
Robust Mean (X_{pt})	**735**
Robust standard deviation (S*)	**51,1**
Number with 2 replicates	8
Repeatability SD (S_r)	14,8
Repeatability (CV_r)	2,00%
Reproducibility SD (S_R)	41,6
Reproducibility (CV_R)	5,64%
Target range:	
Target standard deviation σ_{pt}	**43,6**
Target standard deviation (for Information)	51,5
lower limit of target range	**648**
upper limit of target range	**822**
Quotient S/σ_{pt}*	*1,2*
Standard uncertainty $U_{(Xpt)}$	*22,6*
Results in the target range	*8*
Percent in the target range	*100%*

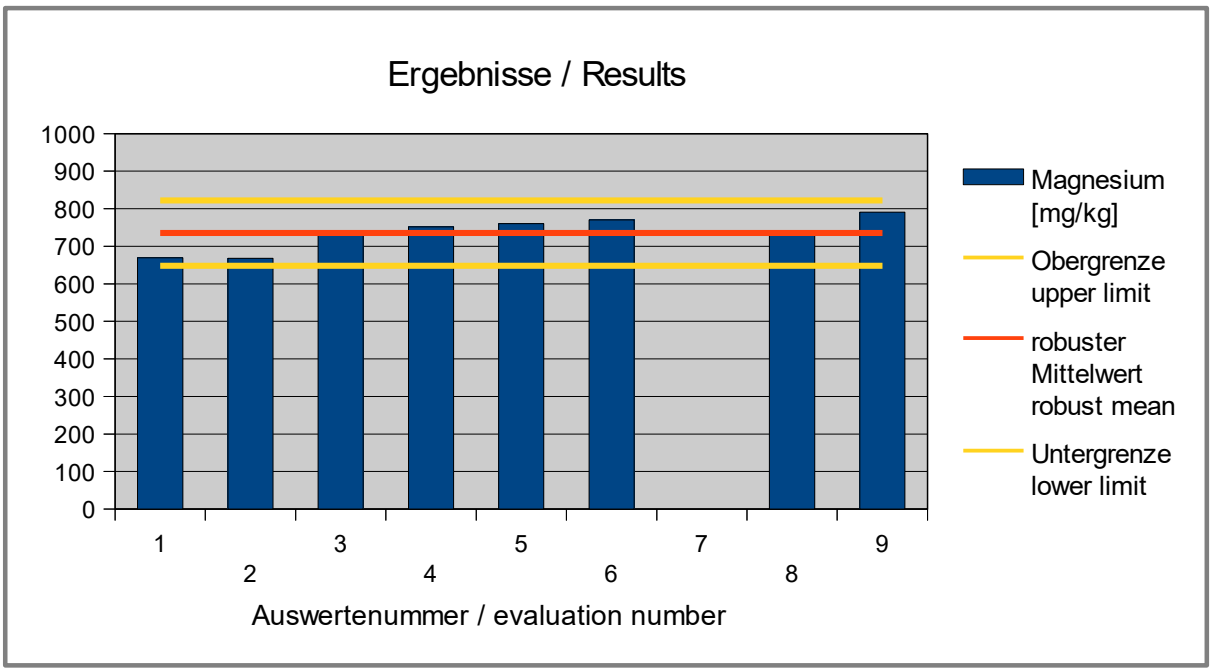


Abb. / Fig. 21: Ergebnisse Magnesium / Results magnesium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Magnesium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	669	-66,2	-1,5	-1,3	
2	668	-67,2	-1,5	-1,3	
3	741	5,8	0,13	0,11	
4	752	16,7	0,38	0,32	
5	760	25,2	0,58	0,49	
6	770	34,8	0,80	0,68	
7					
8	730	-5,2	-0,12	-0,10	
9	791	55,8	1,3	1,1	

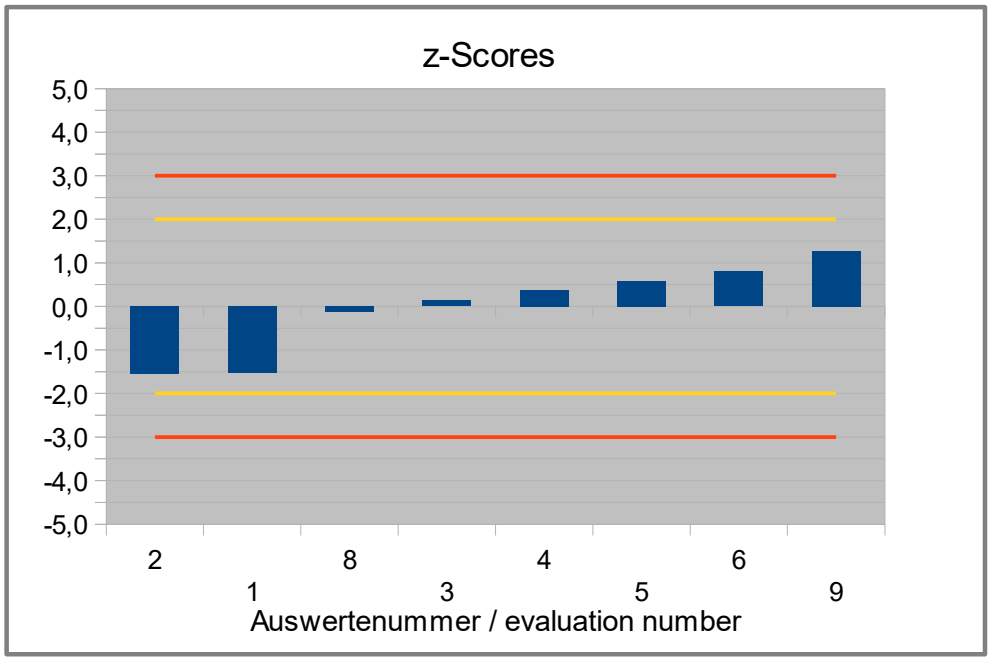


Abb. / Fig. 22: z-Scores Magnesium

4.12 Mn – Manganese in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	0,325
Median	0,316
Robust Mean (X_{pt})	**0,321**
Robust standard deviation (S*)	**0,0313**
Number with 2 replicates	8
Repeatability SD (S_r)	0,0128
Repeatability (CV_r)	3,95%
Reproducibility SD (S_R)	0,0352
Reproducibility (CV_R)	10,9%
Target range:	
Target standard deviation σ_{pt}	**0,0610**
Target standard deviation (for Information)	0,0427
lower limit of target range	**0,199**
upper limit of target range	**0,443**
Quotient S/σ_{pt}*	*0,51*
Standard uncertainty $U_{(Xpt)}$	*0,0138*
Results in the target range	*8*
Percent in the target range	*100%*

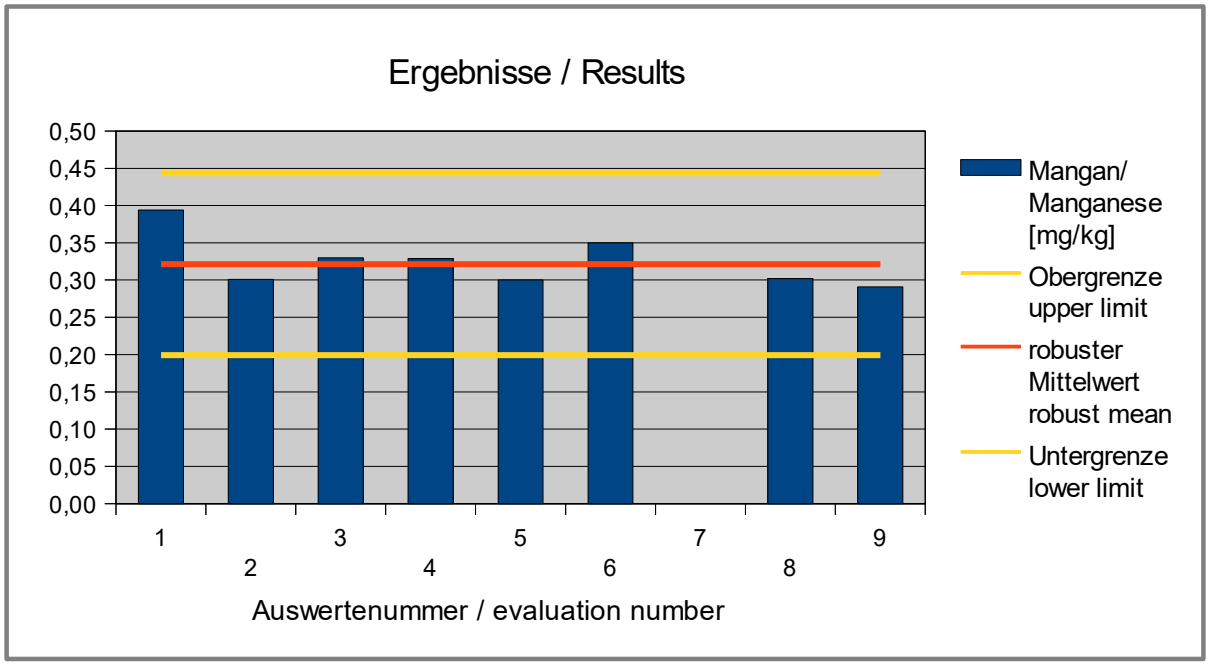


Abb. / Fig. 23: Ergebnisse Mangan / Results manganese

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Mangan/ Manganese [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,394	0,0726	1,2	1,7	
2	0,301	-0,0204	-0,33	-0,48	
3	0,330	0,0086	0,14	0,20	
4	0,329	0,0076	0,12	0,18	
5	0,300	-0,0214	-0,35	-0,50	
6	0,350	0,0286	0,47	0,67	
7					
8	0,302	-0,0194	-0,32	-0,45	
9	0,291	-0,0304	-0,50	-0,71	

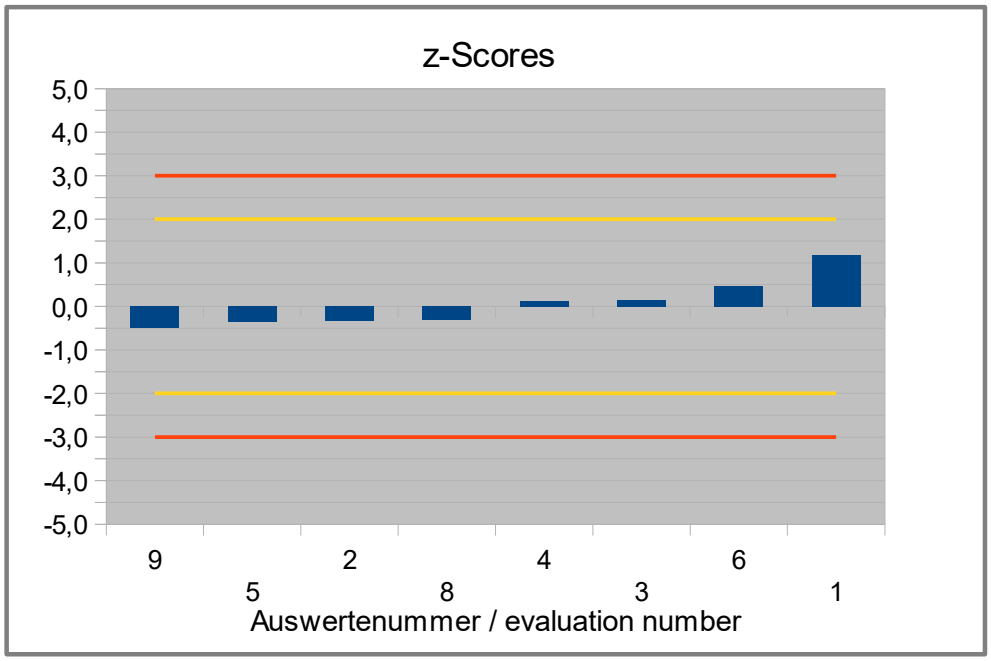


Abb. / Fig. 24: z-Scores Mangan/manganese

4.13 Mo – Molybdenum in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	-
Mean	0,350
Median	0,291
Robust Mean (X_{pt})	**0,297**
Robust standard deviation (S*)	**0,0542**
Number with 2 replicates	7
Repeatability SD (S_r)	0,0104
Repeatability (CV_r)	3,69%
Reproducibility SD (S_R)	0,0351
Reproducibility (CV_R)	12,4%
Target range:	
Target standard deviation σ_{pt}	**0,0571**
Target standard deviation (for Information)	0,0565
lower limit of target range	**0,183**
upper limit of target range	**0,411**
Quotient S/σ_{pt}*	*0,95*
Standard uncertainty $U_{(Xpt)}$	*0,0239*
Results in the target range	7
Percent in the target range	*88%*

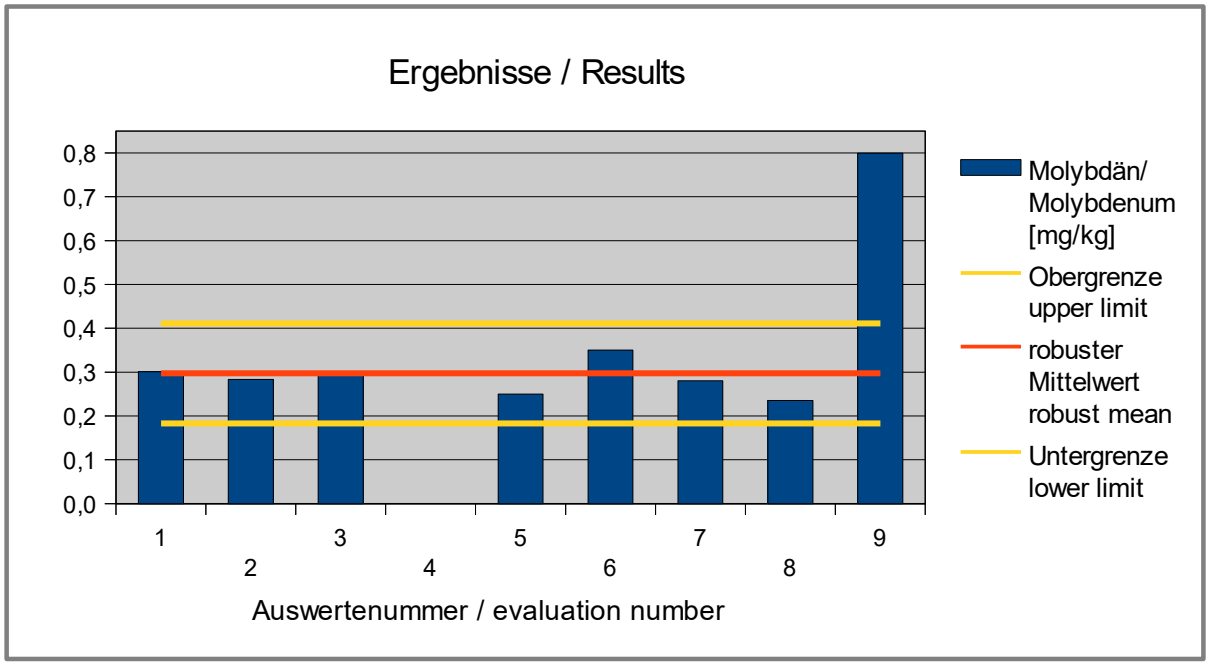


Abb. / Fig. 25: Ergebnisse Molybdän / Results molybdenum

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Molybdän/ Molybdenum [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,301	0,0040	0,07	0,07	
2	0,283	-0,0140	-0,25	-0,25	
3	0,299	0,0020	0,03	0,03	
4					
5	0,250	-0,0470	-0,82	-0,83	
6	0,350	0,0530	0,93	0,94	
7	0,280	-0,0170	-0,30	-0,30	
8	0,235	-0,0620	-1,1	-1,1	
9	0,800	0,5025	8,8	8,9	

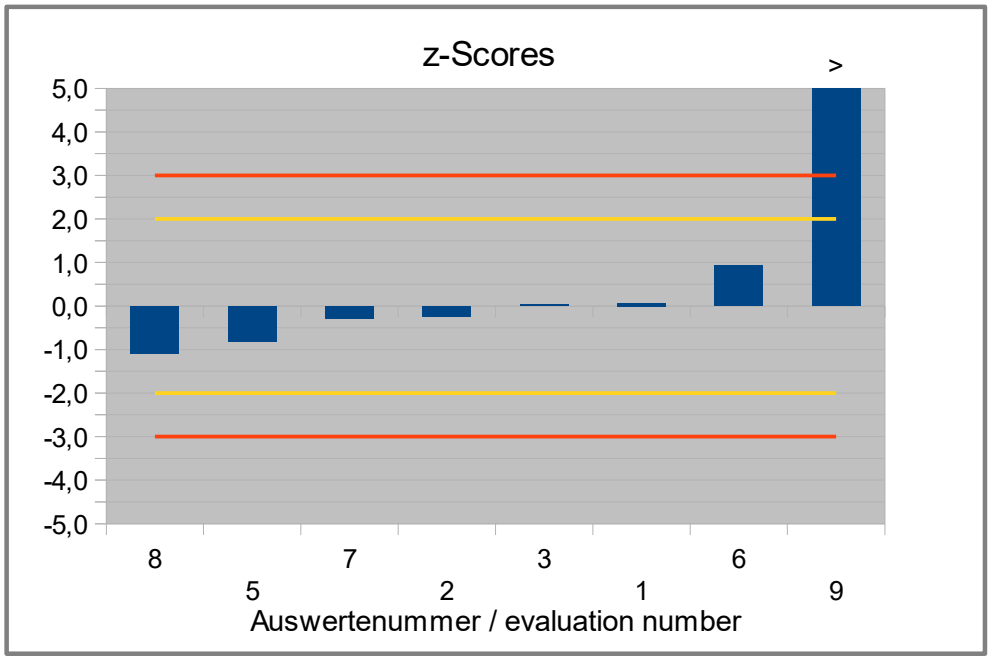


Abb. / Fig. 26: z-Scores Molybdän/ molybdenum

4.14 Na – Sodium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	2040
Median	2040
Robust Mean (X_{pt})	**2040**
Robust standard deviation (S*)	**188**
Number with 2 replicates	8
Repeatability SD (S_r)	33,7
Repeatability (CV_r)	1,65%
Reproducibility SD (S_R)	171
Reproducibility (CV_R)	8,39%
Target range:	
Target standard deviation σ_{pt}	**104**
Target standard deviation (for Information)	84,6
lower limit of target range	**1840**
upper limit of target range	**2250**
Quotient S/σ_{pt}*	*1,8*
Standard uncertainty $U_{(Xpt)}$	*83,0*
Results in the target range	*6*
Percent in the target range	*75%*

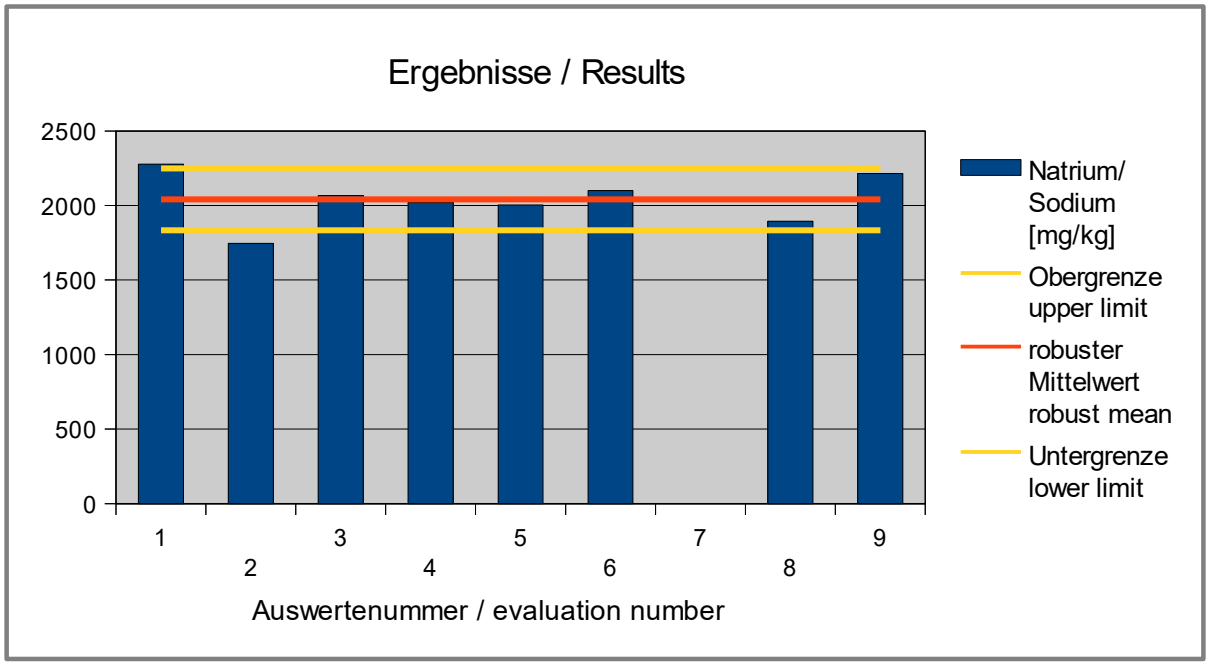


Abb. / Fig. 27: Ergebnisse Natrium / Results sodium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Natrium/ Sodium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	2280	235	2,3	2,8	
2	1750	-296	-2,9	-3,5	
3	2070	24	0,23	0,28	
4	2020	-23	-0,22	-0,27	
5	2000 *	-38	-0,37	-0,45	
6	2100	58	0,56	0,68	
7					
8	1900	-147	-1,4	-1,7	
9	2220	173	1,7	2,0	

* Mean calculated by DLA

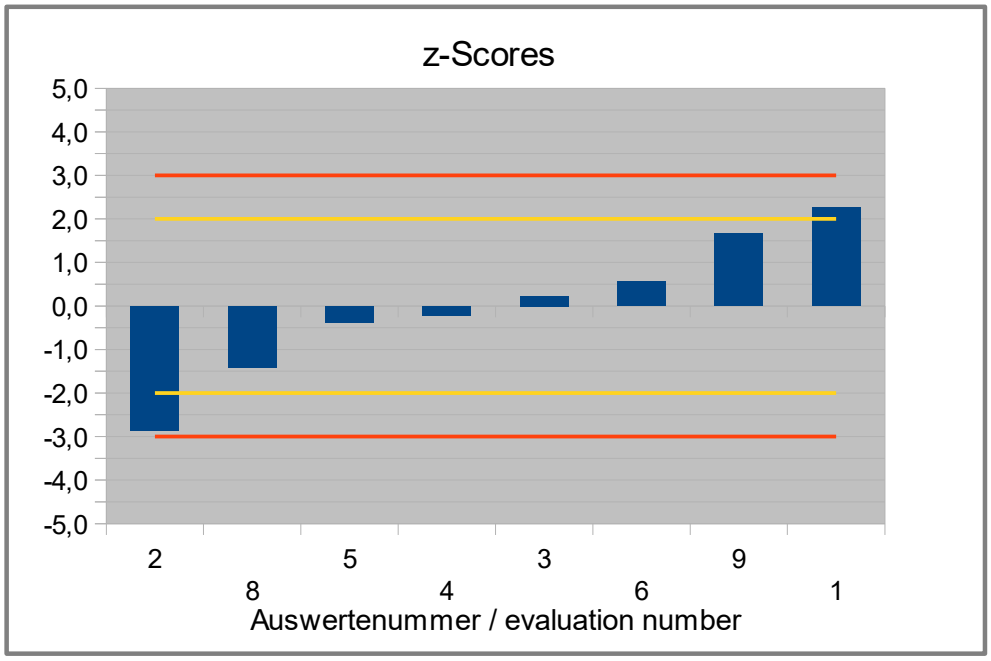


Abb. / Fig. 28: z-Scores Natrium / sodium

4.15 P – Phosphorus in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	7980
Median	7720
Robust Mean (X_{pt})	**7980**
Robust standard deviation (S*)	**995**
Number with 2 replicates	5
Repeatability SD (S_r)	97,3
Repeatability (CV_r)	1,22%
Reproducibility SD (S_R)	861
Reproducibility (CV_R)	10,8%
Target range:	
Target standard deviation σ_{pt}	**597**
Target standard deviation (for Information)	330
lower limit of target range	**6790**
upper limit of target range	**9170**
Quotient S/σ_{pt}*	*1,7*
Standard uncertainty $U_{(Xpt)}$	*556*
Results in the target range	*4*
Percent in the target range	*80%*

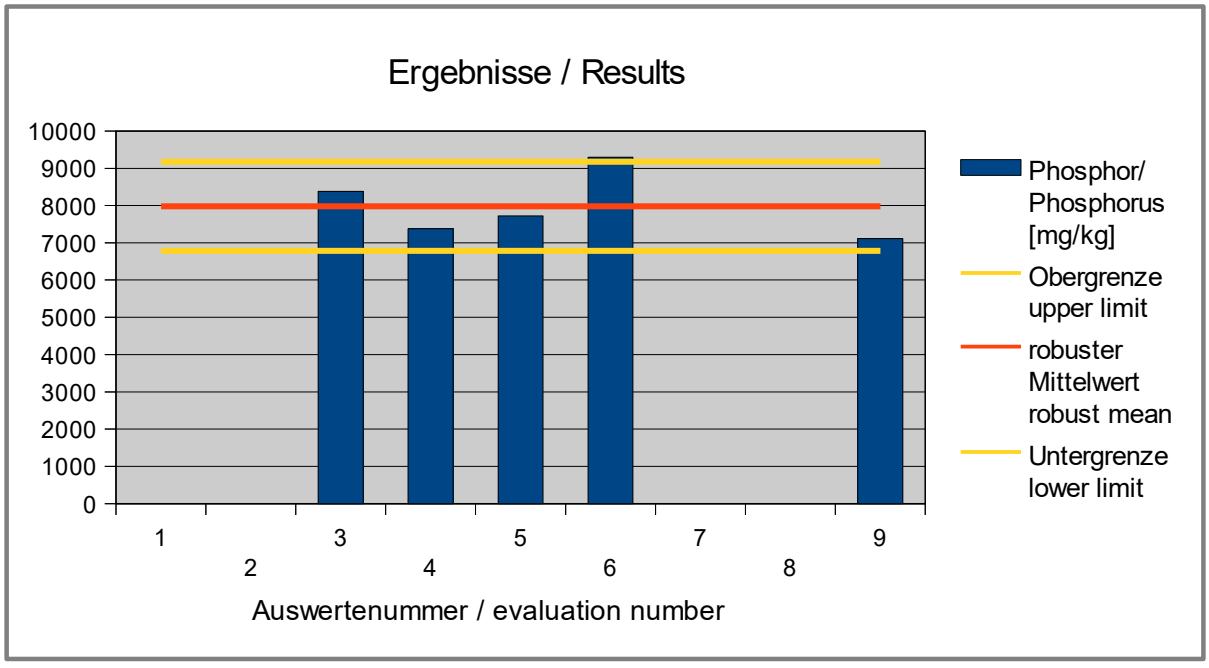


Abb. / Fig. 29: Ergebnisse Phosphor / Results phosphorus

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Phosphor/ Phosphorus [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1					
2					
3	8383	403	0,67	1,2	
4	7381	-599	-1,0	-1,8	
5	7723	-258	-0,43	-0,78	
6	9300	1320	2,2	4,0	
7					
8					
9	7115	-865	-1,4	-2,6	

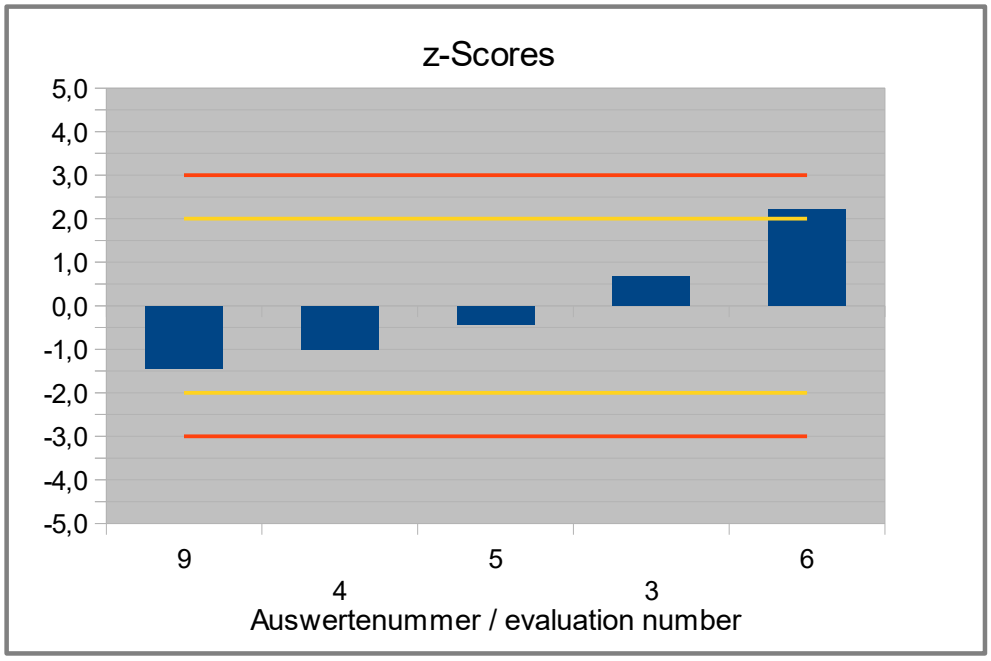


Abb. / Fig. 30: z-Scores Phosphor / phosphorus

4.16 Pb – Lead in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	0,194
Median	0,189
Robust Mean (X_{pt})	**0,194**
Robust standard deviation (S*)	**0,0191**
Number with 2 replicates	8
Repeatability SD (S_r)	0,0158
Repeatability (CV_r)	8,15%
Reproducibility SD (S_R)	0,0201
Reproducibility (CV_R)	10,4%
Target range:	
Target standard deviation σ_{pt}	**0,0398**
Target standard deviation (for Information)	0,0139
lower limit of target range	**0,115**
upper limit of target range	**0,274**
Quotient S/σ_{pt}*	*0,48*
Standard uncertainty $U_{(Xpt)}$	*0,00845*
Results in the target range	*8*
Percent in the target range	*100%*

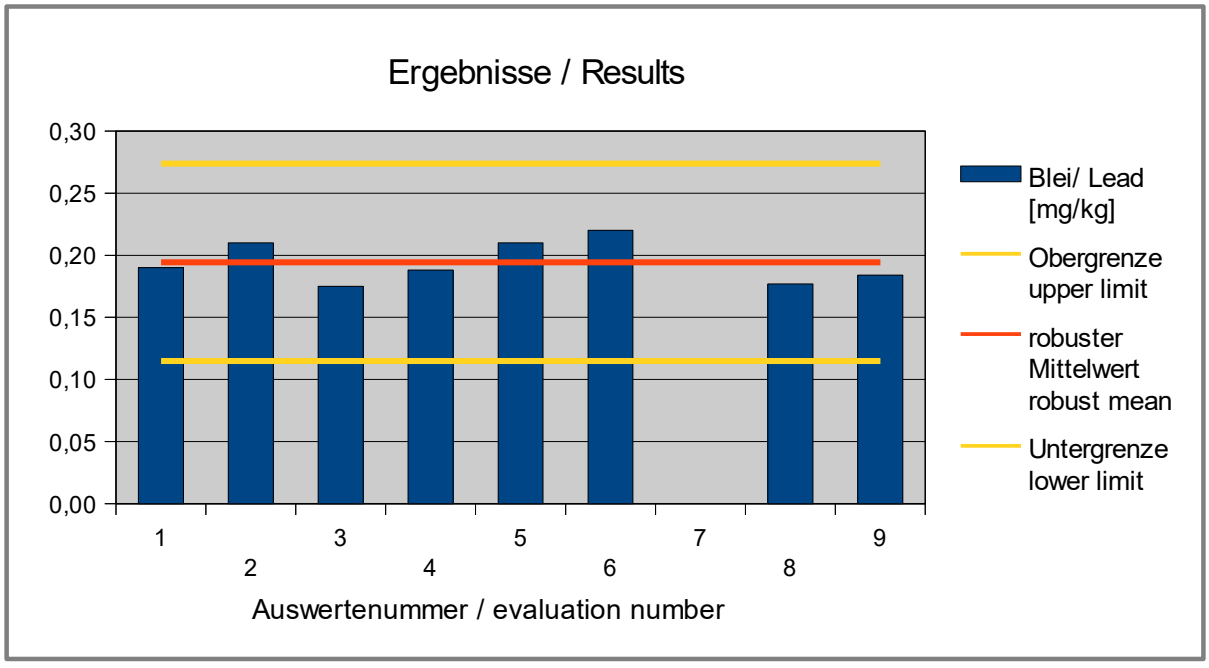


Abb. / Fig. 31: Ergebnisse Blei / Results lead

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Blei/ Lead [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,190	-0,0042	-0,11	-0,30	
2	0,210	0,0158	0,40	1,1	
3	0,175	-0,0193	-0,48	-1,4	
4	0,188	-0,0062	-0,16	-0,45	
5	0,210	0,0158	0,40	1,1	
6	0,220	0,0258	0,65	1,8	
7					
8	0,177	-0,0173	-0,43	-1,2	
9	0,184	-0,0103	-0,26	-0,74	

Abb. / Fig. 32: z-Scores Blei / lead

4.17 S – Sulfur in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	3
Number of outliers	
Mean	2970
Median	2820
Robust Mean (X_{pt})	**2970**
Robust standard deviation (S*)	**326**
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}	
lower limit of target range	
upper limit of target range	
Quotient S/σ_{pt}*	
Standard uncertainty $U_{(Xpt)}$	
Results in the target range	
Percent in the target range	

Due to the small number of available results (<5), no statistical analysis was carried out.

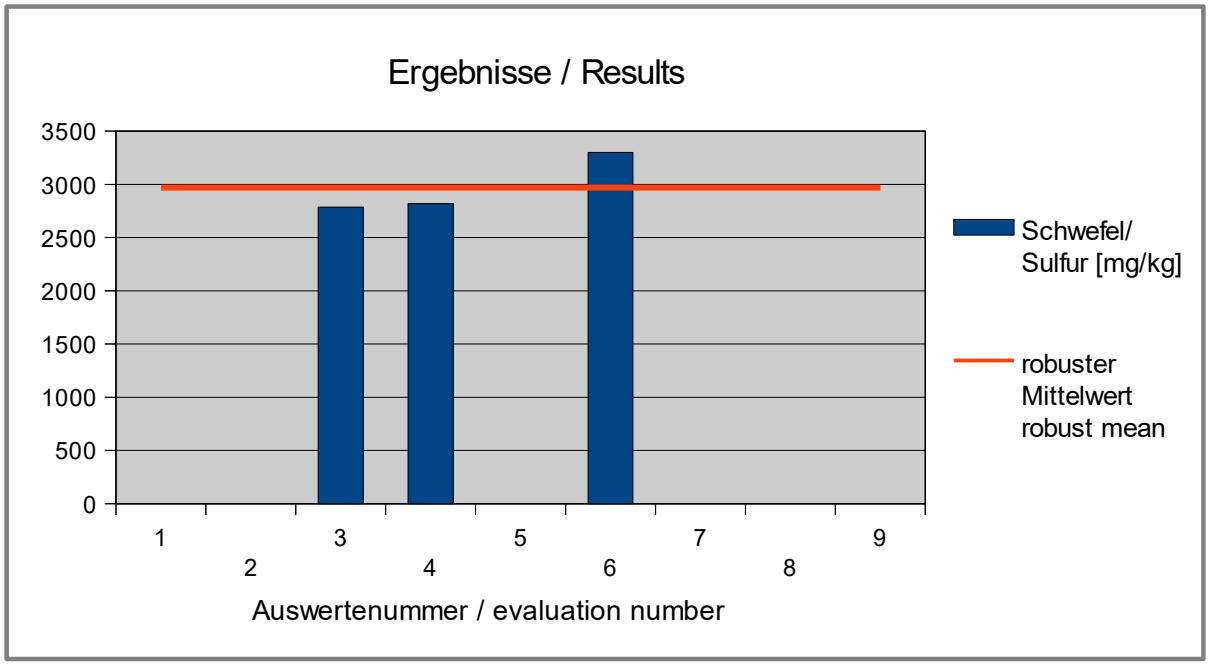


Abb. / Fig. 33: Ergebnisse Schwefel / Results sulfur

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Schwefel/ Sulfur [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	Hinweis Remark
1				
2				
3	2790	-181		
4	2820	-151		
5				
6	3300	332		
7				
8				
9				

4.18 Se – Selenium in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	9
Number of outliers	0
Mean	0,761
Median	0,817
Robust Mean (X_{pt})	**0,761**
Robust standard deviation (S*)	**0,180**
Number with 2 replicates	9
Repeatability SD (S_r)	0,0416
Repeatability (CV_r)	5,49%
Reproducibility SD (S_R)	0,159
Reproducibility (CV_R)	21,0%
Target range:	
Target standard deviation σ_{pt}	**0,127**
Target standard deviation (for Information)	0,0888
lower limit of target range	**0,507**
upper limit of target range	**1,01**
Quotient S/σ_{pt}*	*1,4*
Standard uncertainty $U_{(Xpt)}$	*0,0750*
Results in the target range	*9*
Percent in the target range	*100%*

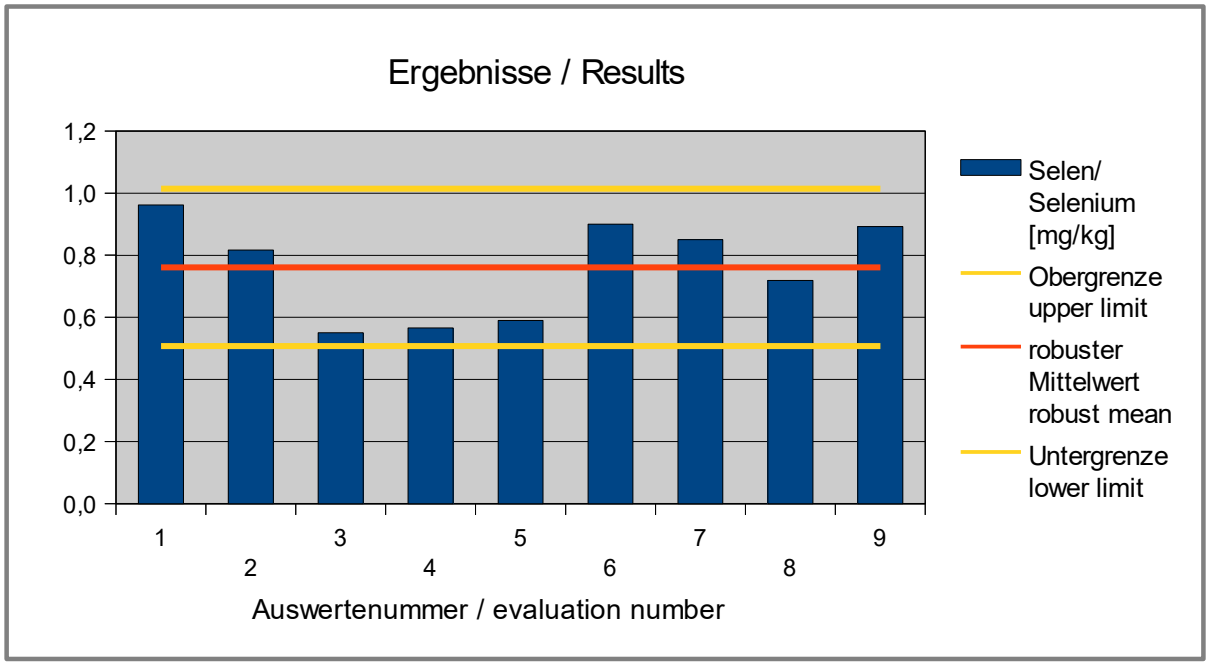


Abb. / Fig. 34: Ergebnisse Selen / Results Selenium

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Selen/ Selenium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	0,962	0,201	1,6	2,3	
2	0,817	0,056	0,44	0,63	
3	0,550	-0,211	-1,7	-2,4	
4	0,566	-0,195	-1,5	-2,2	
5	0,590	-0,171	-1,3	-1,9	
6	0,900	0,139	1,1	1,6	
7	0,850	0,089	0,70	1,0	
8	0,719	-0,042	-0,33	-0,47	
9	0,892	0,131	1,0	1,5	

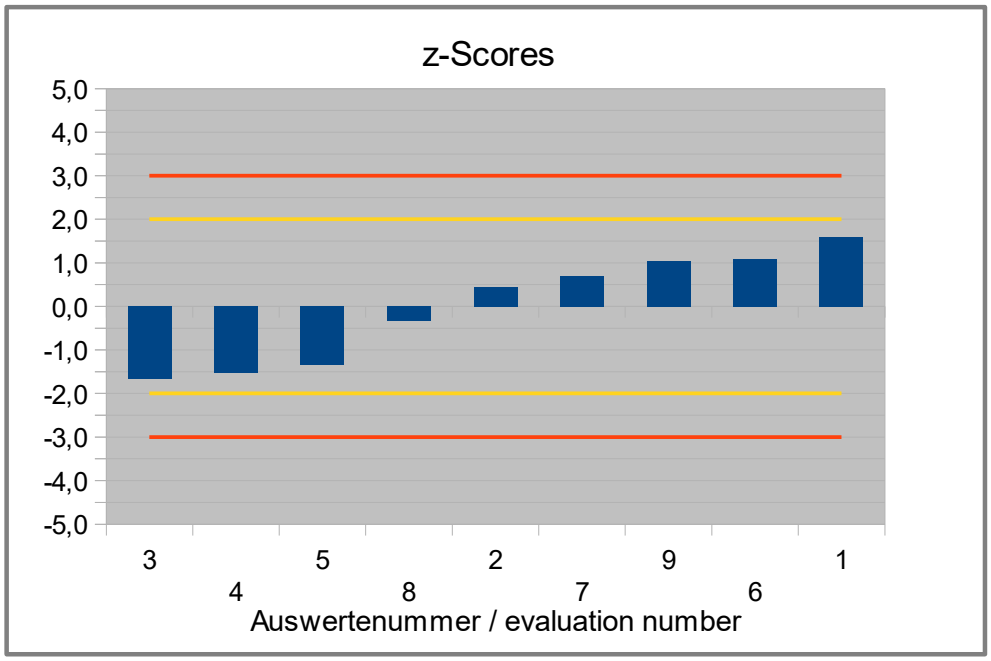


Abb. / Fig. 35: z-Scores Selen / selenium

4.19 Sn – Tin in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	3
Number of outliers	
Mean	0,116
Median	0,0900
Robust Mean (X_{pt})	**0,116**
Robust standard deviation (S*)	**0,146**
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}	
lower limit of target range	
upper limit of target range	
Quotient S/σ_{pt}*	
Standard uncertainty $U_{(Xpt)}$	
Results in the target range	
Percent in the target range	

Due to the small number of available results (<5), no statistical analysis was carried out.

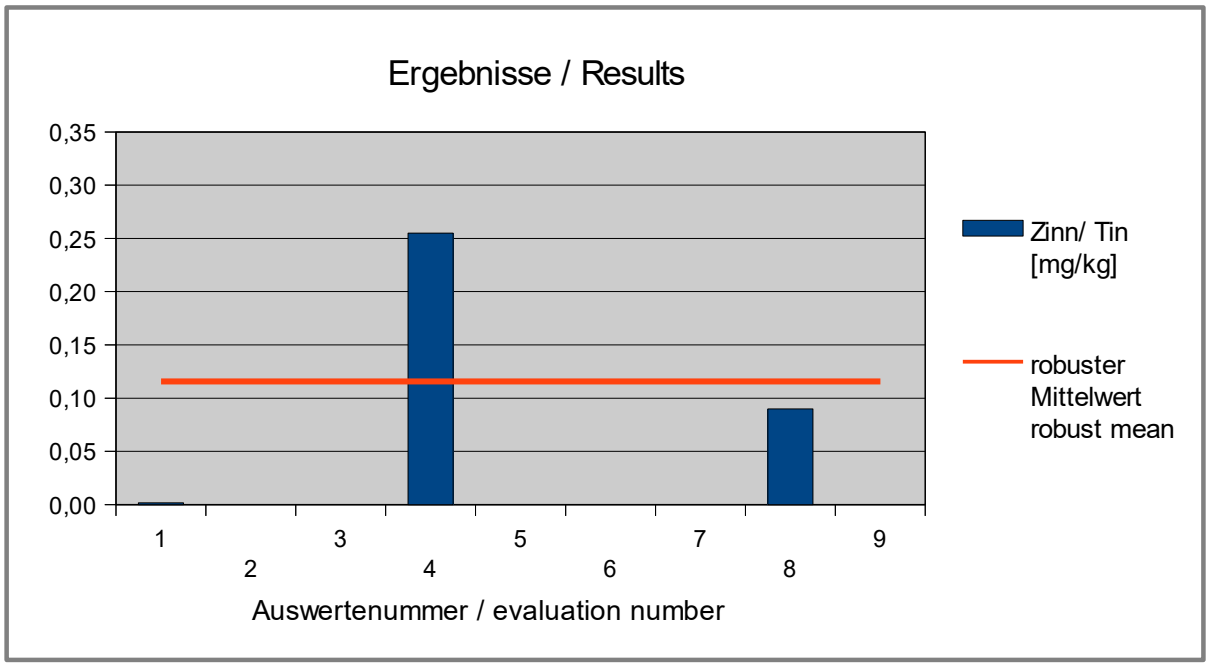


Abb. / Fig. 36: Ergebnisse Zinn / Results tin

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Zinn/ Tin [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	Hinweis Remark
1	0,00165	-0,114		
2	<LOQ			
3	<0,1			
4	0,255	0,139		
5	<0,05			
6	<0,05			
7				
8	0,0900	-0,026		
9				

4.20 Zn – Zinc in mg/kg

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	9
Number of outliers	0
Mean	36,9
Median	38,3
Robust Mean (X_{pt})	**36,9**
Robust standard deviation (S*)	**4,70**
Number with 2 replicates	9
Repeatability SD (S_r)	0,663
Repeatability (CV_r)	1,79%
Reproducibility SD (S_R)	4,21
Reproducibility (CV_R)	11,4%
Target range:	
Target standard deviation σ_{pt}	**3,43**
Target standard deviation (for Information)	2,45
lower limit of target range	**30,1**
upper limit of target range	**43,8**
Quotient S/σ_{pt}*	*1,4*
Standard uncertainty $U_{(Xpt)}$	*1,96*
Results in the target range	*9*
Percent in the target range	*100%*

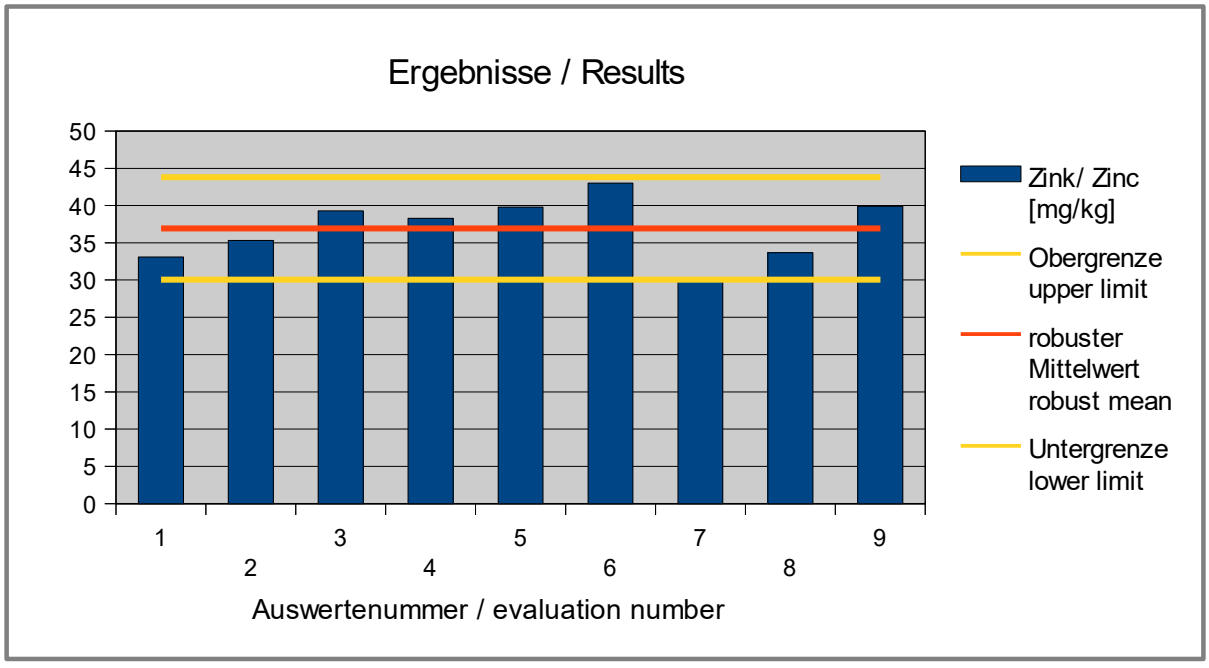


Abb. / Fig. 37: Ergebnisse Zink / Results zinc

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Zink/ Zinc [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1	33,1	-3,83	-1,1	-1,6	
2	35,3	-1,63	-0,47	-0,66	
3	39,3	2,37	0,69	0,97	
4	38,3	1,37	0,40	0,56	
5	39,8	2,86	0,83	1,2	
6	43,0	6,07	1,8	2,5	
7	30,0	-6,93	-2,0	-2,8	
8	33,7	-3,26	-0,95	-1,3	
9	39,9	2,97	0,87	1,2	

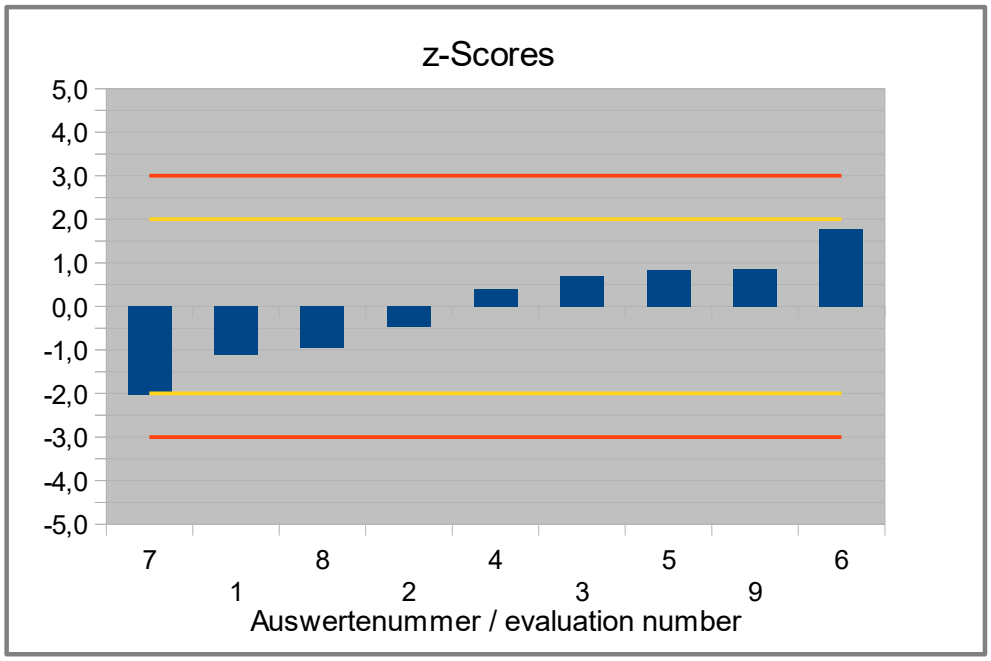


Abb. / Fig. 38: z-Scores Zink / zinc

4.21 Other Elements in mg/kg

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Rubidium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	Hinweis Remark
1	7,50	-0,350		
2	8,20	0,350		
3				
4				
5				
6				
7				
8				
9				

Auswerte-nummer Evaluation number	Strontium [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z-Score (σ_{pt})	Hinweis Remark
1	4,08	-0,125		
2	4,33	0,125		
3				
4				
5				
6				
7				
8				
9				

4.22 Participant z-Scores: overview table

Evaluation number	As	B	Ba	Ca	Cd	Cr	Cu	Fe	Hg	K	Mg	Mn	Mo	Na	P	Pb	S	Se	Sn	Zn
1	2,4	0,62	-0,16	-1,3	0,92	-0,47	0,24	-1,2	0,58	-1,6	-1,5	1,2	0,07	2,3		-0,11		1,6		-1,1
2	0,21	-2,4	0,12	-1,4	0,41	-0,01	-0,93	-0,78	-2,7		-1,5	-0,33	-0,25	-2,9		0,40		0,44		-0,47
3	-0,14	0,79	-0,22	1,8	-0,46	0,15		-0,92	0,71	1,0	0,13	0,14	0,03	0,23	0,67	-0,48		-1,7		0,69
4	-0,53	-1,0	0,04	-0,58	-0,33	-0,57	-0,11	1,8	-0,07	0,38	0,38	0,12		-0,22	-1,0	-0,16		-1,5		0,40
5	-0,22		-0,13	0,77	0,26	0,23	0,32	-0,42	0,64	-0,39	0,58	-0,35	-0,82	-0,37	-0,43	0,40		-1,3		0,83
6	0,43	1,2	0,33	1,5		0,63	0,70	3,4	0,32	1,7	0,80	0,47	0,93	0,56	2,2	0,65		1,1		1,8
7													-0,30					0,70		-2,0
8	-0,18	0,77	-0,68	-0,15	-0,46	-0,25	-0,46	-1,1	-1,0	-1,7	-0,12	-0,32	-1,09	-1,4		-0,43		-0,33		-0,95
9	-0,27		11,6	-0,70	-0,31	0,29	0,24		0,19	0,60	1,3	-0,50	8,81	1,7	-1,4	-0,26		1,0		0,87

Bewertung des z-Scores / valuation of z-score (DIN ISO 13528:2009-01):
-2 ≤ z-score ≤ 2 erfolgreich / successful (in green)
-2 > z-score > 2 „Warnsignal“ / warning signal (in yellow)
-3 > z-score > 3 „Eingriffssignal“ / action signal (in red)

5. Documentation

5.1 Details by the participants

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

5.1.1 Primary Data

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
As - Arsen / Arsenic	1	mg/kg	20	72	13.10.20	0,341	0,329	0,353	0,002	no	
	2	mg/kg	5	87	30.10.20	0.240	0,237	0,242	0,003	no	
	3	mg/kg	26	66	12.10.20	0,224	0,232	0,216	<0,01	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,206	0,186	0,225	keine	yes	80-120
	5	mg/kg	44	48	20.10.20	0,22	0,24	0,21	0,09	no	n.a.
	6	mg/kg	16	76	23.10.20	0,25	0,25	0,26	0,02	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,222	0,237	0,207	0,01	yes	100
	9	mg/kg	35	57	11.11.20	0,218	0,228	0,208	16ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
B - Bor / Boron	1	mg/kg	20	72	13.10.20	0,798	0,685	0,893	0,005	no	
	2	mg/kg	5	87	30.10.20	0,225	0,258	0,191	0,02	no	
	3	mg/kg	26	66	12.10.20	0,831	0,846	0,816	<1,5	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,489	0,508	0,469	keine	yes	80-120
	5	mg/kg	44	48	nicht untersucht	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6	mg/kg	16	76	23.10.20	0,9	0,85	0,91	0,2	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,827	0,834	0,82	0,05	yes	100
	9	mg/kg	35	57							

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Ba - Barium	1	mg/kg	20	72	13.10.20	0,924	0,923	0,926	0,001	no	
	2	mg/kg	5	87	30.10.20	0,968	0,973	0,964	0,003	no	
	3	mg/kg	26	66	12.10.20	0,915	0,92	0,91	<0,50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,956	0,959	0,954	keine	yes	80-120
	5	mg/kg	44	48	19.10.20	0,93	0,93	0,93	0,09	no	n.a.
	6	mg/kg	16	76	23.10.20	1	0,98	1,01	0,05	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,845	0,836	0,855	0,01	yes	100
	9	mg/kg	35	57	11.11.20	2,72	2,62	2,82	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Ca - Calcium	1	mg/kg	20	72	13.10.20	9253	9186	9319	0,02	no	
	2	mg/kg	5	87	30.10.20	9216	9157	9274	0,8	no	
	3	mg/kg	26	66	12.10.20	11738	11778	11698	<50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	9849,8	9858,1	9841,5	keine	yes	80-120
	5	mg/kg	44	48	26.10.20	10905,95	10979,72	10832,17	18	no	n.a.
	6	mg/kg	16	76	23.10.20	11500	11500	11400	200	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	10185	10034	10335	2	yes	100
	9	mg/kg	35	57	09.11.20	9750	9520	9980	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Cd - Cadmium	1	mg/kg	20	72	13.10.20	0.0910	0,0841	0,0979	0,001	no	
	2	mg/kg	5	87	30.10.20	0.0824	0.0838	0,0811	0,00006	no	
	3	mg/kg	26	66	12.10.20	0,068	0,069	0,067	<0,005	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,0701	0,0642	0,0759	0,0025	yes	80-120
	5	mg/kg	44	48	20.10.20	0,08	0,08	0,07	0,03	no	n.a.
	6	mg/kg	16	76	23.10.20	0,87	0,86	0,88	0,02	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,068	0,071	0,064	0,01	yes	100
	9	mg/kg	35	57	11.11.20	0,0705	0,074	0,067	8ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Cr - Chrom / Chromium	1	mg/kg	20	72	13.10.20	1,01	0,98	1,04	0,001	no	
	2	mg/kg	5	87	30.10.20	1,09	1.10	1,09	0,0003	no	
	3	mg/kg	26	66	12.10.20	1,117	1,105	1,129	<0,10	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,993	0,973	1,013	0,0375	yes	80-120
	5	mg/kg	44	48	20.10.20	1,13	1,2	1,06	0,3	no	n.a.
	6	mg/kg	16	76	23.10.20	1,2	1,15	1,22	0,05	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	1,047	1,136	0,958	0,01	yes	100
	9	mg/kg	35	57	10.11.20	1,14	1,28	1	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Cu - Kupfer / Copper	1	mg/kg	20	72	13.10.20	0,463	0,482	0,443	0,001	no	
	2	mg/kg	5	87	30.10.20	0,369	0.370	0,368	0,0008	no	
	3	mg/kg	26	66	12.10.20	<0,5	<0,5	<0,5	<0,50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,435	0,439	0,43	0,025	yes	80-120
	5	mg/kg	44	48	20.10.20	0,47	0,47	0,48	0,06	no	n.a.
	6	mg/kg	16	76	23.10.20	0,5	0,47	0,51	0,1	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,407	0,398	0,416	0,01	yes	100
	9	mg/kg	35	57	10.11.20	0,4635	0,462	0,465	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Fe - Eisen / Iron	1	mg/kg	20	72	13.10.20	1,79	1.90	1,68	0,001	no	
	2	mg/kg	5	87	30.10.20	1,92	1,93	1,91	0,06	no	
	3	mg/kg	26	66	12.10.20	1,875	1,88	1,87	<0,50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	2,704	2,772	2,635	0,25	yes	80-120
	5	mg/kg	44	48	20.10.20	2,03	2,01	2,05	3	no	n.a.
	6	mg/kg	16	76	23.10.20	3,2	3,1	3,2	0,2	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	1,829	1,816	1,841	0,1	yes	100
	9	mg/kg	35	57							

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Hg - Quecksilber / Mercury	1	mg/kg	20	72	13.10.20	0,079	0.080	0,078	0,001	no	
	2	mg/kg	5	87	30.10.20	0,0277	0.0284	0.0270	-	no	
	3	mg/kg	26	66	16.10.20	0,081	0,077	0,084	<0,005	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,069	0,066	0,072	keine	yes	80-120
	5	mg/kg	44	48	20.10.20	0,08	0,08	0,08	0,03	no	n.a.
	6	mg/kg	16	76	23.10.20	0,075	0,074	0,078	0,005	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,054	0,052	0,056	0,007	yes	100
	9	mg/kg	35	57	12.11.20	0,0731	0,0787	0,0675	1ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
K - Kalium / Potassium	1	mg/kg	20	72	13.10.20	8229	8007	8451	0,03	no	
	2	mg/kg	5	87	30.10.20	92760	91330	94190	0,17	no	
	3	mg/kg	26	66	12.10.20	9169	9216	9121	<50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	8931,4	8890,7	8972,1	8,75	yes	80-120
	5	mg/kg	44	48	26.10.20	8654,04	8716,56	8591,48	18	no	n.a.
	6	mg/kg	16	76	23.10.20	9400	9300	9400	100	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	8170	8091	8249	1	yes	100
	9	mg/kg	35	57	09.11.20	9010	8820	9200	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Mg - Magnesium	1	mg/kg	20	72	13.10.20	669	661	677	0,04	no	
	2	mg/kg	5	87	30.10.20	668	691	694	0,0047	no	
	3	mg/kg	26	66	12.10.20	741	744	737	<50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	751,9	743,2	760,5	0,25	yes	80-120
	5	mg/kg	44	48	26.10.20	760,41	765,83	754,98	6	no	n.a.
	6	mg/kg	16	76	23.10.20	770	764	774	10	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	730	721	740	0,1	yes	100
	9	mg/kg	35	57	09.11.20	791	767	815	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Mn - Mangan / Manganese	1	mg/kg	20	72	13.10.20	0,394	0,396	0,392	0,001	no	
	2	mg/kg	5	87	30.10.20	0.301	0.300	0.302	0,001	no	
	3	mg/kg	26	66	12.10.20	0,33	0,32	0,34	<0,50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,329	0,339	0,319	0,0375	yes	80-120
	5	mg/kg	44	48	30.10.20	0,3	0.30	0,29	0,03	no	n.a.
	6	mg/kg	16	76	23.10.20	0,35	0,32	0,36	0,1	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,302	0,299	0,306	0,01	yes	100
	9	mg/kg	35	57	10.11.20	0,291	0,288	0,294	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Mo - Molybdän / Molybdenum	1	mg/kg	20	72	13.10.20	0,301	0,306	0,297	0,01	no	
	2	mg/kg	5	87	30.10.20	0,283	0,284	0,281	0,0006	no	
	3	mg/kg	26	66	12.10.20	0,299	0,299	0,299	<0,01	no	
	4	mg/kg									
	5	mg/kg	44	48	19.10.20	0,25	0,24	0,25	0,03	no	n.a.
	6	mg/kg	16	76	23.10.20	0,35	0,32	0,35	0,1	no	100
	7	mg/kg	# 32	# 60	05.11.20	0.28ppm	0.27ppm	0.29ppm			
	8	mg/kg	6	86	02.12.20	0,235	0,232	0,238	0,01	yes	100
	9	mg/kg	35	57	10.11.20	0,7995	0,849	0,75	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Na - Natrium / Sodium	1	mg/kg	20	72	13.10.20	2277	2284	2270	0,02	no	
	2	mg/kg	5	87	30.10.20	1746	1723	1768	0.10	no	
	3	mg/kg	26	66	12.10.20	2066	2074	2057	<50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	2019,3	1988,3	2050,2	0,375	yes	80-120
	5	mg/kg	44	48	26.10.20	200.79	2022,25	1985,33	9	no	n.a.
	6	mg/kg	16	76	23.10.20	2100	2080	2130	50	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	1895	1867	1922	1	yes	100
	9	mg/kg	35	57	09.11.20	2215	2180	2250	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
P - Phosphor / Phosphorus	1	mg/kg	20	72	13.10.20	-			-	-	
	2	mg/kg	5	87	30.10.20	-	-	-	-	no	
	3	mg/kg	26	66	12.10.20	8383	8399	8367	<50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	7380,8	7330,3	7431,2	keine	yes	80-120
	5	mg/kg	44	48	26.10.20	7722,55	7734,84	7710,26	9	no	n.a.
	6	mg/kg	16	76	23.10.20	9300	9200	9300	200	no	100
	7	mg/kg									
	8	mg/kg									
	9	mg/kg	35	57	09.11.20	7115	6980	7250	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Pb - Blei / Lead	1	mg/kg	20	72	13.10.20	0.190	0,185	0,194	0,001	no	
	2	mg/kg	5	87	30.10.20	0.210	0.210	0.210	0,0008	no	
	3	mg/kg	26	66	12.10.20	0,175	0,18	0,17	<0,01	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,188	0,166	0,209	0,169	yes	80-120
	5	mg/kg	44	48	20.10.20	0,21	0,23	0,2	0,03	no	n.a.
	6	mg/kg	16	76	23.10.20	0,22	0,21	0,22	0,02	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,177	0,189	0,165	0,01	yes	100
	9	mg/kg	35	57	11.11.20	0,184	0,194	0,174	9ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
S - Schwefel / Sulfur	1	mg/kg	20	72	13.10.20	-			-	-	
	2	mg/kg	5	87	30.10.20	-	-	-	-	no	
	3	mg/kg	26	66	12.10.20	2787	2805	2768	<50	no	
	4	mg/kg	No. 38	No. 54	13.11.20	2817,5	2798,8	2836,2	keine	yes	80-120
	5	mg/kg	44	48	not analysed	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6	mg/kg	16	76	23.10.20	3300	3150	3450	200	no	100
	7	mg/kg									
	8	mg/kg									
	9	mg/kg	35	57							

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Se - Selen / Selenium	1	mg/kg	20	72	13.10.20	0,962	0,915	1,01	0,02	no	
	2	mg/kg	5	87	30.10.20	0,817	0,819	0,815	0,004	no	
	3	mg/kg	26	66	10.11.20	0,55	0,56	0,539	<0,10	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,566	0,551	0,58	0,1	ja	80-120
	5	mg/kg	44	48	19.10.20	0,59	0,61	0,57	0,03	no	n.a.
	6	mg/kg	16	76	23.10.20	0,9	0,85	0,91	0,05	no	100
	7	mg/kg	# 32	# 60	05.11.20	0.85ppm	0.88ppm	0.81ppm			
	8	mg/kg	6	86	02.12.20	0,719	0,768	0,669	0,01	ja	100
	9	mg/kg	35	57	10.11.20	0,892	0,907	0,877	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Sn - Zinn / Tin	1	mg/kg	20	72	13.10.20	0,00165	0,00177	0,00154	0,001	no	
	2	mg/kg	5	87	30.10.20	<LOQ	<LOQ	<LOQ	0,0005	no	
	3	mg/kg	26	66	12.10.20	<0,1	<0,1	<0,1	<0,10	no	
	4	mg/kg	No. 38	No. 54	13.11.20	0,255	0,254	0,255	keine	yes	80-120
	5	mg/kg	44	48	19.10.20	< 0,05	< 0,05	< 0,05	0,05	no	n.a.
	6	mg/kg	16	76	23.10.20	<0,05	<0,05	<0,05	0,05	no	100
	7	mg/kg									
	8	mg/kg	6	86	02.12.20	0,09	0,083	0,097	0,01	yes	100
	9	mg/kg	35	57							

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Zn - Zink / Zinc	1	mg/kg	20	72	13.10.20	33,1	33,8	32,5	0,004	no	
	2	mg/kg	5	87	30.10.20	35,3	35,6	35,1	0,006	no	
	3	mg/kg	26	66	12.10.20	39,3	39,5	39,1	<0,5	no	
	4	mg/kg	No. 38	No. 54	13.11.20	38,297	38,332	38,261	0,2	yes	80-120
	5	mg/kg	44	48	20.10.20	39,79	39,96	39,62	0,9	no	n.a.
	6	mg/kg	16	76	23.10.20	43	42,8	43,7	0,5	no	100
	7	mg/kg	# 32	# 60	05.11.20	30ppm	31ppm	29ppm			
	8	mg/kg	6	86	02.12.20	33,67	33,3	34,03	0,2	yes	100
	9	mg/kg	35	57	10.11.20	39,9	39,6	40,2	5ug/kg	No	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Rb - Rubidium	1	mg/kg	20	72	13.10.20	7.50	7,82	7,19		no	
	2	mg/kg	5	87		8.20	8,09	8,29	0,001	no	

Analyte	Partici-pant	Unit	Sample I DLA No.	Sample II DLA No.	Date of analysis	Result (Mean)	Result I	Result II	Limit of quan-tification	Incl. RR	Recovery rate
					Day/Month					yes / no	in %
Sr - Strontium	1	mg/kg	20	72	13.10.20	4,08	4,23	3,92		no	
	2	mg/kg	5	87		4.33	4.30	4,34	0,0002	no	

5.1.2 Analytical Methods

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
As	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 17294-2 (E 29)(2005-02)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	no	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
B	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 11885 (E 22)(2009-09)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	no	
	5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9							

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Ba / Ca	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 11885 (E 22)(2009-09)	VDLUFA VII, 2.1.3 (2011)		Ja		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	no	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	no	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	No	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Cd / Cr / Pb	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 17294-2 (E 29)(2005-02)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	yes	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Cu / Fe / K / Mg / Mn / Na	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 11885 (E 22)(2009-09)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	yes	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Hg	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 12846 (E 12)(2012-08)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	no	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	EPA 7473	Direct Analysis	DMA	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Mo	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 17294-2 (E 29)(2005-02)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4							
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7	ICP-OES with acid digestion			Spex Certiprep		The method is, but not for this analyte	
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
P	1	-	-				-	not analysed
	2	in-house method	-				no	not analysed
	3	DIN EN ISO 11885 (E 22)(2009-09)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-OES	microwave pressure digestion	Quantitative Analysis ICP-OES	external calibration and reference water	no	no	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	no	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8							
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
S	1	-	-				-	not analysed
	2	in-house method	-				no	not analysed
	3	DIN EN ISO 11885 (E 22)(2009-09)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-OES	microwave pressure digestion	Quantitative Analysis ICP-OES	external calibration and reference water	no	Nein	
	5	n.a.	n.a.	n.a.	n.a.	n.a.	no	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8							
	9							

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Se	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN 38405-D 23 (1194-10)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	no	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7	ICP-OES with acid digestion			Spex Certiprep		The method is, but not for this analyte	
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	No	Yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Sn	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 11885 (E 22)(2009-09)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	yes	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7							
	8	§64 L00.00-19/1	aqua regia digestion	ICP-MS	External Standards	yes	yes	-
	9							

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Zn	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	3	DIN EN ISO 17294-2 (E 29)(2005-02)	VDLUFA VII, 2.1.3 (2011)		yes		yes	
	4	Quantitative Analysis ICP-MS	microwave pressure digestion	Quantitative Analysis ICP-MS	external calibration and reference water	no	no	
	5	Analytes by ICP-MS after microwave digestion	mixing	ICP-MS	ext. with IS In	n.a.	yes	n.a.
	6	EN 15763 - EN 17294-2	microwave digestion	ICP-MS	TMDA51.5 ICP-MS	no	yes	
	7	ICP-OES with acid digestion			Spex Certiprep		yes	
	8	§64 L00.00-19/1	HNO3-digestion	ICP-MS	External Standards	yes	yes	-
	9	AOAC 993.14	Hot Block Digestion	ICP-MS	Sigma Aldrich	no	yes	

Analyte	Participant	Method description as in test report / norm / literature	Sample preparation	Measuring method	Calibration / Reference material	Recovery rate with same matrix	Method accredited ISO/IEC 17025	Further Remarks
			Digestion: Method / Solution			yes / no	yes / no	
Rb / Sr	1	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container
	2	in-house method	microwave acid digestion with HNO3 and H2O2 (4:1, v:v). sample weight: ~500 mg				no	Homogenized by stirring after transferring to sample container

5.2 Homogeneity

5.2.1 Homogeneity of bottled PT-samples

Homogeneity test of copper and lead by ICP-MS (EN ISO 17294-2):

Copper

Independant Samples	mg/kg
1	0,47
2	0,49
3	0,48
4	0,48
5	0,47
6	0,48
7	0,47
8	0,48

General Mean	0,48	
Repeatability standard deviation	0,0071	1,48%

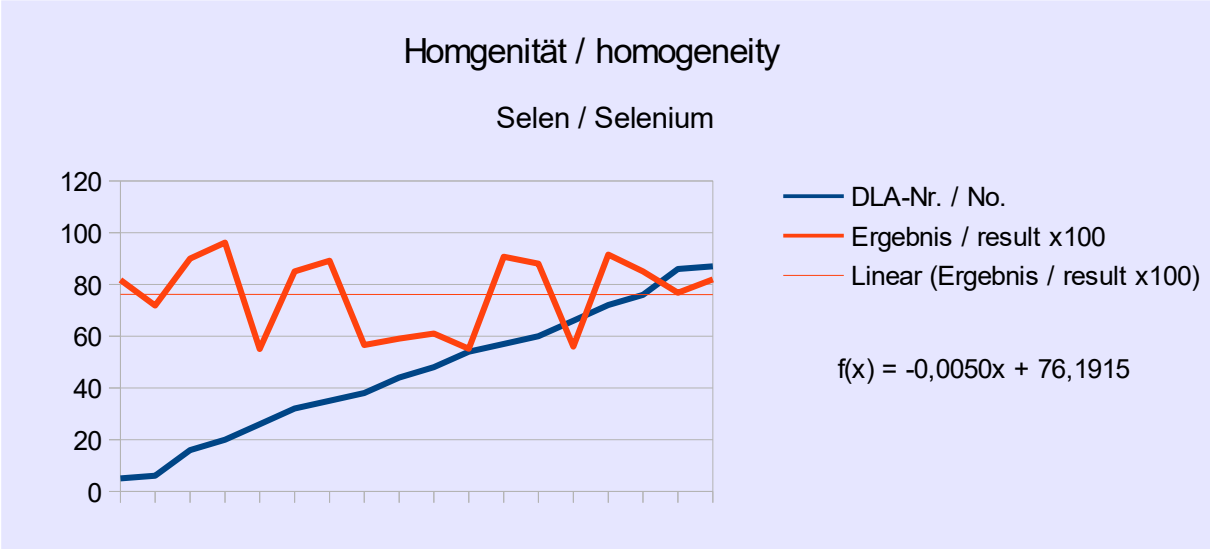
Lead

Independant Samples	mg/kg
1	0,24
2	0,20
3	0,19
4	0,23
5	0,25
6	0,19
7	0,20
8	0,22

General Mean	0,22	
Repeatability standard deviation	0,023	10,8%

5.2.2 Trend line function of the participants results

By comparison of the increasing sample numbers and the measurement results of participants, the homogeneity of the chronological bottled PT items can be shown by the trend line for information:



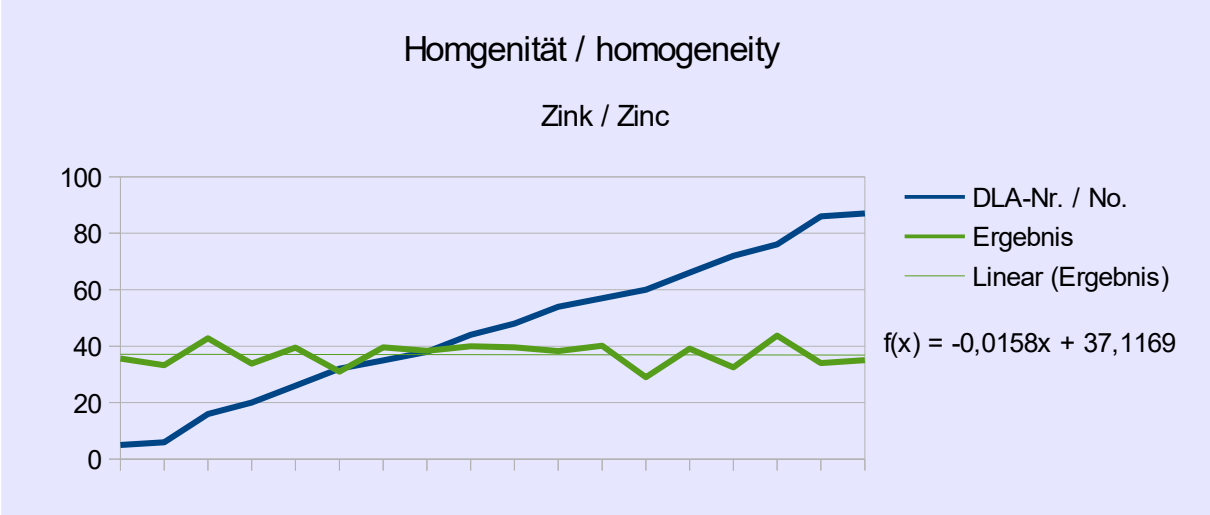


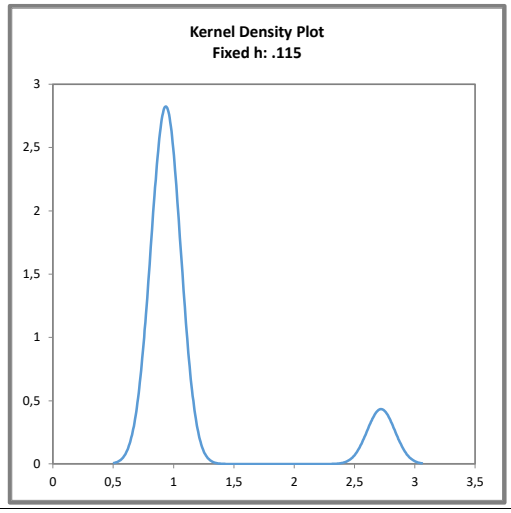
Abb./Fig. 39: Trendfunktion Probennummern vs. Ergebnisse: Selen (1*100 dargestellt) und Zink
trend line function sample number vs. results: selenium (1*100 shown) and zinc

5.3 Kernel Density Plots of Results

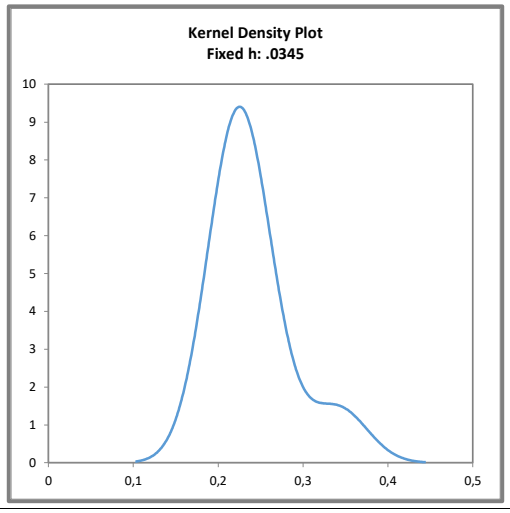
Abbildungen:
Kerndichte-Schätzungen
der Teilnehmerergebnisse
(mit h = 0,75 x σ_{pt} von Xpt)

Figures:
Kernel density plots
of participants' results
(with h = 0,75 x σ_{pt} of Xpt)

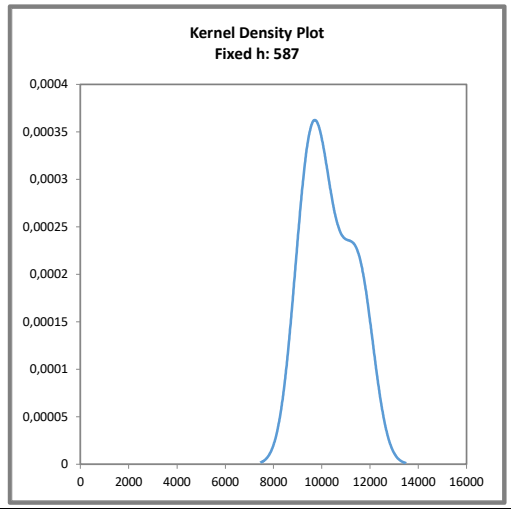
B



As



Ca

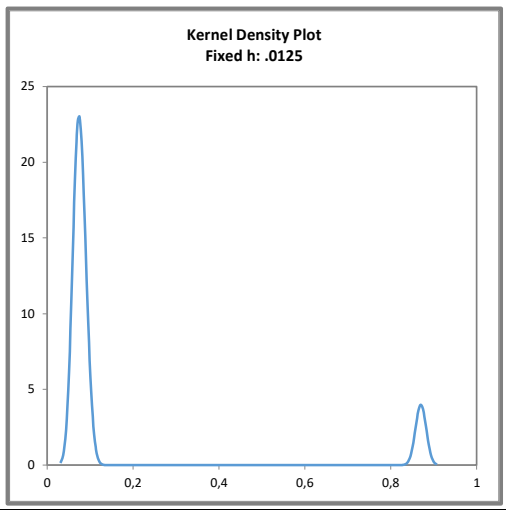


B

< 8 Ergebnisse

< 8 Results

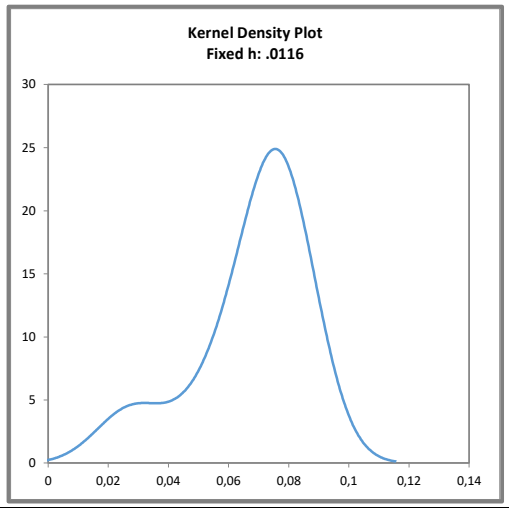
Cd



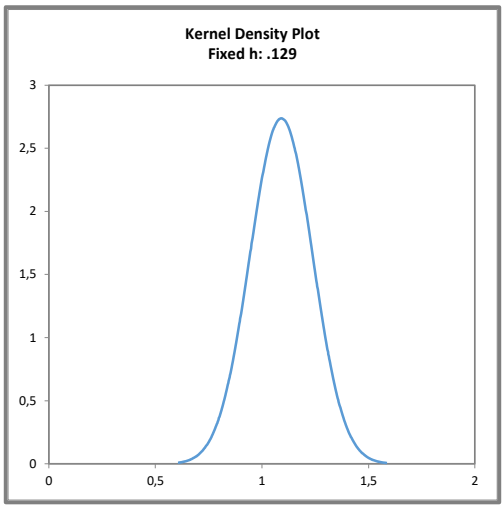
Abbildungen:
Kerndichte-Schätzungen
der Teilnehmerergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

Figures:
Kernel density plots
of participants' results
(with h = 0,75 x σ_{pt} of X_{pt})

Hg



Cr



K

ohne Ausreißer < 8 Ergebnisse

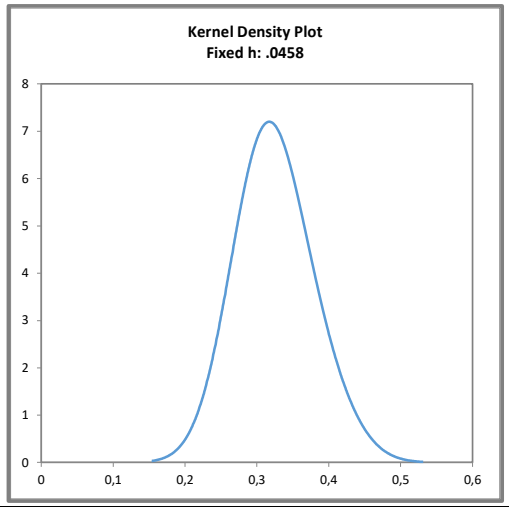
without outlier < 8 Results

Cu

< 8 Ergebnisse

< 8 Results

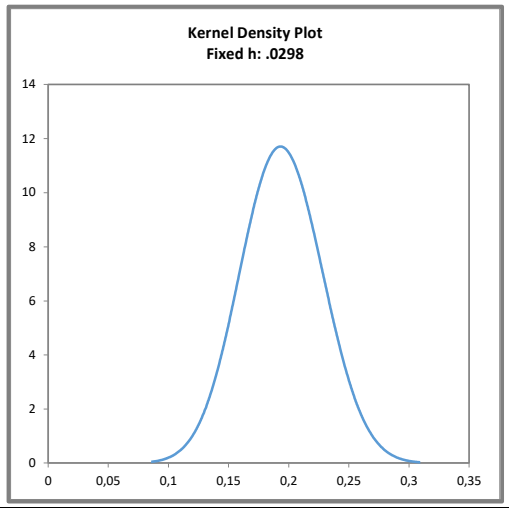
Mn



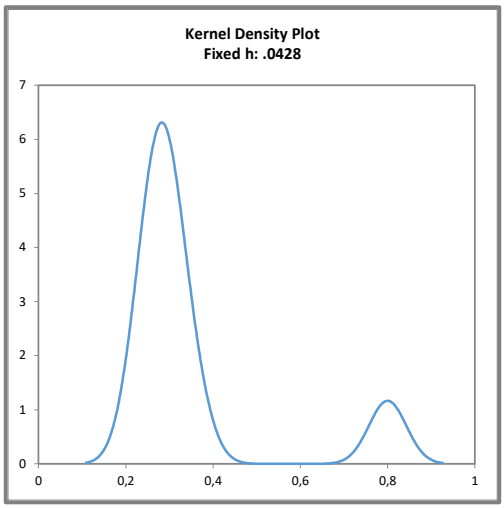
Abbildungen:
Kerndichte-Schätzungen
der Teilnehmerergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

Figures:
Kernel density plots
of participants' results
(with h = 0,75 x σ_{pt} of X_{pt})

Pb



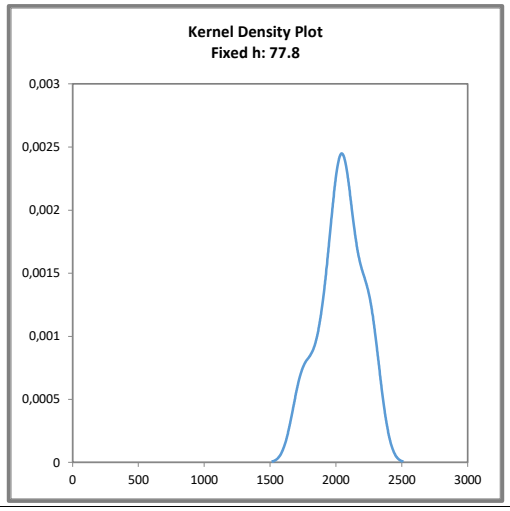
Mo



P

< 8 Ergebnisse
< 8 Results

Na



S

< 8 Ergebnisse
< 8 Results

Abbildungen:
Kerndichte-Schätzungen
der Teilnehmerergebnisse
(mit h = 0,75 x σ_{pt} von X_{pt})

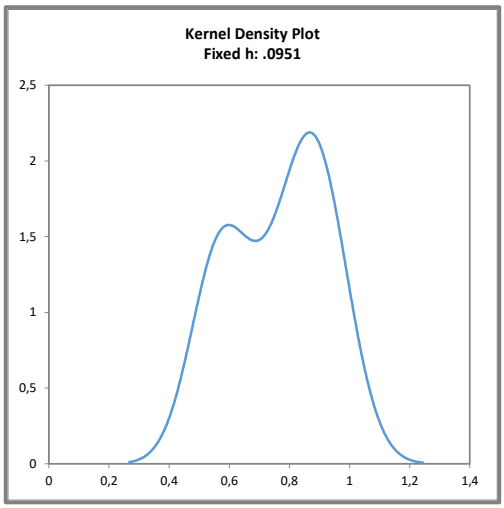
Figures:
Kernel density plots
of participants' results
(with h = 0,75 x σ_{pt} of X_{pt})

Sn

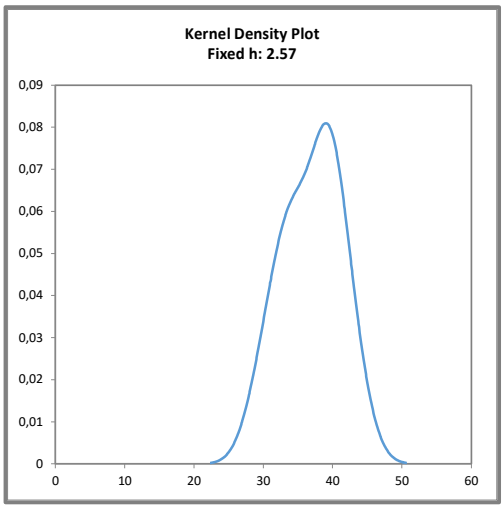
< 8 Ergebnisse

< 8 Results

Se



Zn



5.4 Information on the Proficiency Test (PT)

Before the PT the participants received the following information in the sample cover letter:

PT number	***DLA ptSU08 (2020)***
PT name	***Heavy Metals and Trace Elements in high-fat Food***
*Sample matrix**	*Samples I + II: Sports nutrition (drink powder) / ingredients: cream powder, casein powder (fat content >50%)*
Number of samples and sample amount	*2 identical samples I + II, 8 g each.*
Storage	*Samples I + II: room temperature*
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative: As, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, P, Pb, S, Se, Sn and Zn*
Methods of analysis	*Analytical methods are optional*
Notes to analysis	*The analysis of PT samples should be performed like a routine laboratory analysis.* *In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights.*
Result sheet	*The results for sample I and II as well as the final results calculated as mean of the double determination (samples I and II) should be filled in the result submission file. The recovery rates, if carried out, has to be included in the calculation.*
Units	*mg/kg*
Number of significant digits	*at least 2*
Further information	*For information please specify:* – *Date of analysis* – *DLA-sample-numbers (for sample I and II)* – *Limit of detection* – *Assignment incl. Recovery* – *Recovery with the same matrix* – *Method is accredited*
Result submission	*The result submission file should be sent by e-mail to:* ***pt@dla-lvu.de***
Last Deadline	***the latest December 11th 2020***
Evaluation report	*The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.*
Coordinator and contact person of PT	*Matthias Besler-Scharf, PhD.*

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

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		USA
		USA
		Germany
		Germany
		Germany
		Germany
		SWITZERLAND
		Germany
		Germany

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

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

7. Index of references

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 inter-laboratory comparisons
4. ASU §64 LFGB: Planung und statistische Auswertung von Ringversuchen zur Methoden-validierung / DIN ISO 5725 series part 1, 2 and 6 Accuracy (trueness and preci-sion) of measurement methods and results
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14. GMP+ Feed Certification scheme, Module: Feed Safety Assurance, chapter 5.7 Check-ing 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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17. AOAC Official Methods of Analysis: Guidelines for Standard Method Performance Re-quirements, Appendix F, p. 2, AOAC Int (2016)
18. ASU §64 L 00.00-157 (2016-2): Bestimmung von Aluminium in Lebensmitteln mit der Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS) [Determination of aluminium in foods by inductively coupled plasma mass spectrometry (ICPMS) after pressure digestion]
19. ASU §64 L 00.00-158 (2016-2): Bestimmung von Aluminium in Lebensmitteln mit der optischen Emmissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP-OES) [De-termination of aluminium in foods by inductively coupled plasma emmission spectro-metry (ICP-OES) after pressure digestion]
20. ASU §64 L 00.00-135 (2011-01) / DIN EN 15763:2010: Bestimmung von Arsen, Cadmium, Quecksilber und Blei in Lebensmitteln mit ICP-MS nach Druckaufschluss / Food-stuffs. Determination of trace elements. Determination of arsenic, cadmium, mer-cury and lead in foodstuffs by inductively coupled plasma mass spectrometry (ICPMS) after pressure digestion
21. ASU §64 L 00.00-19/2: Bestimmung von Eisen, Kupfer, Mangan und Zink mit der Atom-absorptionsspektrometrie (AAS) in der Flamme [Determination of iron, copper, man-ganese and zinc by atomic absorption spectrometry (AAS) in the flame]
22. ASU §64 L 00.00-19/3 / DIN EN 14083: Bestimmung von Blei, Cadmium, Chrom und Mo-lybdän mit Graphitofen-Atomabsorptionsspektrometrie (GFAAS) nach Druckaufschluss / Foodstuffs. Determination of trace elements. Determination of lead, cadmium, chro-

mium and molybdenum by graphite furnace atomic absorption spectrometry (GFAAS) after pressure digestion
23. ASU §64 L 00.00-19/5: Bestimmung von Selen mit der Atomabsorptionsspektrometrie (AAS) - Hydridtechnik [Determination of selenium by atomic absorption spectrometry (AAS) - hydride technique]
24. ASU §64 L 00.00-144 : Bestimmung der Mineralstoffe Ca, K, Mg, Na, P und S sowie der Spurenelemente Fe, Cu, Mn und Zn in Lebensmitteln mit ICP-OES [Determination of minerals Ca, K, Mg, Na, P and S and trace elements Fe, Cu, Mn and Zn in foods by ICP-OES]
25. ASU §64 L 00.00-93 / DIN EN 15111: Bestimmung von Iod in Lebensmitteln - ICP-M-S-Verfahren / Foodstuffs. Determination of trace elements. Determination of iodine by ICP-MS (inductively coupled plasma mass spectrometry)
26. ASU §64 L 00.00-127 / EN 15764: Bestimmung von Zinn in Lebensmitteln mit der Flammen- und Graphitrohr-Atomabsorptionsspektrometrie (GFAAS) nach Druckaufschluss / Foodstuffs. Determination of trace elements. Determination of tin by flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) after pressure digestion
27. ASU §64 L 00.00-128 / DIN EN 15765: Bestimmung Zinn in Lebensmitteln mit der Massensprektrometrie mit induktiv gekoppeltem Plasma (ICP-MS) nach Druckaufschluss / Foodstuffs. Determination of trace elements. Determination of tin by inductively coupled plasma mass spectrometry (ICPMS) after pressure digestion
28. ASU §64 L 31.00-10: Bestimmung der Gehalte an Natrium, Kalium, Calcium und Magnesium in Frucht- und Gemüsesäften – Atomabsorptionsspektrometrisches Verfahren (AAS) [Determination of sodium, potassium, calcium and magnesium in fruit and vegetable juices - atomic absorption spectrometry (AAS)]