

**Proficiency Tests**

**DLA**

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cosmetics  
consumer goods  
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**Evaluation Report**

proficiency test

**DLA 57/2018**

**Children's Product I:**

**PAH in Plastic Toy**

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

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<i>Vertraulichkeit</i> <i>Confidentiality</i>	<p>Die Teilnehmerergebnisse sind im EP-Bericht in anonymisierter Form mit Auswertenummern benannt. Daten einzelner Teilnehmer werden ausschließlich nach vorheriger Zustimmung des Teilnehmers an Dritte weitergegeben.  Participant result are named anonymously with evaluation numbers in the PT report. Data of individual participants will be passed on to third parties only with prior consent of the participant.</p>

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## 1. Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the verification and/or validation of the particular testing method [1, 5].

The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.

Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009 / ISO 13528:2015 [2, 3].

## 2. Realisation

### 2.1 Test material

The test material is a mixture of two different plastics. The base used was black plastic granules. The granules were further crushed and then sieved (mesh 1.8 x 20 mm). The second plastic used was a black rubber with known content of polycyclic aromatic hydrocarbons (PAH). The rubber was cut by hand into pieces about 1 to 2 mm wide and 2 to 3 mm long.

For the first set of samples (batch 1), both raw materials were mixed and homogenized.

Afterwards the samples were portioned to approximately 3 g into 28 ml plastic containers and packed in film bags.

For the second sample batch (batch 2), a defined quantity of each of the two plastics was weighed into each individual 28 mL plastic container and packed in film bags.

**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 of the bottled DLA-Samples** was examined 5-fold by photometric determination as total sum parameter. The repeatability standard deviation of 9,5 % can be regarded sufficient. The results of the homogeneity test of batch 2 is given in the documentation.

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

Experience with DLA reference materials and comparable raw materials shows a good storage stability of the material and the content of parameters. 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 (batch 1) were sent to every participating laboratory in the 35<sup>th</sup> week of 2018. In the 40<sup>th</sup> week of 2018 an additional sample (batch 2) was sent.

For determination of PAH the method of the Product Safety Commission of the Federal Institute for Occupational Safety and Health (AfPS 2014: 01 PAK) should be applied or an equivalent method. The tests should be finished at 26<sup>th</sup> November 2018 (extended deadline) the latest.

With the first cover letter along with the sample shipment (batch 1) the following information was given to participants:

*The two portions contain identical samples of a mixture of plastic and rubber parts of toys with the parameters Polycyclic Aromatic Hydrocarbons (PAH) to be determined, as individual compounds as well as the sums of 18 PAH and 7 PAH. The contents are predominantly in the range of the maximum permitted levels (AfPS). The samples are provided in crushed form of max. 2-3 mm sized particles.*

*We recommend thorough mixing of the whole sample amount before analysis.*

With the second sample cover letter (batch 2) the participants were given i.a. information below:

*The enclosed additional sample is a second bottling (Batch 2) with basically the same composition as before. But the two different plastic materials were separately filled directly in each sample container.*

Important Note: Before analysis the whole sample must be thoroughly mixed or the whole amount must be taken for extraction.

***Please note the attached information on the proficiency test.***

(see documentation, section 5.4 Information on the PT)

Due to inquiries, the participants were given the following recommendation for sample preparation of batch 2 by e-mail:

*We recommend preferably the extraction of the whole sample amount of approx. 3 g with 20 ml toluene and further analysis according to the method instructions. The concentration will be higher, but before determination it can be e.g. diluted 1:6.*

*The sample contains about 10% of PAH containing plastic, therefore 20 ml are sufficient for extraction.*

### 2.3 Submission of results

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

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.

Out of 18 participants, 17 participants submitted their results in time. One registration was canceled after sample shipment.

### 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:  $\Delta \text{median} - \text{rob. mean} > 0,3 \sigma_{pt}$ ) [3].

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

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

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

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

#### 3.2 Robust standard deviation

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

#### 3.3 Repeatability standard deviation

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

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

The relative repeatability standard deviation as a percentage of the mean value is indicated as coefficient of variation  $CV_r$  in the table of stat-



istical 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  $\sigma_{pt}$  (= standard deviation for proficiency assessment) can be determined according to the following methods.

If an acceptable quotient  $S^*/\sigma_{pt}$  is present, the target standard deviation of the general model by Horwitz is preferably used for the proficiency assessment. It is usually suitable for evaluation of interlaboratory studies, where different methods are applied by the participants. On the other hand the target standard deviation from the evaluation of precision data of an precision experiment is derived from collaborative studies with specified analytical methods.

In cases where both above-mentioned models are not suitable, the target standard deviation is determined based on values by perception, see under 3.6.3.

For information, the z-scores of both models are given in the evaluation, if available.

***For valuation of all parameters in the present PT the target standard deviation according to the general model of Horwitz was applied (see 3.6.1). Additionally for all parameters the standard uncertainty was considered by evaluation using z'-scores (see 3.6.8).***

For information besides z'-scores the z-scores were also given in the evaluation part.

### 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  $\sigma_R$  [6]. Later the model was modified by Thompson for certain concentration ranges [10]. The reproducibility standard deviation  $\sigma_R$  can be applied as the relative target standard deviation  $\sigma_{pt}$  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  $c$ .

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

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

### 3.6.2 Value by precision experiment

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

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

The determination of PAHs in contact materials is carried out in accordance with the AfPS method for granting of the GS label of product safety. Comparative and repeatability standard deviations are not given there [16].

The relative repeatability standard deviations ( $RSD_r$ ) and relative reproducibility standard deviations ( $RSD_R$ ) given in table 1 were determined in collaborative studies using the specified method for the determination of PAHs in shredder waste [19].

**Table 1:** Relative repeatability standard deviations ( $RSD_r$ ) and relative reproducibility standard deviations ( $RSD_R$ ) from precision experiments and resulting target standard deviations  $\sigma_{pt}$  [19]

Parameter	Matrix	Mean	$RSD_r$	$RSD_R$	$\sigma_{pt}$	Method / Literatur
PAH single	Shredder light fraction	0,247 - 8,84 mg/kg	3,6 - 19,8 %	20,8 - 74,1 %	19,8 - 72,8 %	EN 15527 [19]
Sum 16 PAH	Shredder light fraction	36,5 mg/kg	6,3 %	20,5 %	20,0 %	EN 15527 [19]

### 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 using the z'-scores.

Table 2 shows selected statistic data of participants results of the present PT compared to PT results of previous years.

### Legal regulations and GS examination

Maximum levels for certain PAHs in plastic and rubber parts in consumer products are given in Annex XVII of the REACH Regulation (1906/2006 / EU) as last amended by Regulation EU 1272/2013 [18]. The assessment and evaluation of PAHs in the awarding of the GS lable is carried out according to the method of the Product Safety Committee (AfPS) [18]. There, consumer products are listed in 3 categories, each with its maximum PAHs to be respected [18].

### 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 ( $\sigma_{pt}$ ) the result ( $x_i$ ) of the participant is deviating from the assigned value ( $X_{pt}$ ) [3].

Participants' z-scores are derived from:

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

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

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

The valid z-Score for each parameter is indicated as z-Score ( $\sigma_{pt}$ ). The value indicated as z-Score (Info) only obtains a informative character. The both z-Scores were calculated with the different target standard deviations in accordance with 3.6.

**Table 2:** Characteristics of the present PT (on dark grey) in comparison to a previous PT 2016 (SD = standard deviation, CV = coefficient of variation)

<b>Parameter</b>	<b>Matrix</b>	<b>robust Mean [mg/kg]</b>	<b>rob. SD (S*) [mg/kg]</b>	<b>rel. SD (VK<sub>S*</sub>) [%]</b>	<b>Quotient S*/σ<sub>pt'</sub></b>	<b>DLA-Report</b>
Naphthalene	Plastics	0,489	0,0969	34,3 %	1,9	DLA 73/2016
Naphthalene	Plastics	0,178	0,168	54,5 %	1,7 <sup>1</sup>	DLA 57/2018
Acenaphthylene	Plastics	0,240	0,0808	33,7 %	1,7	DLA 73/2016
Acenaphthylene	Plastics	0,0831	0,0444	53,4 %	1,4 <sup>1</sup>	DLA 57/2018
Acenaphthene	Plastics	0,338	0,126	37,4 %	2,0	DLA 73/2016
Acenaphthene	Plastics	0,361	0,0927	25,7 %	1,2 <sup>1</sup>	DLA 57/2018
Fluorene	Plastics	1,96	0,733	37,5 %	1,9 <sup>1</sup>	DLA 73/2016
Fluorene	Plastics	3,22	0,753	23,4 %	1,5 <sup>1</sup>	DLA 57/2018
Phenanthrene	Plastics	11,1	1,56	14,1 %	1,3	DLA 73/2016
Phenanthrene	Plastics	25,6	5,24	20,5 %	1,7 <sup>1</sup>	DLA 57/2018
Anthracene	Plastics	3,61	0,825	22,9 %	1,7	DLA 73/2016
Anthracene	Plastics	8,70	2,63	30,2 %	1,3 <sup>1</sup>	DLA 57/2018
Fluoranthene	Plastics	6,25	1,08	17,3 %	1,4	DLA 73/2016
Fluoranthene	Plastics	12,6	2,22	17,7 %	1,4 <sup>1</sup>	DLA 57/2018
Pyrene	Plastics	6,34	1,36	21,4 %	1,8	DLA 73/2016
Pyrene	Plastics	11,0	1,83	16,6 %	1,3 <sup>1</sup>	DLA 57/2018
Chrysene	Plastics	1,95	0,518	26,5 %	1,8	DLA 73/2016
Chrysene	Plastics	10,6	3,24	30,7 %	2,1 <sup>1</sup>	DLA 57/2018
Benzo[a]anthracene	Plastics	2,06	0,507	24,6 %	1,7	DLA 73/2016
Benzo[a]anthracene	Plastics	8,57	2,00	23,4 %	1,7 <sup>1</sup>	DLA 57/2018
Benzo[b]fluoranthene	Plastics	0,812	0,350	43,1 %	1,8 <sup>1</sup>	DLA 73/2016
Benzo[b]fluoranthene	Plastics	2,09	0,881	42,1 %	2,1 <sup>1</sup>	DLA 57/2018
Benzo[k]fluoranthene	Plastics	0,385	0,185	48,1 %	1,9 <sup>1</sup>	DLA 73/2016
Benzo[k]fluoranthene	Plastics	0,867	0,172	19,8 %	1,1 <sup>1</sup>	DLA 57/2018
Benzo[j]fluoranthene	Plastics	0,270	0,121	44,6 %	1,6 <sup>1</sup>	DLA 73/2016
Benzo[j]fluoranthene	Plastics	0,775	0,220	28,4 %	1,4 <sup>1</sup>	DLA 57/2018

*Continuation of the table on next page*

Parameter	Matrix	robust Mean [mg/kg]	rob. SD (S*) [mg/kg]	rel. SD (VK <sub>S*</sub> ) [%]	Quotient S*/ $\sigma_{pt}^1$	DLA-Report
Benzo[a]pyrene	Plastics	0,785	0,324	41,3 %	1,9 <sup>1</sup>	DLA 73/2016
Benzo[a]pyrene	Plastics	3,73	0,710	19,0 %	1,3 <sup>1</sup>	DLA 57/2018
Benzo[e]pyrene	Plastics	0,629	0,226	36,0 %	1,6 <sup>1</sup>	DLA 73/2016
Benzo[e]pyrene	Plastics	3,56	0,916	25,7 %	1,6 <sup>1</sup>	DLA 57/2018
Indeno[1,2,3-cd]pyrene	Plastics	0,290	0,131	45,1 %	1,8 <sup>1</sup>	DLA 73/2016
Indeno[1,2,3-cd]pyrene	Plastics	0,872	0,338	38,7 %	1,9 <sup>1</sup>	DLA 57/2018
Dibenzo[ah]anthracene	Plastics	0,176	0,0894	50,7 %	**	DLA 73/2016
Dibenzo[ah]anthracene	Plastics	0,554	0,246	44,5 %	2,0 <sup>1</sup>	DLA 57/2018
Benzo[ghi]perylene	Plastics	0,596	0,230	38,6 %	1,8 <sup>1</sup>	DLA 73/2016
Benzo[ghi]perylene	Plastics	1,30	0,365	28,0 %	1,6 <sup>1</sup>	DLA 57/2018
Sum 7 PAH	Plastics	30,2	3,89	12,9 %	1,3	DLA 73/2016
Sum 7 PAH	Plastics	61,9	12,0	19,5 %	1,8 <sup>1</sup>	DLA 57/2018
Sum 18 PAH	Plastics	38,3	4,54	11,8 %	1,3	DLA 73/2016
Sum 18 PAH	Plastics	95,5	15,7	16,4 %	1,7 <sup>1</sup>	DLA 57/2018

<sup>1</sup> with target standard deviation  $\sigma_{pt}$

\*\* no statistical valuation (< 7 results)

### 3.7.1 Warning and action signals

In accordance with the norm ISO 13528 it is recommended that a result that gives rise to a z-score above 3,0 or below -3,0, shall be considered to give an "action signal" [3]. Likewise, a z-score above 2,0 or below -2,0 shall be considered to give a "warning signal". A single "action signal", or "warning signal" in two successive PT-rounds, shall be taken as evidence that an anomaly has occurred which requires investigation. For example a fault isolation or a root cause analysis through the examination of transmission error or an error in the calculation, in the trueness and precision must be performed and if necessary appropriate corrective measures should be applied [3].

In the figures of z-scores DLA gives the limits of warning and action signals as yellow and red lines respectively. According to ISO 13528 the signals are valid only in case of a number of  $\geq 10$  results [3].

### 3.8 z'-Score

The z'-score can be used for the valuation of the results of the participants, in cases the standard uncertainty has to be considered (s. 3.8). The z'-score represents the relation of the deviation of the result (x) of the participant from the respective consensus value (X) to the square root of quadrat sum of the target standard deviation ( $\sigma_{pt}$ ) and the standard uncertainty ( $U_{x_{pt}}$ ) [3].

The calculation is performed by:

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

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

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

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

For warning and action signals see 3.7.1.

### 3.9 Reproducibility coefficient of variation (CV<sub>R</sub>)

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 $S^*/\sigma_{pt}$

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

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

If  $U_{(x_{pt})} \leq 0,3 \sigma_{pt}$  the standard uncertainty of the 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

The participant's results of the first sample set (batch 1) showed higher deviations between sample I and II in about 1/3 of the cases. The reason for this was probably the different nature of the plastics contained, which can lead to segregation.

Therefore only the results of batch 2 were evaluated statistically and given in the documentation.

### Comments to the distribution of the results:

The kernel density plots showed for all parameters nearly a symmetrical distribution of results (figures see documentation 5.3). Partly slight shoulders and separated smaller peaks can be seen, which are due to individual results, outliers or values outside the target range. In the case of chrysene and benzo[a]anthracene, a distribution of the results with two peaks is visible. However, the participants' notes on the methods do not give any obvious indications of such a grouping of the results. The distributions, when using the robust standard deviation as estimator  $h$ , are converted into one peak distributions, thus the evaluation has been carried out.

### Comments to the statistic data:

For acenaphthylene there were  $< 7$  results. Nevertheless a statistical evaluation was done, because the statistic characteristics showed a sufficient comparability of results.

For all parameters the target standard deviation was calculated according to the general model of Horwitz.

Because the quotients  $S^*/\sigma_{pt}$  were in part clearly above 2,0, it was evaluated considering the standard uncertainty by  $z'$ -scores. The quotients  $S^*/\sigma_{pt}'$  were then in the range of 2,0 (see table 2).

The robust standard deviations are in the range of the values of the previous PT in 2016 and are comparable to usual values for the applied determination methods (s. 3.6.3) [19].

The comparability of results is given.

71% to 100% of results were in the respective 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:

<b>Statistic Data</b>
<i>Number of results</i>
<i>Number of outliers</i>
Mean
Median
Robust mean ( $X_{pt}$ )
Robust standard deviation ( $S^*$ )
<i>Target range:</i>
Target standard deviation $\sigma_{pt}$ or $\sigma_{pt}'$
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 $(X_{pt} + 2\sigma_{pt}')$ *
<i>Quotient <math>S^*/\sigma_{pt}</math> or <math>S^*/\sigma_{pt}'</math></i>
<i>Standard uncertainty <math>U(X_{pt})</math></i>
<i>Number of results in the target range</i>
<i>Percent in the target range</i>

\* 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\*\*:

<b>Auswertenummer</b>	<b>Parameter [Einheit / Unit]</b>	<b>Abweichung</b>	<b>z-Score</b>	<b>z-Score</b>	<b>Hinweis</b>
<b>Evaluation number</b>		<b>Deviation</b>	<b><math>\sigma_{pt}</math></b>	<b>(Info)</b>	<b>Remark</b>

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

## 4.1 Naphthalene in mg/kg

### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	-
Mean	0,187
Median	0,175
<b>Robust Mean (X)</b>	<b>0,178</b>
<b>Robust standard deviation (S*)</b>	<b>0,0969</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>0,0565</b>
Target standard deviation (for Information)	0,0369
<b>lower limit of target range</b>	<b>0,0647</b>
<b>upper limit of target range</b>	<b>0,291</b>
Quotient $S^*/\sigma_{pt}'$	1,71
Standard uncertainty $U(x_{pt})$	0,0428
Results in the target range	6
Percent in the target range	75%

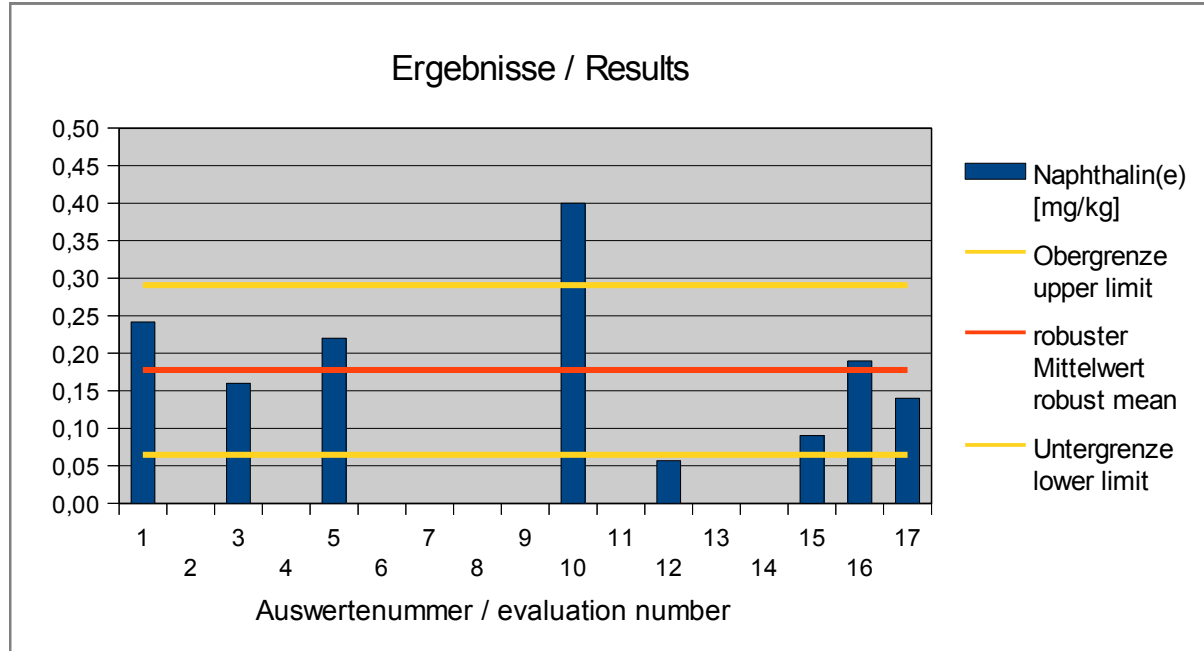
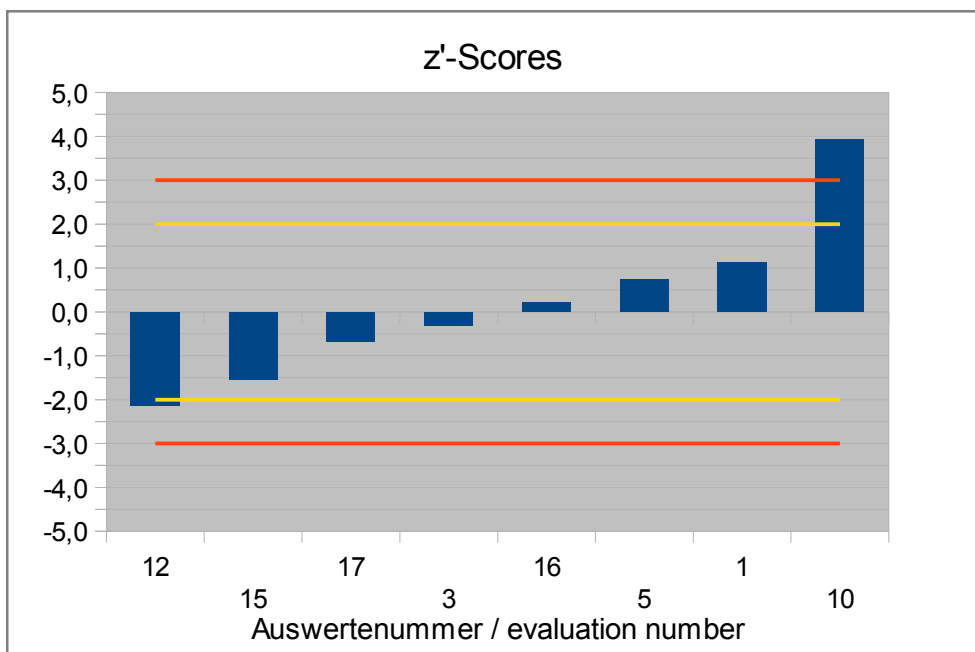


Abb. / Fig. 1: Ergebnisse Naphthalin / Results Naphthalene

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

Auswertenummer Evaluation number	Naphthalin / Naphthalene [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	0,242	0,0640	1,1	1,7	
2	< 0,2				
3	0,160	-0,0178	-0,31	-0,48	
4	< 0,2				
5	0,220	0,0422	0,75	1,1	
6	nd				
7	< 0,20				
8					
9					
10	0,400	0,2222	3,9	6,0	
11	< 0,1				
12	0,057	-0,1208	-2,1	-3,3	
13	< 0,2				
14	< 0,2				
15	0,090	-0,0874	-1,5	-2,4	
16	0,190	0,0122	0,22	0,33	
17	0,140	-0,0378	-0,67	-1,0	



**Abb. / Fig. 2:** Z'-Scores Naphthalin / Naphthalene

## 4.2 Acenaphtylen(e) in mg/kg

### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	0,0831
Median	0,0610
<b>Robust Mean (X)</b>	<b>0,0831</b>
<b>Robust standard deviation (S*)</b>	<b>0,0444</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>0,0315</b>
Target standard deviation (for Information)	0,0193
<b>lower limit of target range</b>	<b>0,0202</b>
<b>upper limit of target range</b>	<b>0,146</b>
<i>Quotient <math>S^*/\sigma_{pt}'</math></i>	<i>1,4</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>0,0248</i>
Results in the target range	5
Percent in the target range	100%

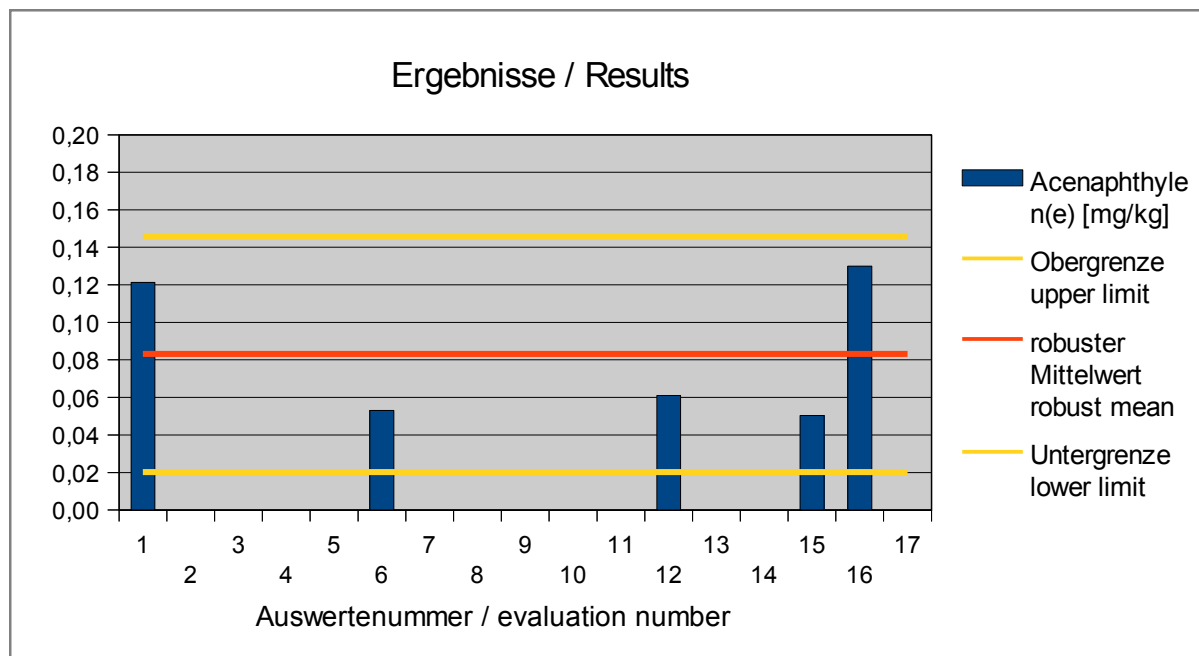
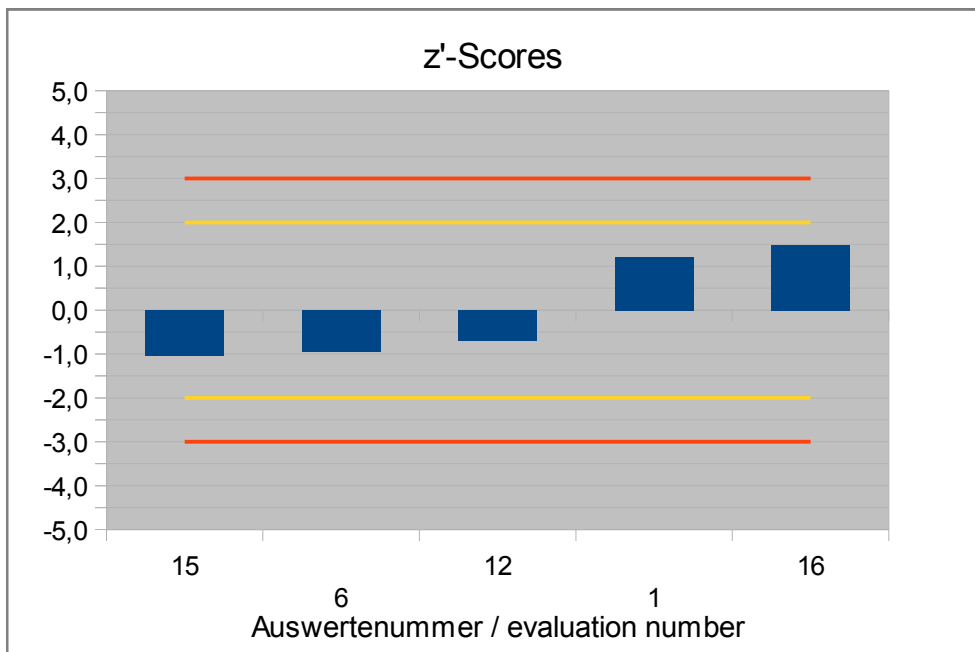


Abb. / Fig. 3: Ergebnisse Acenaphtylen / Results Acenaphtylene

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

Auswertenummer	Acenaphtylen(e) [mg/kg]	Abweichung [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis
Evaluation number	[mg/kg]	Deviation [mg/kg]			Remark
1	0,121	0,038	1,2	2,0	
2	<0,2				
3	<0,1				
4	<0,2				
5	<0,2				
6	0,053	-0,030	-1,0	-1,6	
7	< 0,20				
8					
9					
10	<0,2				
11	< 0,1				
12	0,061	-0,022	-0,70	-1,1	
13	<0,2				
14	<0,2				
15	0,050	-0,033	-1,0	-1,7	
16	0,130	0,047	1,5	2,4	
17	<0,1				



**Abb. / Fig. 4:** z'-Scores Acenaphtylen / Acenaphtylene

### 4.3 Acenaphthen(e) in mg/kg

#### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results <sup>°</sup>	12
Number of outliers	1
Mean	0,381
Median	0,373
<b>Robust Mean (X)</b>	<b>0,361</b>
<b>Robust standard deviation (S*)</b>	<b>0,0927</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>0,0751</b>
Target standard deviation (for Information)	0,0673
<b>lower limit of target range</b>	<b>0,210</b>
<b>upper limit of target range</b>	<b>0,511</b>
Quotient $S^*/\sigma_{pt}'$	1,2
Standard uncertainty $U(X_{pt})$	0,0334
Results in the target range	11
Percent in the target range	92%

<sup>°</sup> without outliers (result no. 3)

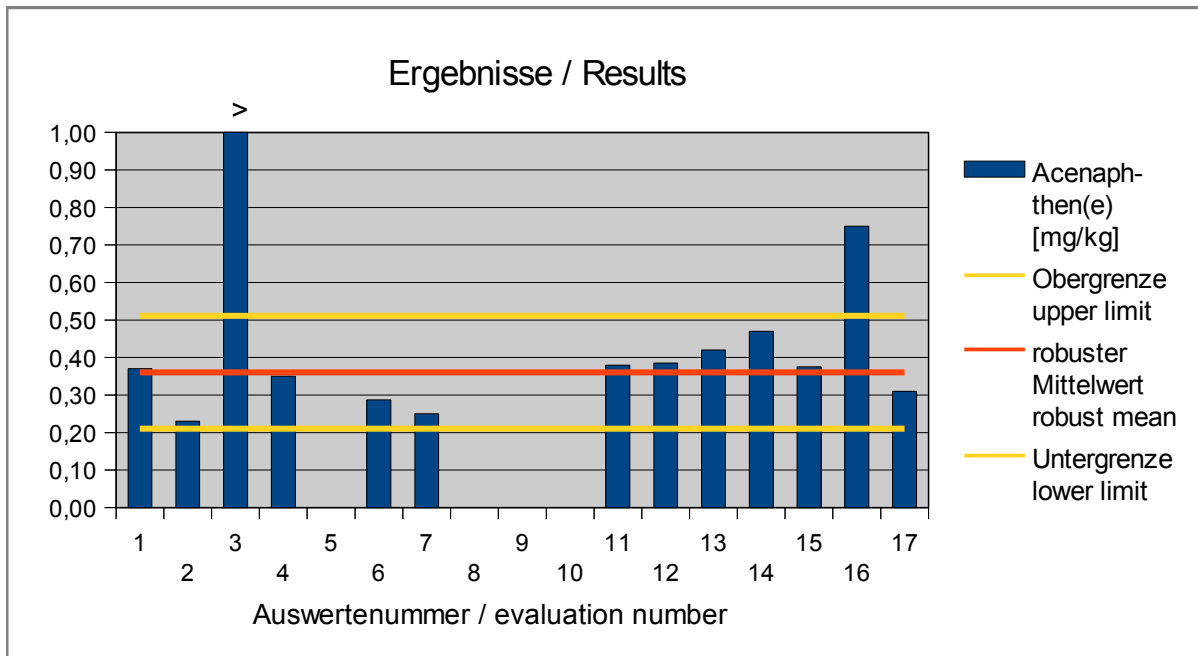
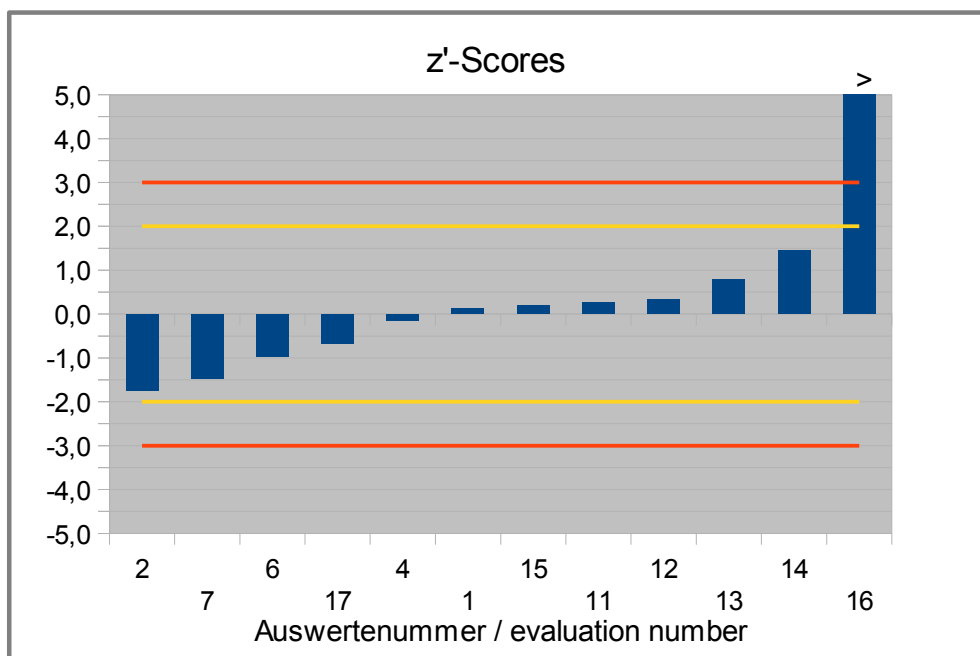


Abb. / Fig. 5: Ergebnisse Acenaphthen / Results Acenaphthene



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

Auswertenummer Evaluation number	Acenaphthen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	0,370	0,010	0,13	0,14	
2	0,230	-0,131	-1,7	-1,9	
3	3,45				Ausreißer ausgeschlossen / Outlier excluded
4	0,350	-0,011	-0,14	-0,16	
5					
6	0,287	-0,074	-1,0	-1,1	
7	0,250	-0,111	-1,5	-1,6	
8					
9					
10					
11	0,380	0,019	0,26	0,29	
12	0,385	0,024	0,33	0,36	
13	0,420	0,059	0,79	0,88	
14	0,470	0,109	1,46	1,63	
15	0,375	0,015	0,19	0,22	
16	0,750	0,389	5,2	5,8	
17	0,310	-0,051	-0,67	-0,75	

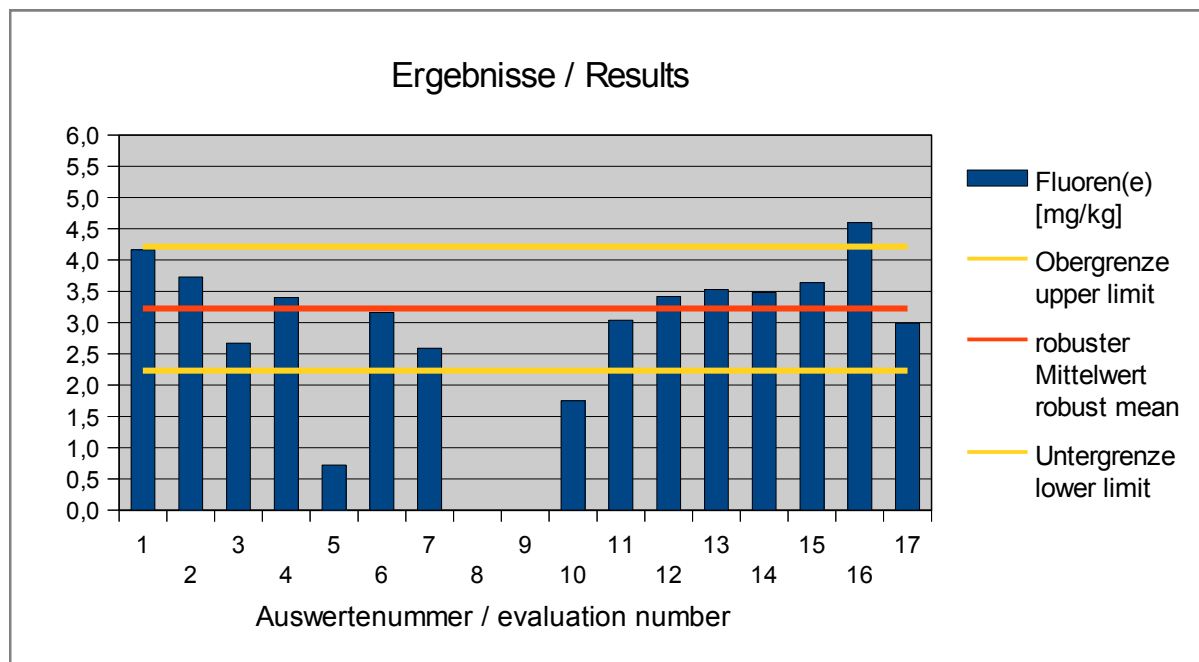


**Abb. / Fig. 6:** z'-Scores Acenaphthen / Acenaphthene

**4.4 Fluoren(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

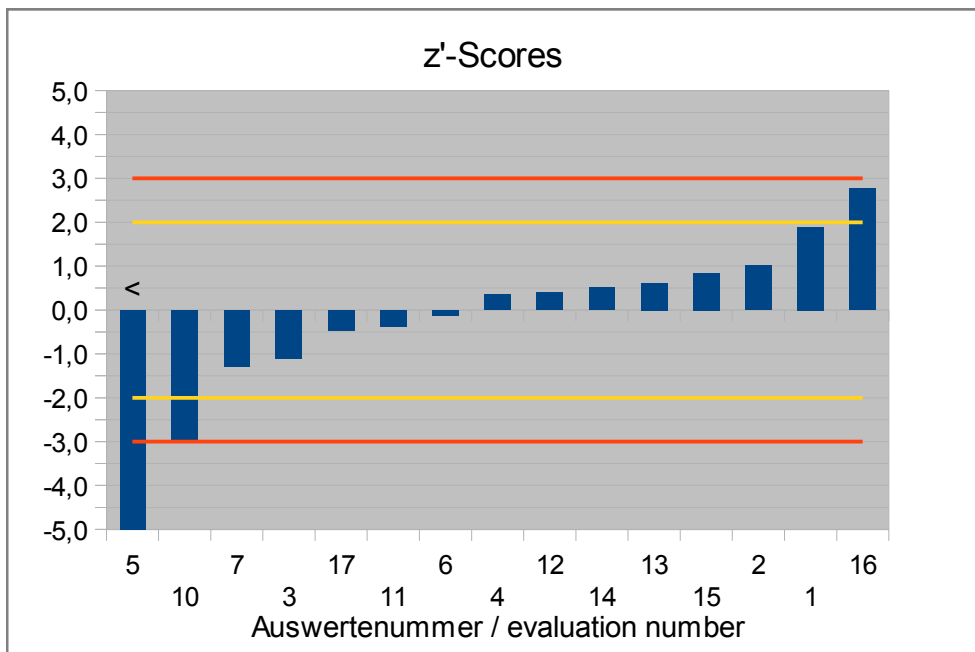
<b>Statistic Data</b>	
Number of results	15
Number of outliers	-
Mean	3,13
Median	3,40
<b>Robust Mean (X)</b>	<b>3,22</b>
<b>Robust standard deviation (S*)</b>	<b>0,753</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}</math></b>	<b>0,496</b>
Target standard deviation (for Information)	0,432
<b>lower limit of target range</b>	<b>2,23</b>
<b>upper limit of target range</b>	<b>4,22</b>
<i>Quotient <math>S^*/\sigma_{pt}</math></i>	<i>1,5</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>0,243</i>
<i>Results in the target range</i>	<i>12</i>
<i>Percent in the target range</i>	<i>80%</i>



**Abb. / Fig. 7:** Ergebnisse Fluoren / Results Fluorene

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

Auswertenummer Evaluation number	Fluoren(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	4,16	0,940	1,9	2,2	
2	3,73	0,506	1,0	1,2	
3	2,67	-0,554	-1,1	-1,3	
4	3,40	0,176	0,36	0,41	
5	0,72	-2,50	-5,0	-5,8	
6	3,16	-0,064	-0,13	-0,15	
7	2,59	-0,634	-1,3	-1,5	
8					
9					
10	1,75	-1,474	-3,0	-3,4	
11	3,04	-0,184	-0,37	-0,43	
12	3,42	0,196	0,40	0,45	
13	3,53	0,306	0,62	0,71	
14	3,48	0,256	0,52	0,59	
15	3,64	0,417	0,84	1,0	
16	4,60	1,38	2,8	3,2	
17	2,99	-0,234	-0,47	-0,54	

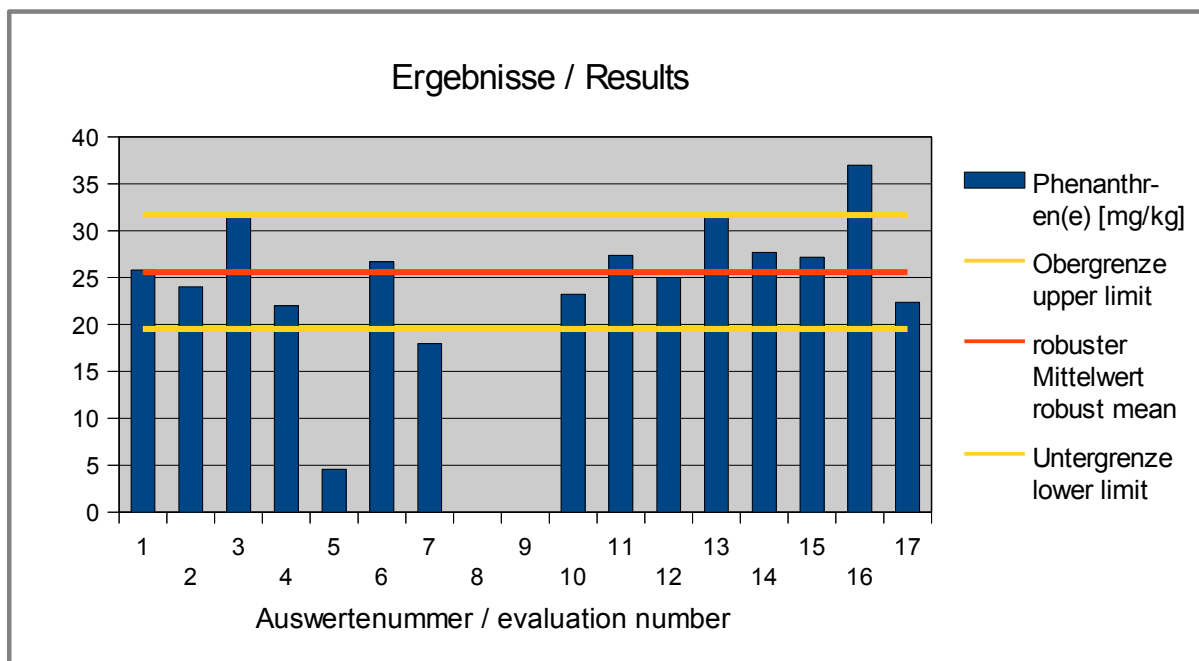


**Abb. / Fig. 8:** Z'-Scores Fluoren / Fluorene

**4.5 Phenanthren(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

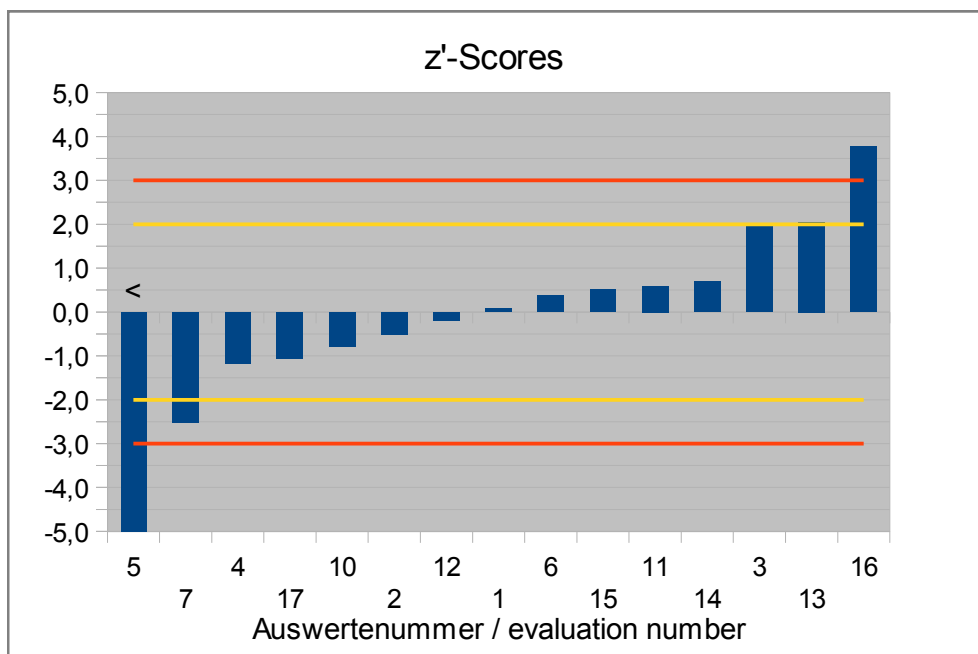
Statistic Data	
Number of results	15
Number of outliers	-
Mean	24,9
Median	25,8
<b>Robust Mean (X)</b>	<b>25,6</b>
<b>Robust standard deviation (S*)</b>	<b>5,24</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>3,03</b>
Target standard deviation (for Information)	2,51
<b>lower limit of target range</b>	<b>19,5</b>
<b>upper limit of target range</b>	<b>31,7</b>
<i>Quotient <math>S^*/\sigma_{pt}'</math></i>	<i>1,7</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>1,69</i>
<i>Results in the target range</i>	<i>11</i>
<i>Percent in the target range</i>	<i>73%</i>



**Abb. / Fig. 9:** Ergebnisse Phenanthren / Results Phenanthrene

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

Auswertenummer Evaluation number	Phenanthren(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	25,81	0,224	0,1	0,1	
2	24,01	-1,581	-0,5	-0,6	
3	31,55	5,959	2,0	2,4	
4	22,00	-3,591	-1,2	-1,4	
5	4,57	-21,02	-6,9	-8,4	
6	26,70	1,109	0,4	0,4	
7	17,96	-7,631	-2,5	-3,0	
8					
9					
10	23,22	-2,371	-0,8	-0,9	
11	27,38	1,789	0,6	0,7	
12	25,00	-0,591	-0,2	-0,2	
13	31,81	6,219	2,1	2,5	
14	27,70	2,109	0,7	0,8	
15	27,17	1,583	0,5	0,6	
16	37,00	11,41	3,8	4,5	
17	22,36	-3,231	-1,1	-1,3	

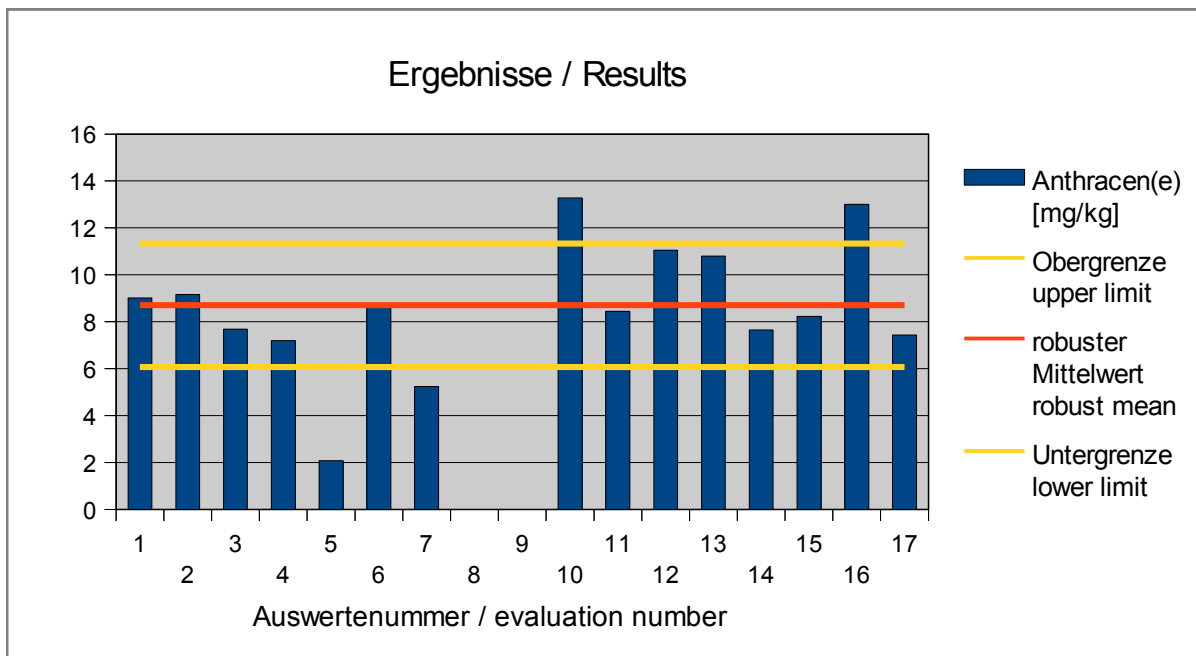


**Abb. / Fig. 10:** Z'-Scores Phenanthren / Phenanthrene

**4.6 Anthracen(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

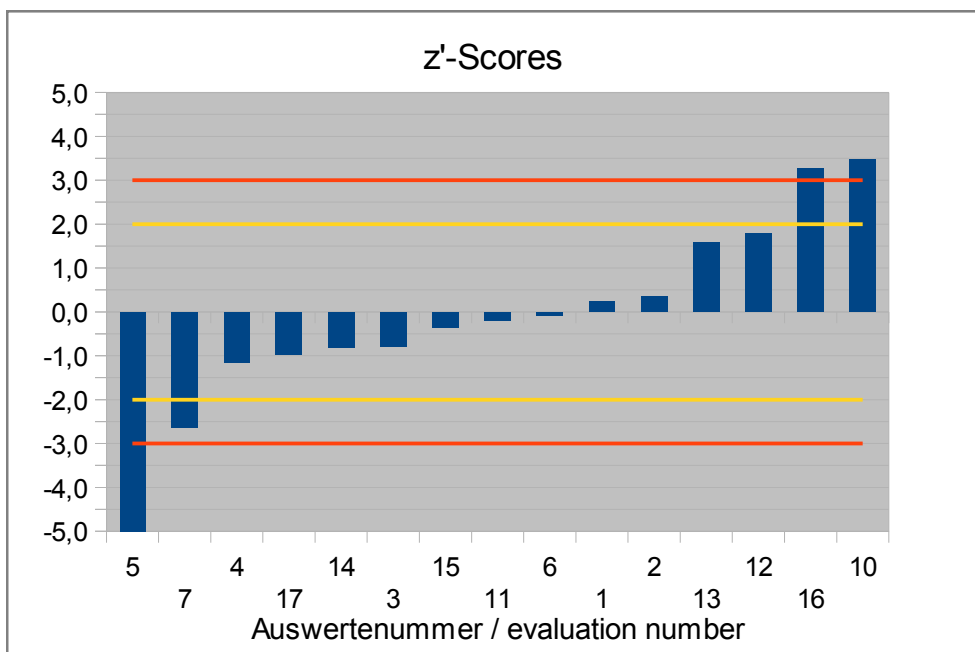
Statistic Data	
Number of results	15
Number of outliers	-
Mean	8,59
Median	8,45
<b>Robust Mean (X)</b>	<b>8,70</b>
<b>Robust standard deviation (S*)</b>	<b>2,63</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>1,31</b>
Target standard deviation (for Information)	1,01
<b>lower limit of target range</b>	<b>6,07</b>
<b>upper limit of target range</b>	<b>11,3</b>
<i>Quotient <math>S^*/\sigma_{pt}'</math></i>	<i>2,0</i>
<i>Standard uncertainty <math>U(X_{pt})</math></i>	<i>0,85</i>
<i>Results in the target range</i>	<i>11</i>
<i>Percent in the target range</i>	<i>73%</i>



**Abb. / Fig. 11:** Ergebnisse Anthracen / Results Anthracene

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

Auswertenummer Evaluation number	Anthracen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ <sub>pt</sub> )	z-Score (Info)	Hinweis Remark
1	9,01	0,306	0,23	0,30	
2	9,16	0,456	0,35	0,45	
3	7,68	-1,02	-0,78	-1,0	
4	7,20	-1,50	-1,1	-1,5	
5	2,08	-6,62	-5,0	-6,6	
6	8,60	-0,104	-0,08	-0,10	
7	5,24	-3,46	-2,6	-3,4	
8					
9					
10	13,3	4,58	3,5	4,6	
11	8,45	-0,254	-0,19	-0,25	
12	11,1	2,35	1,8	2,3	
13	10,8	2,10	1,6	2,1	
14	7,65	-1,05	-0,80	-1,0	
15	8,24	-0,469	-0,36	-0,47	
16	13,0	4,30	3,3	4,3	
17	7,44	-1,26	-1,0	-1,3	



**Abb. / Fig. 12:** Z'-Scores Anthracen / Anthracene

**4.7 Fluoranthen(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Statistic Data	
Number of results	15
Number of outliers	-
Mean	12,3
Median	12,7
<b>Robust Mean (X)</b>	<b>12,6</b>
<b>Robust standard deviation (S*)</b>	<b>2,22</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>1,55</b>
Target standard deviation (for Information)	1,37
<b>lower limit of target range</b>	<b>9,47</b>
<b>upper limit of target range</b>	<b>15,7</b>
<i>Quotient <math>S^*/\sigma_{pt}'</math></i>	<i>1,4</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>0,72</i>
<i>Results in the target range</i>	<i>12</i>
<i>Percent in the target range</i>	<i>80%</i>

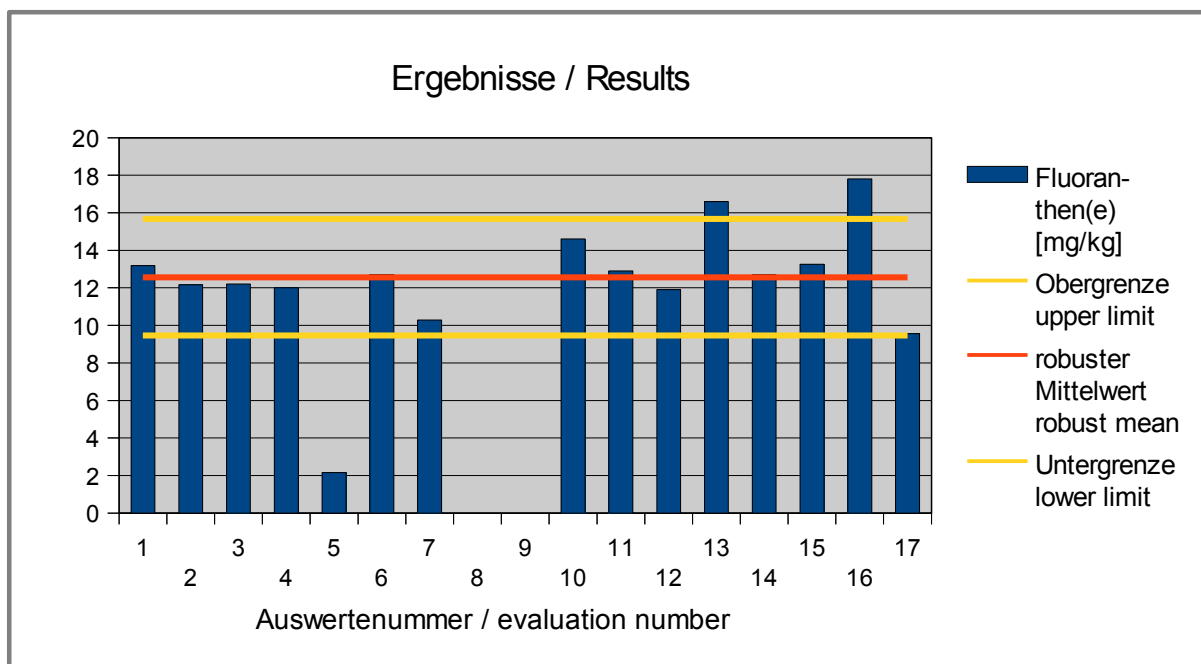
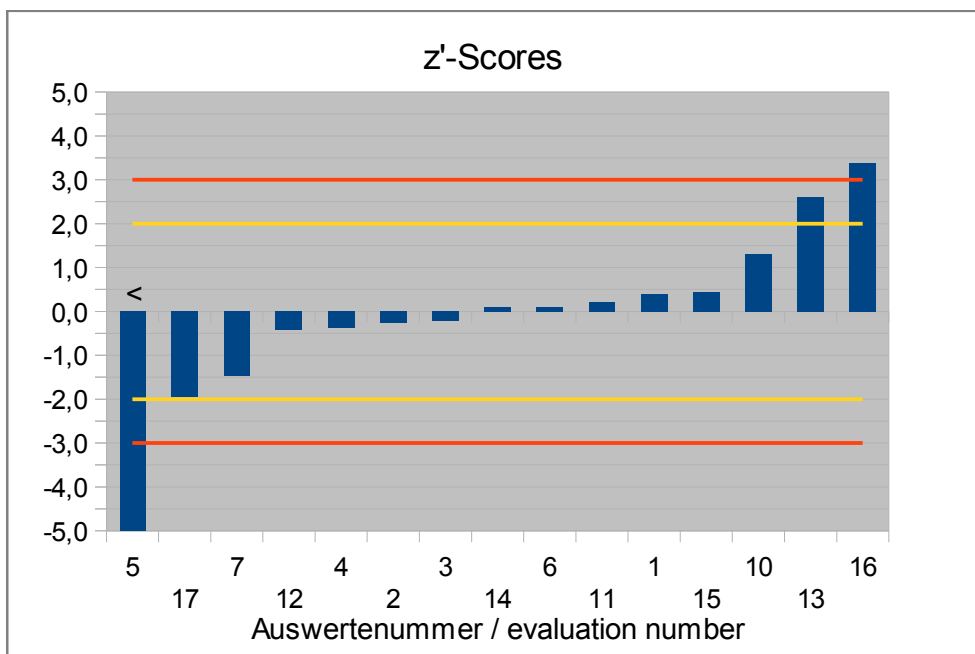


Abb. / Fig. 13: Ergebnisse Fluoranthen / Results Fluoranthene



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

Auswertenummer Evaluation number	Fluoranthen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	13,2	0,61	0,40	0,45	
2	12,2	-0,40	-0,26	-0,29	
3	12,2	-0,35	-0,23	-0,26	
4	12,0	-0,56	-0,36	-0,41	
5	2,16	-10,40	-6,7	-7,6	
6	12,7	0,14	0,09	0,10	
7	10,3	-2,28	-1,5	-1,7	
8					
9					
10	14,6	2,04	1,3	1,5	
11	12,9	0,34	0,22	0,24	
12	11,9	-0,66	-0,43	-0,48	
13	16,6	4,04	2,6	2,9	
14	12,7	0,14	0,09	0,10	
15	13,3	0,69	0,44	0,50	
16	17,8	5,24	3,4	3,8	
17	9,56	-3,00	-1,9	-2,2	

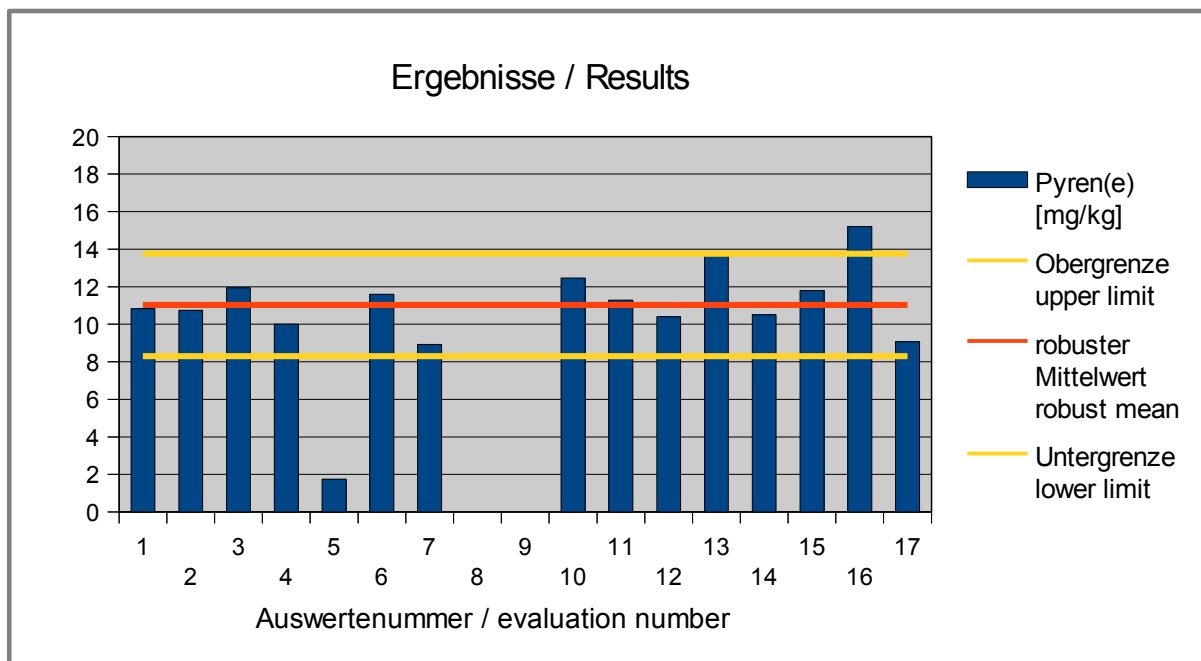


**Abb. / Fig. 14:** Z'-Scores Fluoranthen / Fluoranthene

**4.8 Pyren(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

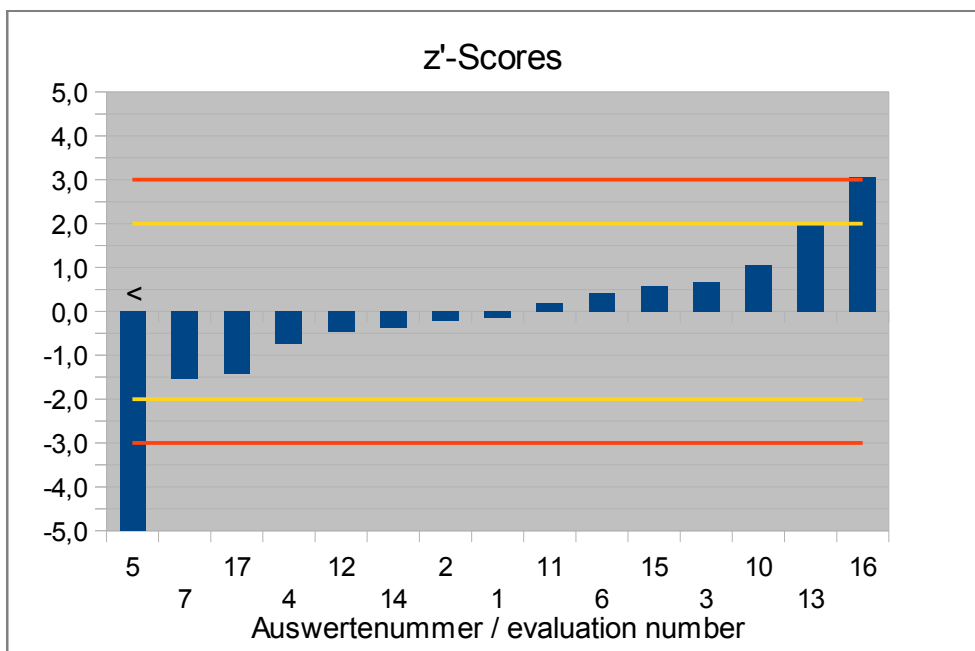
Statistic Data	
Number of results	15
Number of outliers	-
Mean	10,7
Median	10,8
<b>Robust Mean (X)</b>	<b>11,0</b>
<b>Robust standard deviation (S*)</b>	<b>1,83</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>1,36</b>
Target standard deviation (for Information)	1,23
<b>lower limit of target range</b>	<b>8,30</b>
<b>upper limit of target range</b>	<b>13,8</b>
Quotient $S^*/\sigma_{pt}'$	1,3
Standard uncertainty $U(X_{pt})$	0,59
Results in the target range	12
Percent in the target range	80%



**Abb. / Fig. 15:** Ergebnisse Pyren / Results Pyrene

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

Auswertenummer Evaluation number	Pyren(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	10,8	-0,20	-0,15	-0,16	
2	10,7	-0,28	-0,21	-0,23	
3	11,9	0,91	0,66	0,74	
4	10,0	-1,02	-0,75	-0,83	
5	1,75	-9,27	-6,8	-7,5	
6	11,6	0,58	0,42	0,47	
7	8,93	-2,09	-1,5	-1,7	
8					
9					
10	12,5	1,44	1,1	1,2	
11	11,3	0,26	0,19	0,21	
12	10,4	-0,62	-0,46	-0,51	
13	13,8	2,76	2,0	2,2	
14	10,5	-0,52	-0,38	-0,43	
15	11,8	0,77	0,57	0,63	
16	15,2	4,18	3,1	3,4	
17	9,07	-1,95	-1,4	-1,6	



**Abb. / Fig. 16:** z'-Scores Pyren / Pyrene

### 4.9 Chrysen(e) in mg/kg

#### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results <sup>°</sup>	15
Number of outliers	2
Mean	10,6
Median	10,1
<b>Robust Mean (X)</b>	<b>10,6</b>
<b>Robust standard deviation (S*)</b>	<b>3,24</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}</math>'</b>	<b>1,58</b>
Target standard deviation (for Information)	1,19
<b>lower limit of target range</b>	<b>7,40</b>
<b>upper limit of target range</b>	<b>13,7</b>
<i>Quotient <math>S^*/\sigma_{pt}</math>'</i>	<i>2,1</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>1,05</i>
<i>Results in the target range</i>	<i>12</i>
<i>Percent in the target range</i>	<i>80%</i>

<sup>°</sup> without outliers (results no. 5 and 9)

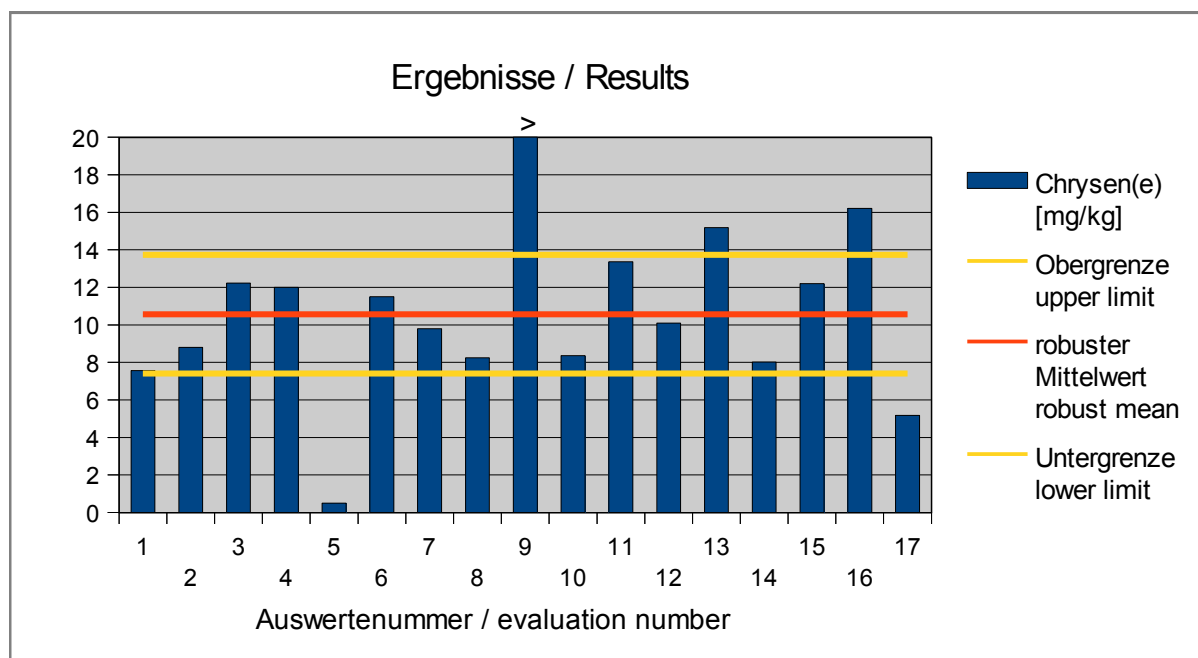
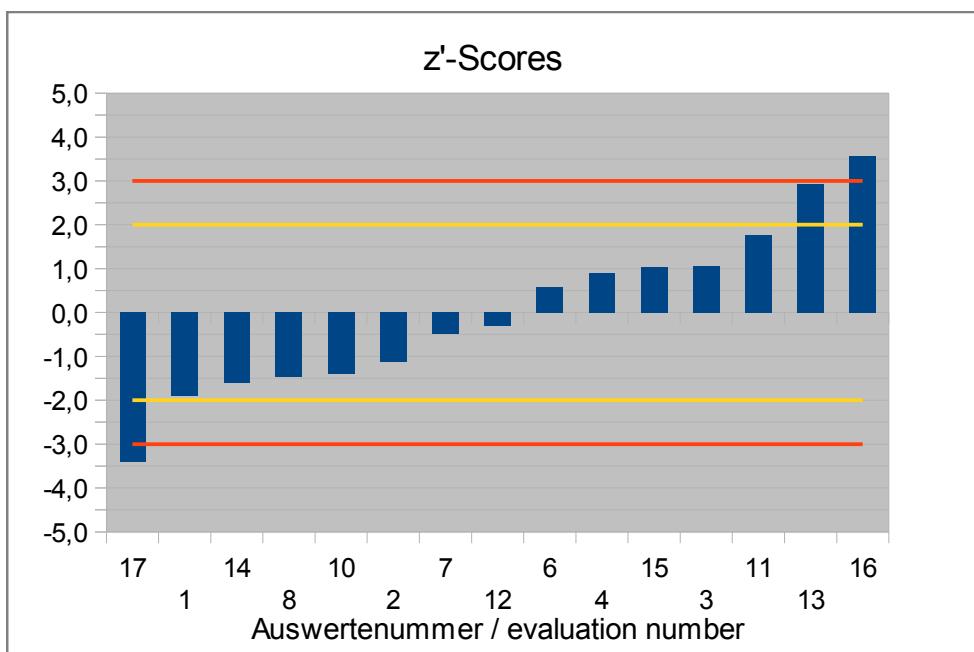


Abb. / Fig. 17: Ergebnisse Chrysen / Results Chrysene

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

Auswertenummer Evaluation number	Chrysen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	7,6	-3,00	-1,90	-2,53	
2	8,8	-1,77	-1,12	-1,49	
3	12,2	1,66	1,05	1,40	
4	12,0	1,43	0,91	1,21	
5	0,500				Ausreißer ausgeschlossen / Outlier excluded
6	11,5	0,93	0,59	0,79	
7	9,80	-0,77	-0,5	-0,6	
8	8,3	-2,32	-1,5	-2,0	
9	100				Ausreißer ausgeschlossen / Outlier excluded
10	8,4	-2,21	-1,4	-1,9	
11	13,4	2,79	1,77	2,35	
12	10,1	-0,47	-0,30	-0,39	
13	15,2	4,62	2,9	3,9	
14	8,0	-2,55	-1,61	-2,15	
15	12,2	1,64	1,04	1,38	
16	16,2	5,63	3,6	4,8	
17	5,18	-5,39	-3,4	-4,5	



**Abb. / Fig. 18:** z'-Scores Chrysen / Chrysene

### 4.10 Benzo[a]anthracen(e) in mg/kg

#### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results <sup>°</sup>	15
Number of outliers	2
Mean	8,57
Median	8,47
<b>Robust Mean (X)</b>	<b>8,57</b>
<b>Robust standard deviation (S*)</b>	<b>2,00</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>1,18</b>
Target standard deviation (for Information)	0,992
<b>lower limit of target range</b>	<b>6,20</b>
<b>upper limit of target range</b>	<b>10,9</b>
Quotient $S^*/\sigma_{pt}'$	1,7
Standard uncertainty $U(X_{pt})$	0,647
Results in the target range	13
Percent in the target range	87%

<sup>°</sup> without outliers (results no. 5 and 9)

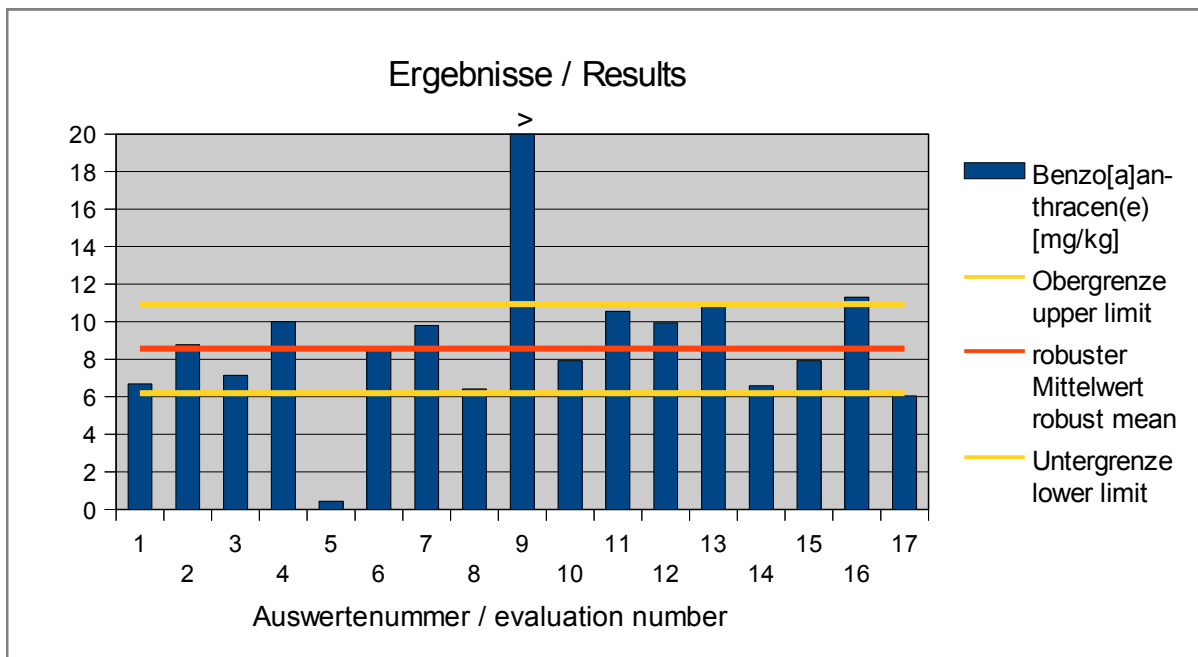
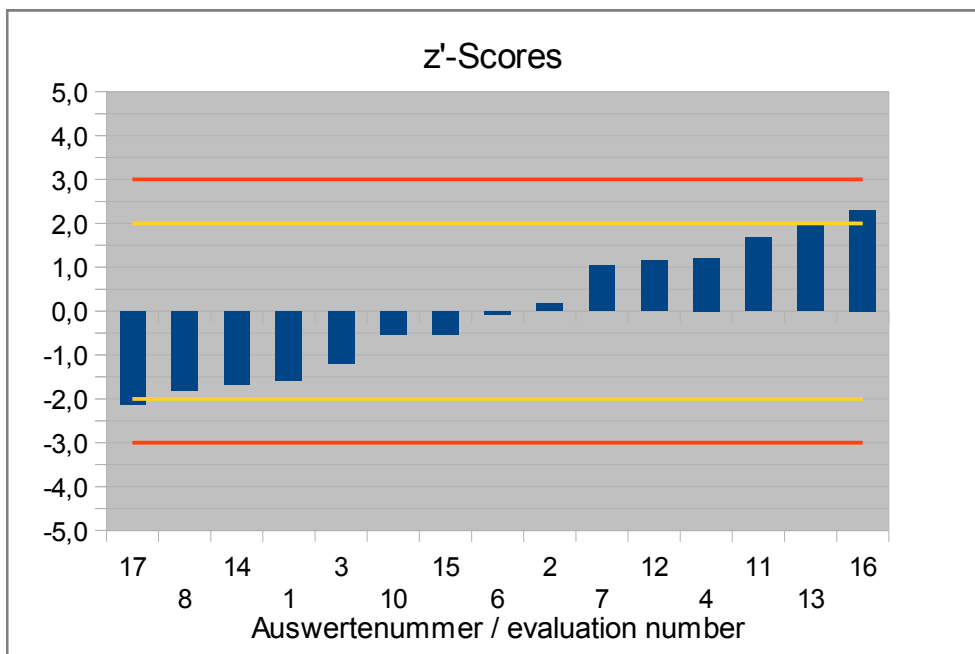


Abb. / Fig. 19: Ergebnisse Benzo[a]anthracen / Results Benzo[a]anthracen(e)

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

Auswertenummer Evaluation number	Benzo[a]anthracen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	6,69	-1,88	-1,6	-1,9	
2	8,77	0,20	0,17	0,21	
3	7,14	-1,43	-1,2	-1,4	
4	10,0	1,43	1,2	1,4	
5	0,430				Ausreißer ausgeschlossen / Outlier excluded
6	8,47	-0,10	-0,08	-0,10	
7	9,80	1,23	1,0	1,2	
8	6,42	-2,15	-1,8	-2,2	
9	58,9				Ausreißer ausgeschlossen / Outlier excluded
10	7,92	-0,65	-0,55	-0,65	
11	10,6	1,99	1,7	2,0	
12	9,94	1,37	1,2	1,4	
13	10,9	2,34	2,0	2,4	
14	6,59	-1,98	-1,7	-2,0	
15	7,92	-0,65	-0,55	-0,65	
16	11,3	2,73	2,3	2,8	
17	6,05	-2,52	-2,1	-2,5	



**Abb. / Fig. 20:** z'-Scores Benzo[a]anthracen / Benzo[a]anthracene

#### 4.11 Benzo[b]fluoranthen(e) in mg/kg

##### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results <sup>°</sup>	14
Number of outliers	1
Mean	2,13
Median	1,98
<b>Robust Mean (X)</b>	<b>2,09</b>
<b>Robust standard deviation (S*)</b>	<b>0,881</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}</math>'</b>	<b>0,420</b>
Target standard deviation (for Information)	0,300
<b>lower limit of target range</b>	<b>1,25</b>
<b>upper limit of target range</b>	<b>2,93</b>
Quotient $S^*/\sigma_{pt}'$	2,1
Standard uncertainty $U(X_{pt})$	0,29
Results in the target range	10
Percent in the target range	71%

<sup>°</sup> without outliers (result no. 9)

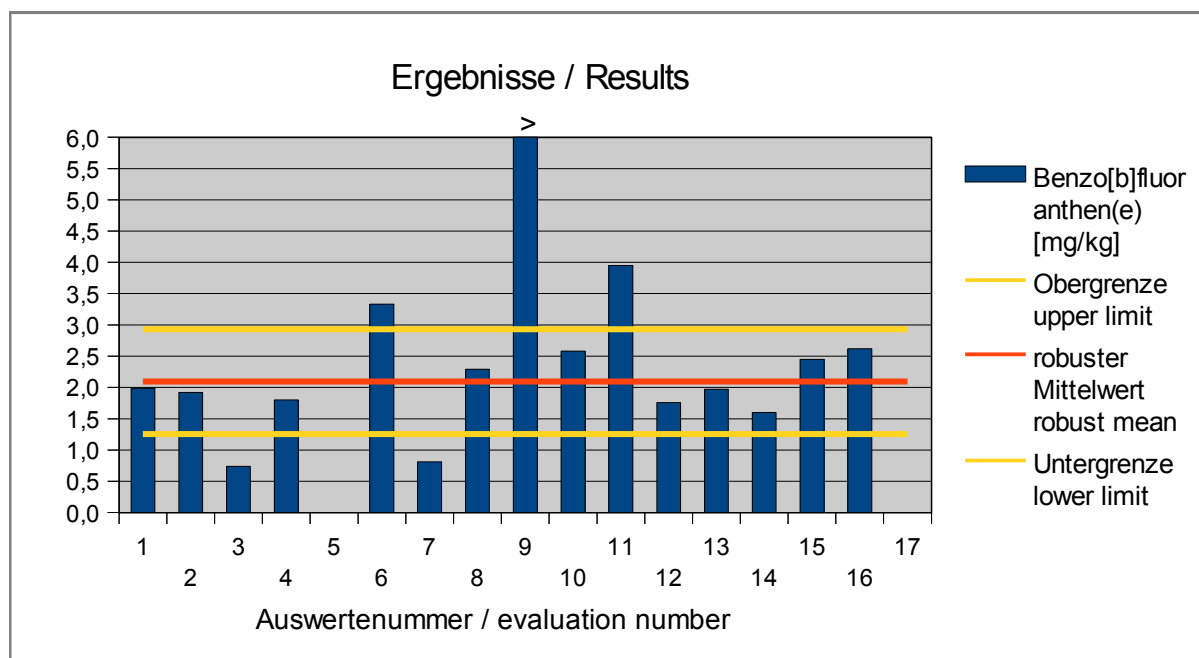
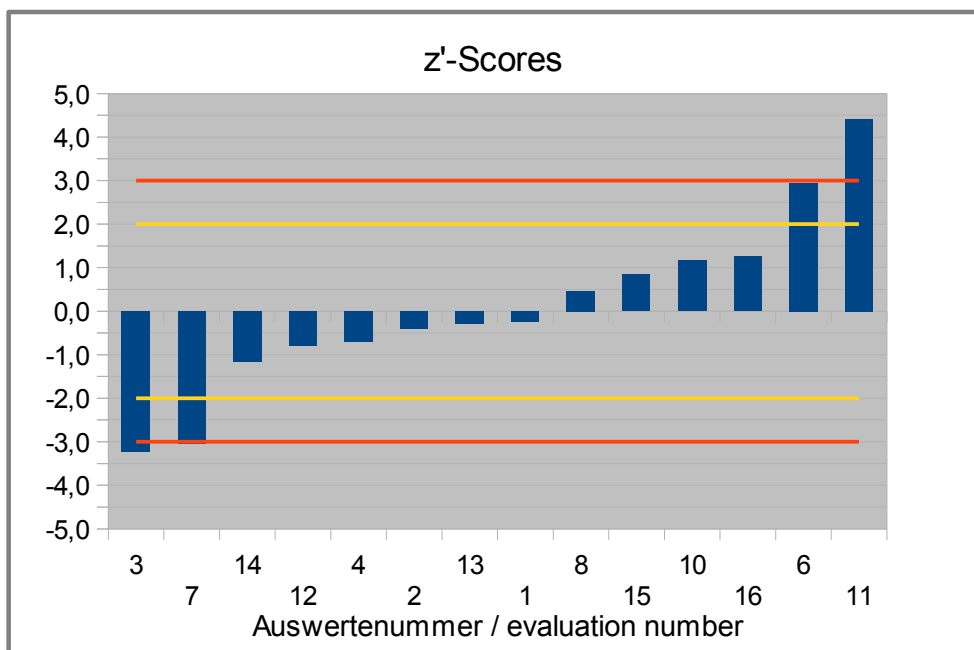


Abb. / Fig. 21: Ergebnisse Benzo[b]fluoranthen / Results Benzo[b]fluoranthen(e)



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

Auswertenummer Evaluation number	Benzo[b]fluoranthen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	1,99	-0,105	-0,25	-0,35	
2	1,92	-0,173	-0,41	-0,58	
3	0,740	-1,353	-3,2	-4,5	
4	1,80	-0,293	-0,70	-1,0	
5	< 0,2				
6	3,33	1,237	2,95	4,13	
7	0,810	-1,283	-3,1	-4,3	
8	2,29	0,197	0,47	0,7	
9	17,9				Ausreißer ausgeschlossen / Outlier excluded
10	2,58	0,487	1,16	1,6	
11	3,95	1,857	4,4	6,2	
12	1,76	-0,333	-0,79	-1,1	
13	1,97	-0,123	-0,29	-0,41	
14	1,60	-0,493	-1,2	-1,6	
15	2,45	0,354	0,84	1,18	
16	2,62	0,527	1,26	1,8	
17					



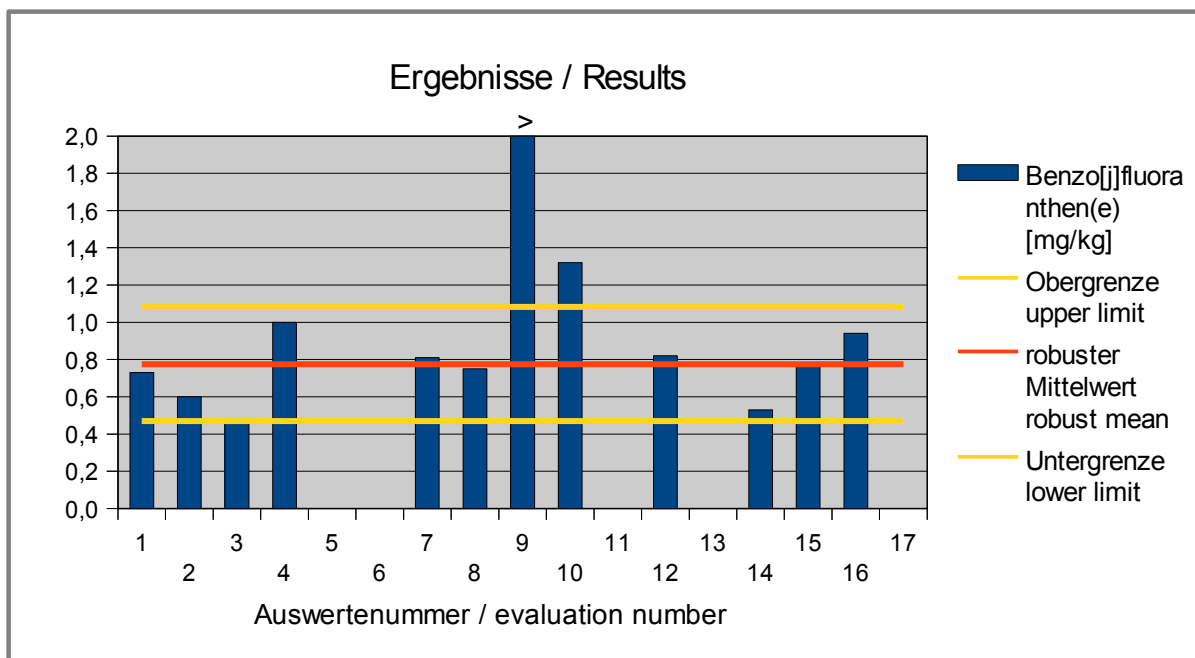
**Abb. / Fig. 22:** Z'-Scores Benzo[b]fluoranthen / Benzo[b]fluoranthene

**4.12 Benzo[j]fluoranth(en)e in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Statistic Data	
Number of results <sup>°</sup>	11
Number of outliers	1
Mean	0,795
Median	0,774
<b>Robust Mean (X)</b>	<b>0,775</b>
<b>Robust standard deviation (S*)</b>	<b>0,220</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}</math>'</b>	<b>0,153</b>
Target standard deviation (for Information)	0,129
<b>lower limit of target range</b>	<b>0,469</b>
<b>upper limit of target range</b>	<b>1,08</b>
Quotient $S^*/\sigma_{pt}'$	1,4
Standard uncertainty $U(x_{pt})$	0,08
Results in the target range	10
Percent in the target range	91%

<sup>°</sup> without outliers (result no. 9)



**Abb. / Fig. 23:** Ergebnisse Benzo[j]fluoranth(en)e / Results Benzo[j]fluoranthene

Ergebnisse der Teilnehmer:  
Results of Participants:

Auswertenummer Evaluation number	Benzo[j]fluoranthen(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	0,730	-0,045	-0,29	-0,4	
2	0,600	-0,175	-1,14	-1,36	
3	0,470	-0,305	-2,0	-2,4	
4	1,00	0,225	1,46	1,7	
5	< 0,2				
6					
7	0,810	0,035	0,2	0,3	
8	0,750	-0,025	-0,17	-0,2	
9	8,96				Ausreißer ausgeschlossen / Outlier excluded
10	1,32	0,545	3,55	4,2	
11					
12	0,820	0,045	0,3	0,3	
13	< 0,2				
14	0,530	-0,245	-1,6	-1,9	
15	0,774	-0,001	-0,01	-0,01	
16	0,940	0,165	1,07	1,3	
17					

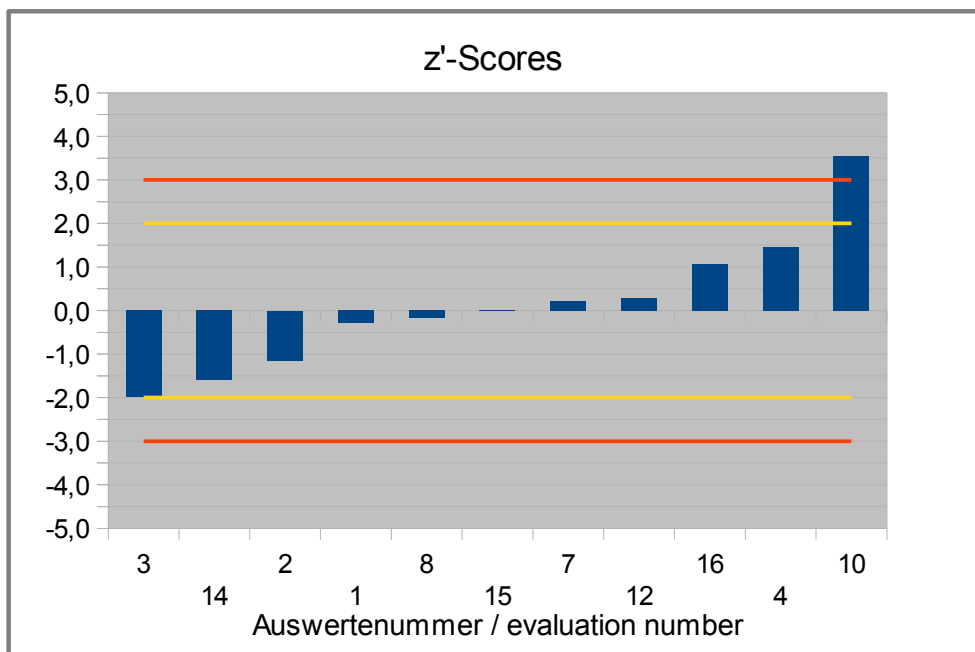


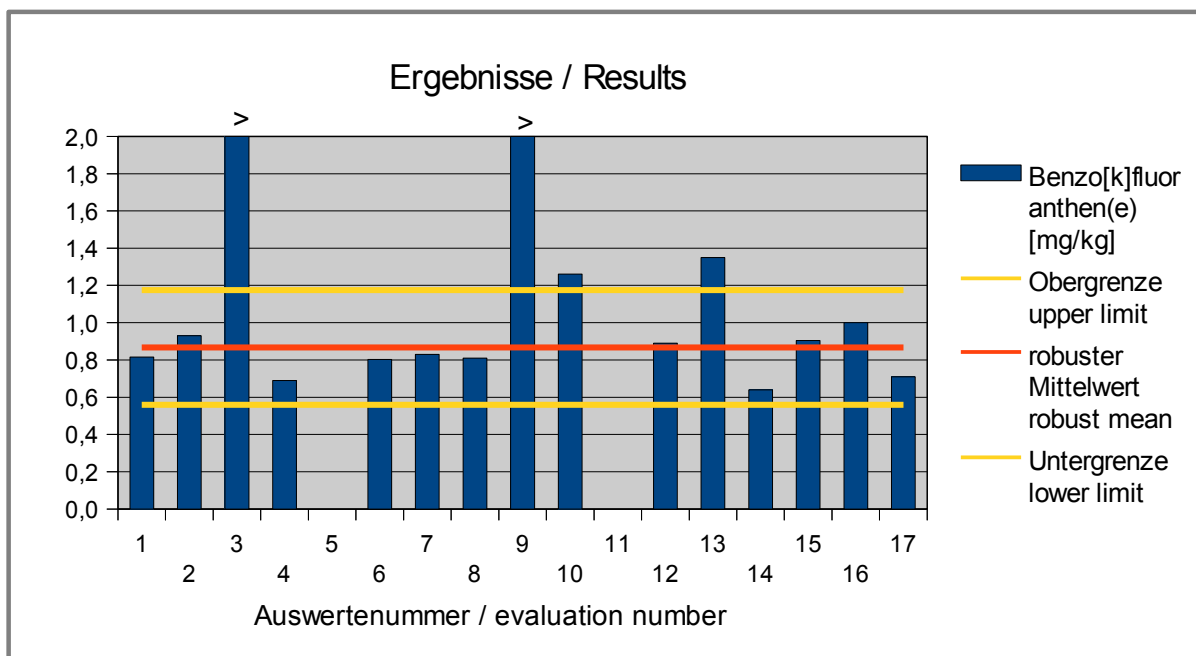
Abb. / Fig. 24: z'-Scores Benzo[j]fluoranthen / Benzo[j]fluoranthene

**4.13 Benzo[k]fluoranth(en) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Statistic Data	
Number of results <sup>°</sup>	13
Number of outliers	2
Mean	0,895
Median	0,830
<b>Robust Mean (X)</b>	<b>0,867</b>
<b>Robust standard deviation (S*)</b>	<b>0,172</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}</math>'</b>	<b>0,154</b>
Target standard deviation (for Information)	0,142
<b>lower limit of target range</b>	<b>0,560</b>
<b>upper limit of target range</b>	<b>1,17</b>
Quotient $S^*/\sigma_{pt}'$	1,1
Standard uncertainty $U(x_{pt})$	0,0595
Results in the target range	11
Percent in the target range	85%

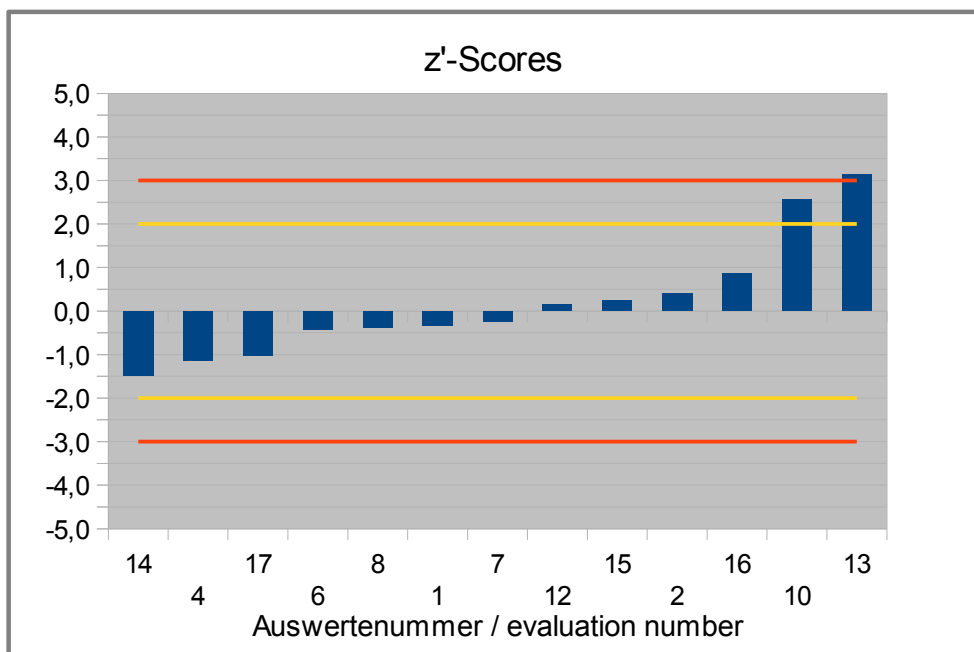
<sup>°</sup> without outliers (results no. 3 and 9)



**Abb. / Fig. 25:** Ergebnisse Benzo[k]fluoranth(en) / Results Benzo[k]fluoranthene

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

Auswertenummer Evaluation number	Benzo[k]fluoranth(en)e [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	0,816	-0,051	-0,33	-0,4	
2	0,930	0,063	0,41	0,44	
3	3,25				Ausreißer ausgeschlossen / Outlier excluded
4	0,690	-0,177	-1,15	-1,2	
5	< 0,2				
6	0,803	-0,064	-0,42	-0,45	
7	0,830	-0,037	-0,2	-0,3	
8	0,810	-0,057	-0,37	-0,4	
9	6,65				Ausreißer ausgeschlossen / Outlier excluded
10	1,26	0,393	2,56	2,8	
11					
12	0,890	0,023	0,1	0,2	
13	1,35	0,483	3,1	3,4	
14	0,640	-0,227	-1,5	-1,6	
15	0,904	0,037	0,24	0,26	
16	1,00	0,133	0,86	0,9	
17	0,710	-0,157	-1,0	-1,1	



**Abb. / Fig. 26:** z'-Scores Benzo[k]fluoranth(en)e / Benzo[k]fluoranth(en)e

### 4.14 Benzo[e]pyren(e) in mg/kg

#### Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results <sup>°</sup>	15
Number of outliers	1
Mean	3,58
Median	3,55
<b>Robust Mean (X)</b>	<b>3,56</b>
<b>Robust standard deviation (S*)</b>	<b>0,916</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>0,556</b>
Target standard deviation (for Information)	0,470
<b>lower limit of target range</b>	<b>2,45</b>
<b>upper limit of target range</b>	<b>4,67</b>
Quotient $S^*/\sigma_{pt}'$	1,6
Standard uncertainty $U(\bar{x}_{pt})$	0,296
Results in the target range	12
Percent in the target range	80%

<sup>°</sup> without outliers (result no. 9)

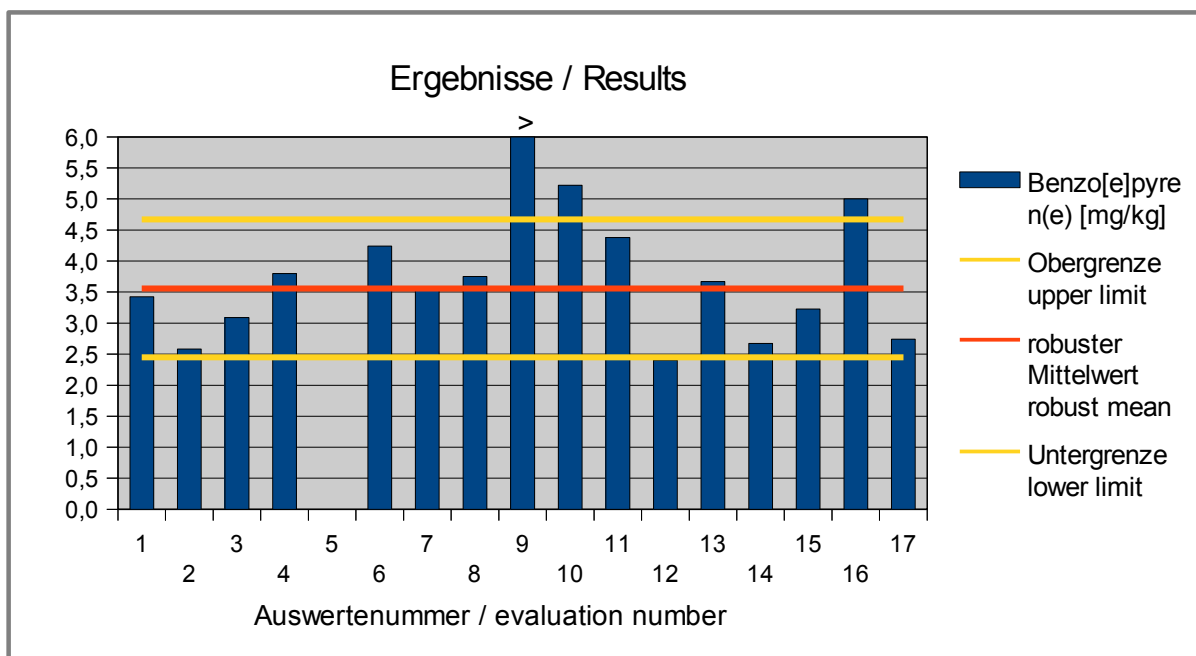
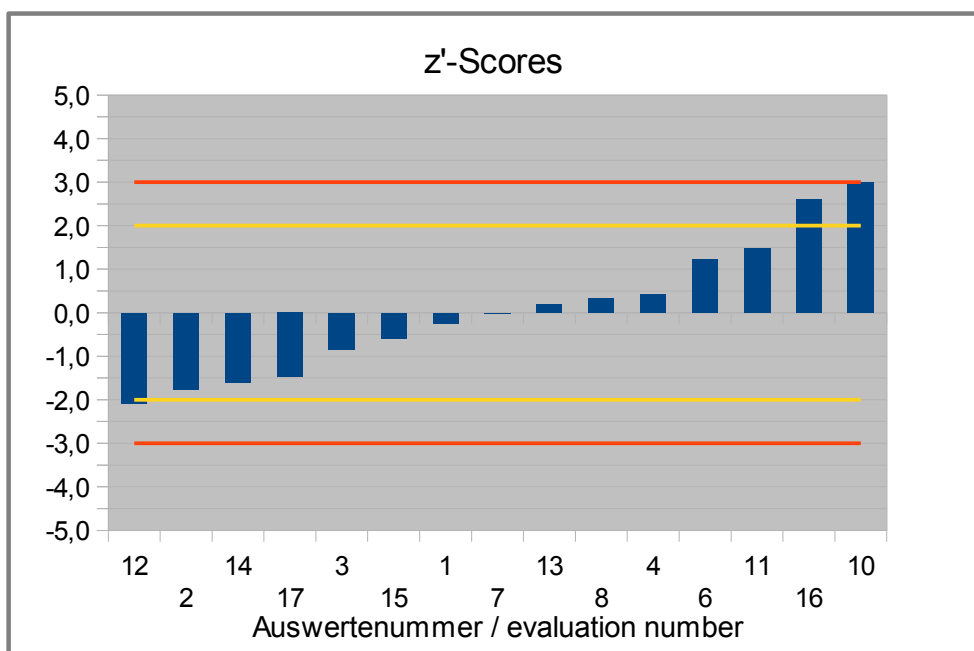


Abb. / Fig. 27: Ergebnisse Benzo[e]pyren / Results Benzo[e]pyrene

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

Auswertenummer Evaluation number	Benzo[e]pyren(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	3,43	-0,133	-0,24	-0,3	
2	2,58	-0,979	-1,8	-2,08	
3	3,09	-0,469	-0,8	-1,0	
4	3,80	0,241	0,43	0,5	
5	< 0,2				
6	4,24	0,681	1,2	1,45	
7	3,55	-0,009	0,0	0,0	
8	3,75	0,191	0,34	0,4	
9	26,2				Ausreißer ausgeschlossen / Outlier excluded
10	5,22	1,661	3,0	3,5	
11	4,38	0,821	1,5	1,7	
12	2,40	-1,159	-2,1	-2,5	
13	3,67	0,111	0,2	0,2	
14	2,67	-0,889	-1,6	-1,9	
15	3,23	-0,331	-0,60	-0,70	
16	5,00	1,441	2,6	3,1	
17	2,74	-0,819	-1,5	-1,7	



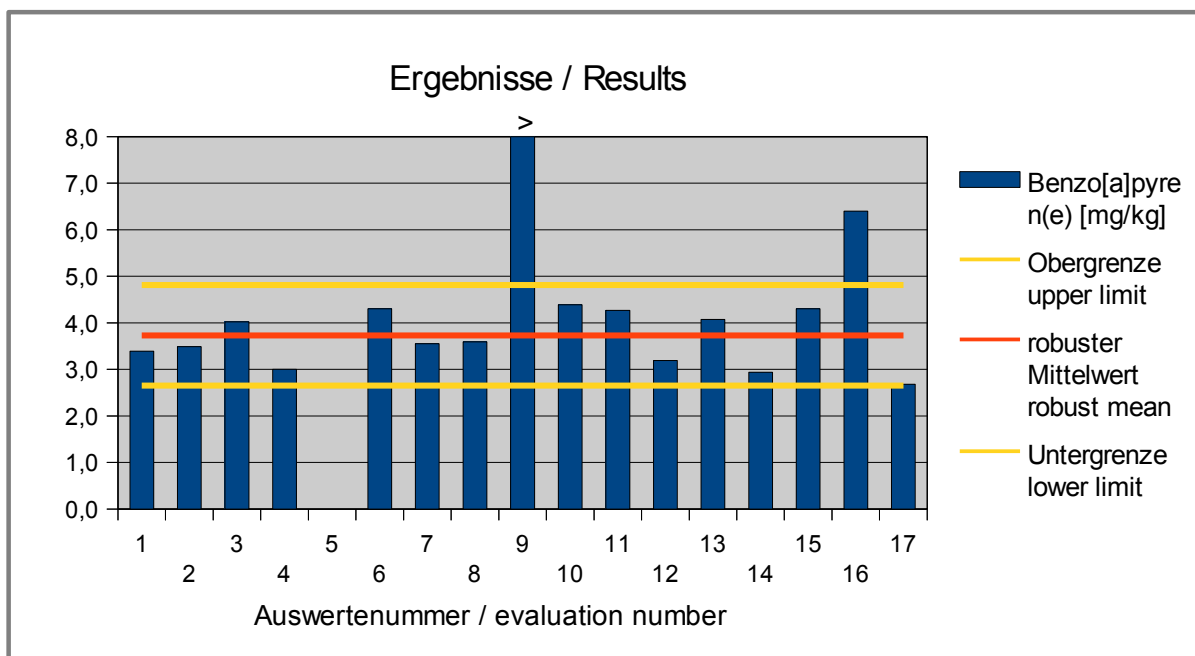
**Abb. / Fig. 28:** z'-Scores Benzo[e]pyren / Benzo[e]pyrene

**4.15 Benzo[a]pyren(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Statistic Data	
Number of results <sup>°</sup>	15
Number of outliers	1
Mean	3,84
Median	3,59
<b>Robust Mean (X)</b>	<b>3,73</b>
<b>Robust standard deviation (S*)</b>	<b>0,710</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}</math>'</b>	<b>0,541</b>
Target standard deviation (for Information)	0,490
<b>lower limit of target range</b>	<b>2,65</b>
<b>upper limit of target range</b>	<b>4,81</b>
Quotient $S^*/\sigma_{pt}'$	1,3
Standard uncertainty $U(x_{pt})$	0,229
Results in the target range	14
Percent in the target range	93%

<sup>°</sup> without outliers (result no. 9)

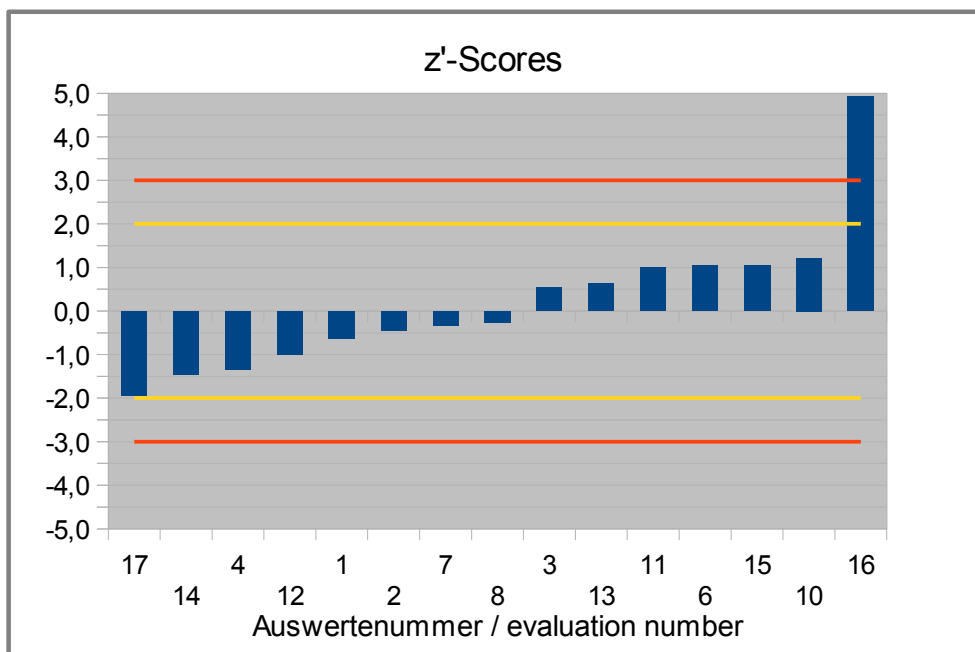


**Abb. / Fig. 29:** Ergebnisse Benzo[a]pyren / Results Benzo[a]pyrene



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

Auswertenummer Evaluation number	Benzo[a]pyren(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	3,39	-0,341	-0,63	-0,7	
2	3,49	-0,242	-0,4	-0,49	
3	4,02	0,288	0,5	0,6	
4	3,00	-0,732	-1,35	-1,5	
5	< 0,2				
6	4,30	0,568	1,1	1,16	
7	3,55	-0,182	-0,3	-0,4	
8	3,59	-0,142	-0,26	-0,3	
9	38,7				Ausreißer ausgeschlossen / Outlier excluded
10	4,39	0,658	1,2	1,3	
11	4,27	0,538	1,0	1,1	
12	3,19	-0,542	-1,0	-1,1	
13	4,07	0,338	0,6	0,7	
14	2,94	-0,792	-1,5	-1,6	
15	4,30	0,570	1,05	1,16	
16	6,40	2,668	4,9	5,4	
17	2,68	-1,052	-1,9	-2,1	



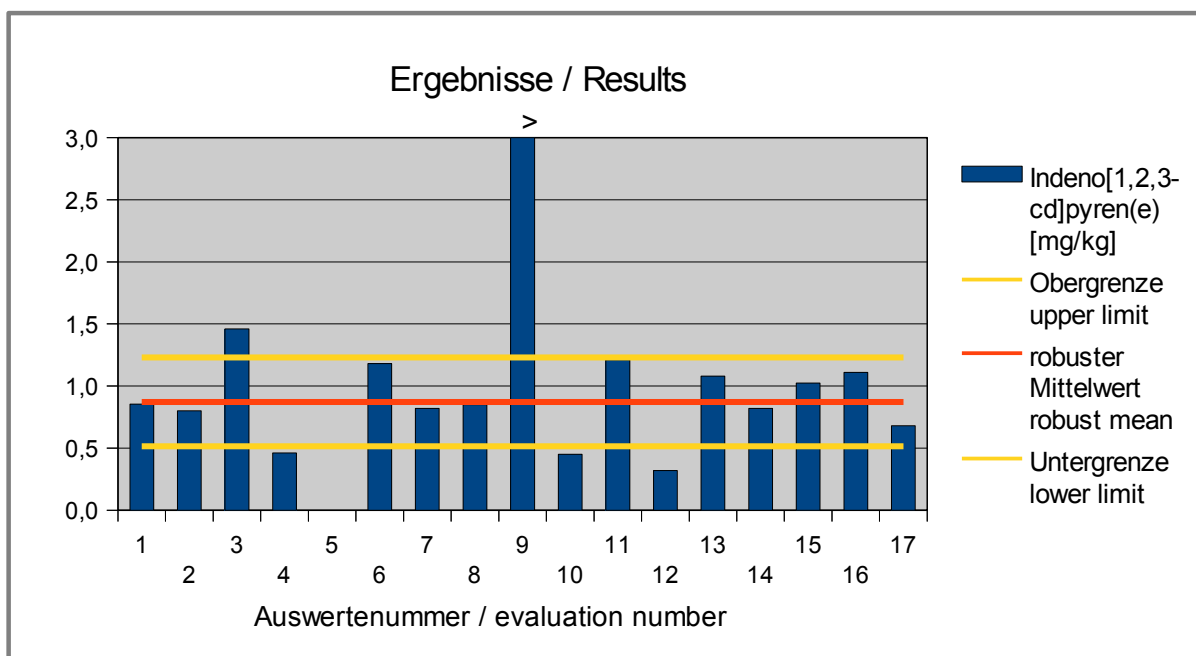
**Abb. / Fig. 30:** z'-Scores Benzo[a]pyren / Benzo[a]pyrene

**4.16 Indeno[1,2,3-cd]pyrene in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Statistic Data	
Number of results <sup>°</sup>	15
Number of outliers	1
Mean	0,874
Median	0,850
<b>Robust Mean (X)</b>	<b>0,872</b>
<b>Robust standard deviation (S*)</b>	<b>0,338</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}</math>'</b>	<b>0,179</b>
Target standard deviation (for Information)	0,142
<b>lower limit of target range</b>	<b>0,513</b>
<b>upper limit of target range</b>	<b>1,23</b>
Quotient $S^*/\sigma_{pt}'$	1,9
Standard uncertainty $U(x_{pt})$	0,1090
Results in the target range	11
Percent in the target range	73%

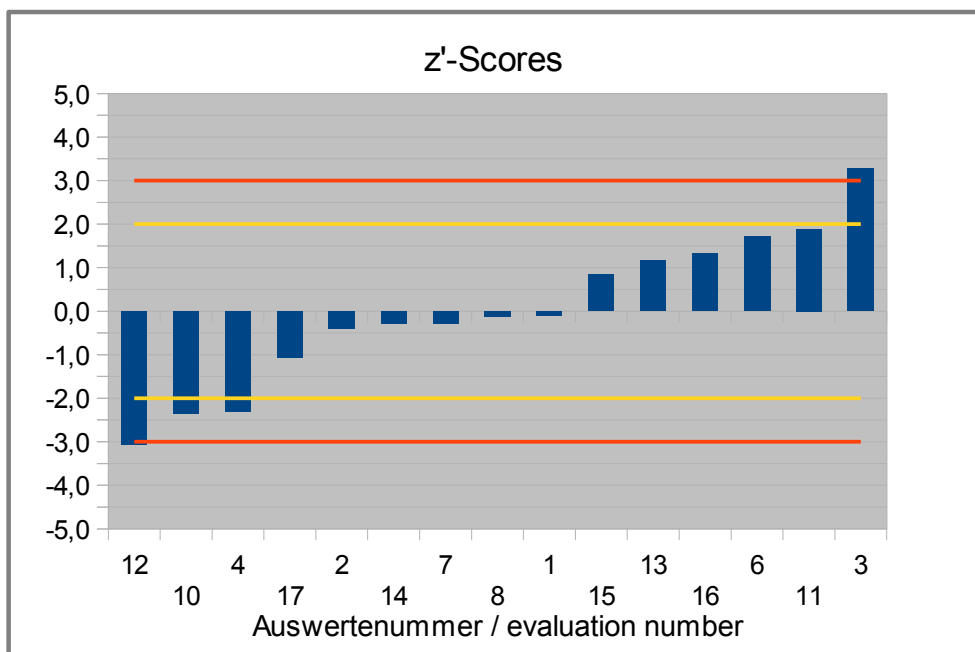
<sup>°</sup> without outliers (result no. 9)



**Abb. / Fig. 31:** Ergebnisse Indeno[1,2,3-cd]pyren / Results Indeno[1,2,3-cd]pyrene

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

Auswertenummer Evaluation number	Indeno[1,2,3-cd]pyren(e) [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	0,854	-0,018	-0,10	-0,1	
2	0,800	-0,072	-0,40	-0,51	
3	1,460	0,588	3,3	4,1	
4	0,460	-0,412	-2,3	-2,9	
5	< 0,2				
6	1,180	0,308	1,7	2,16	
7	0,820	-0,052	-0,29	-0,4	
8	0,850	-0,022	-0,12	-0,2	
9	5,10				Ausreißer ausgeschlossen / Outlier excluded
10	0,450	-0,422	-2,4	-3,0	
11	1,210	0,338	1,9	2,4	
12	0,320	-0,552	-3,1	-3,9	
13	1,080	0,208	1,2	1,5	
14	0,820	-0,052	-0,29	-0,4	
15	1,023	0,151	0,84	1,06	
16	1,110	0,238	1,3	1,7	
17	0,680	-0,192	-1,1	-1,3	

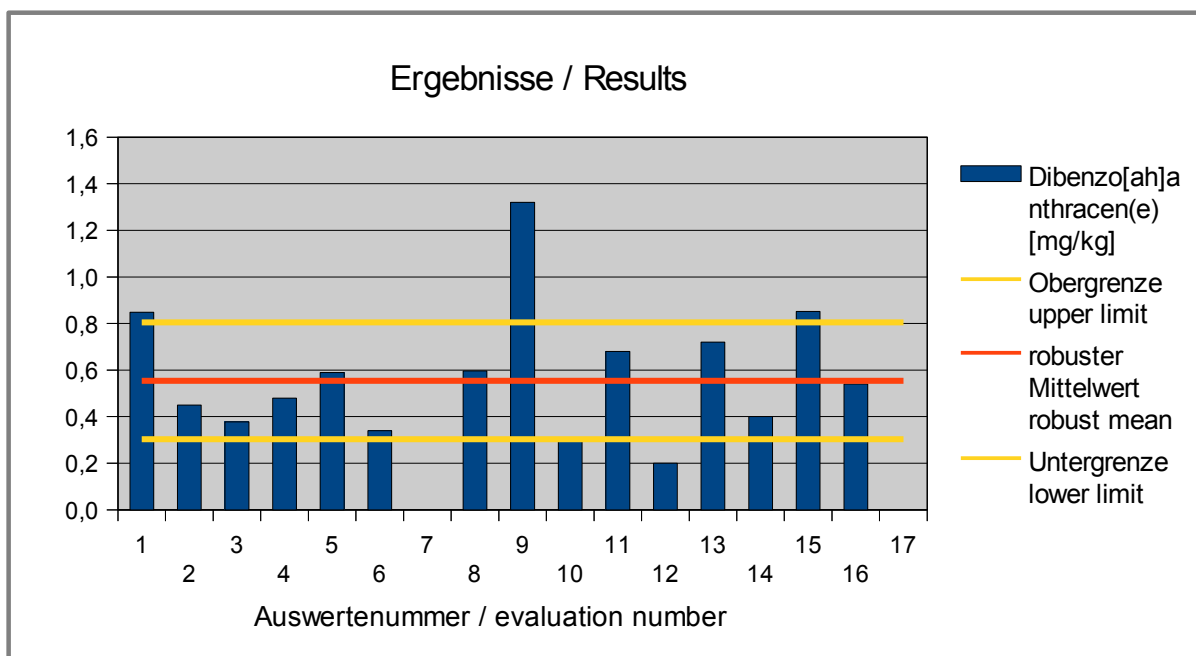


**Abb. / Fig. 32:** Z'-Scores Indeno[1,2,3-cd]pyren / Indeno[1,2,3-cd]pyrene

**4.17 Dibenzo[ah]anthracen(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

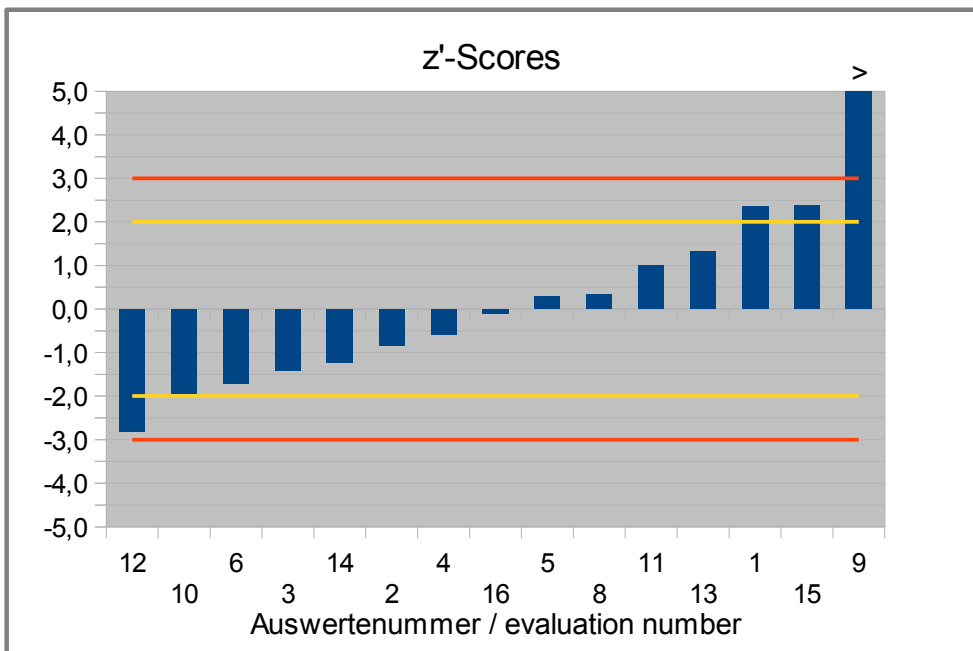
<b>Statistic Data</b>	
Number of results°	15
Number of outliers	-
Mean	0,580
Median	0,540
<b>Robust Mean (X)</b>	<b>0,554</b>
<b>Robust standard deviation (S*)</b>	<b>0,246</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>0,125</b>
Target standard deviation (for Information)	0,097
<b>lower limit of target range</b>	<b>0,303</b>
<b>upper limit of target range</b>	<b>0,804</b>
<i>Quotient <math>S^*/\sigma_{pt}'</math></i>	<i>2,0</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>0,0794</i>
<i>Results in the target range</i>	<i>11</i>
<i>Percent in the target range</i>	<i>73%</i>



**Abb. / Fig. 33:** Ergebnisse Dibenzo[ah]anthracen / Results Dibenzo[ah]anthracene

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

Auswertenummer	Dibenzo[ah]-anthracen(e) [mg/kg]	Abweichung [mg/kg]	z'-Score (σ <sub>pt</sub> )	z-Score (Info)	Hinweis
Evaluation number		Deviation [mg/kg]			Remark
1	0,848	0,294	2,3	3,0	
2	0,450	-0,104	-0,8	-1,07	
3	0,378	-0,176	-1,4	-1,8	
4	0,480	-0,074	-0,59	-0,8	
5	0,590	0,036	0,3	0,4	
6	0,340	-0,214	-1,7	-2,21	
7	< 0,2				
8	0,596	0,042	0,34	0,4	
9	1,32	0,766	6	8	
10	0,310	-0,244	-1,9	-2,5	
11	0,680	0,126	1,0	1,3	
12	0,200	-0,354	-2,8	-3,7	
13	0,720	0,166	1,3	1,7	
14	0,400	-0,154	-1,2	-1,6	
15	0,852	0,298	2,38	3,08	
16	0,540	-0,014	-0,1	-0,1	
17					



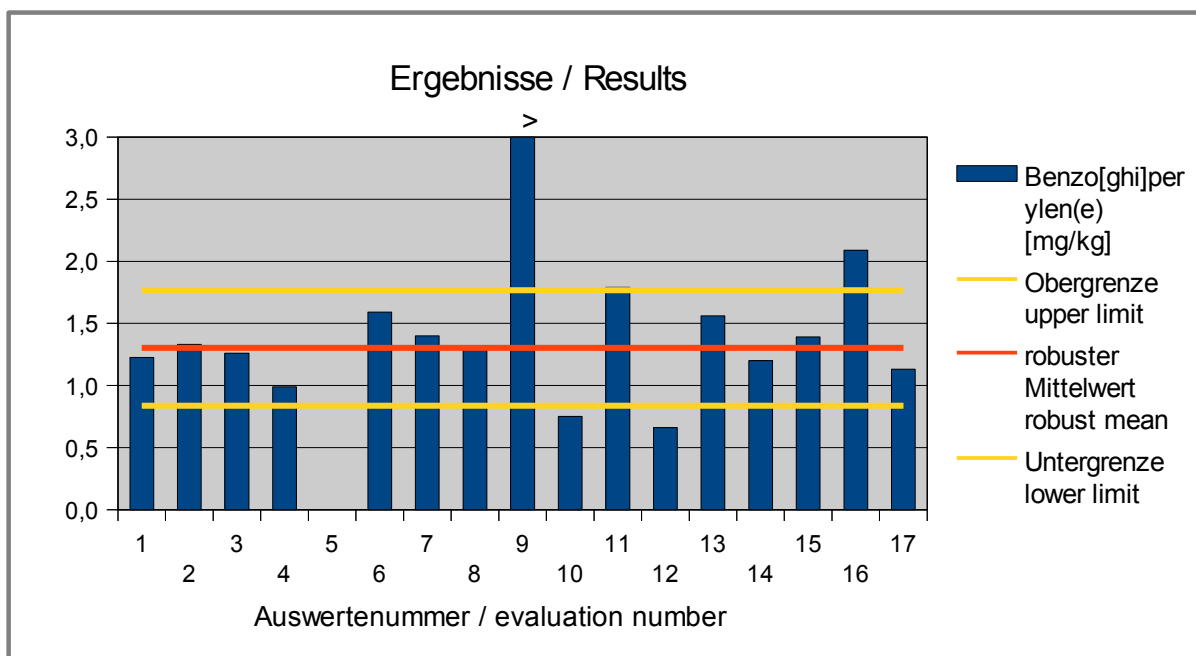
**Abb. / Fig. 34:** z'-Scores Dibenzo[ah]anthracen / Dibenzo[ah]anthracene

**4.18 Benzo[ghi]perylen(e) in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Statistic Data	
Number of results <sup>°</sup>	15
Number of outliers	1
Mean	1,31
Median	1,31
<b>Robust Mean (X)</b>	<b>1,30</b>
<b>Robust standard deviation (S*)</b>	<b>0,365</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}</math></b>	<b>0,232</b>
Target standard deviation (for Information)	0,200
<b>lower limit of target range</b>	<b>0,838</b>
<b>upper limit of target range</b>	<b>1,77</b>
Quotient $S^*/\sigma_{pt}$	1,6
Standard uncertainty $U(x_{pt})$	0,118
Results in the target range	11
Percent in the target range	73%

<sup>°</sup> without outliers (result no. 9)



**Abb. / Fig. 35:** Ergebnisse Benzo[ghi]perylen / Results Benzo[ghi]perylene

Ergebnisse der Teilnehmer:  
Results of Participants:

Auswertenummer Evaluation number	Benzo[ghi]perylene [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	1,22	-0,078	-0,33	-0,4	
2	1,33	0,028	0,12	0,14	
3	1,26	-0,042	-0,2	-0,2	
4	0,990	-0,312	-1,3	-1,6	
5	< 0,2				
6	1,590	0,288	1,2	1,44	
7	1,40	0,098	0,42	0,5	
8	1,31	0,008	0,03	0,0	
9	11,3				Ausreißer ausgeschlossen / Outlier excluded
10	0,750	-0,552	-2,4	-2,8	
11	1,79	0,488	2,1	2,4	
12	0,660	-0,642	-2,8	-3,2	
13	1,56	0,258	1,1	1,3	
14	1,20	-0,102	-0,44	-0,5	
15	1,39	0,088	0,38	0,44	
16	2,09	0,788	3,4	3,9	
17	1,13	-0,172	-0,7	-0,9	

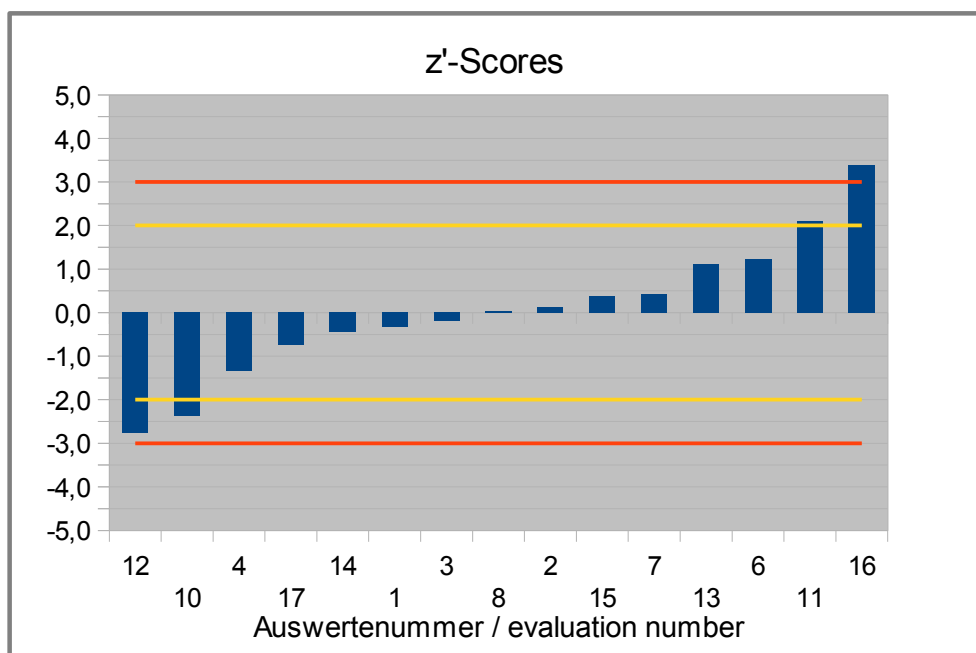
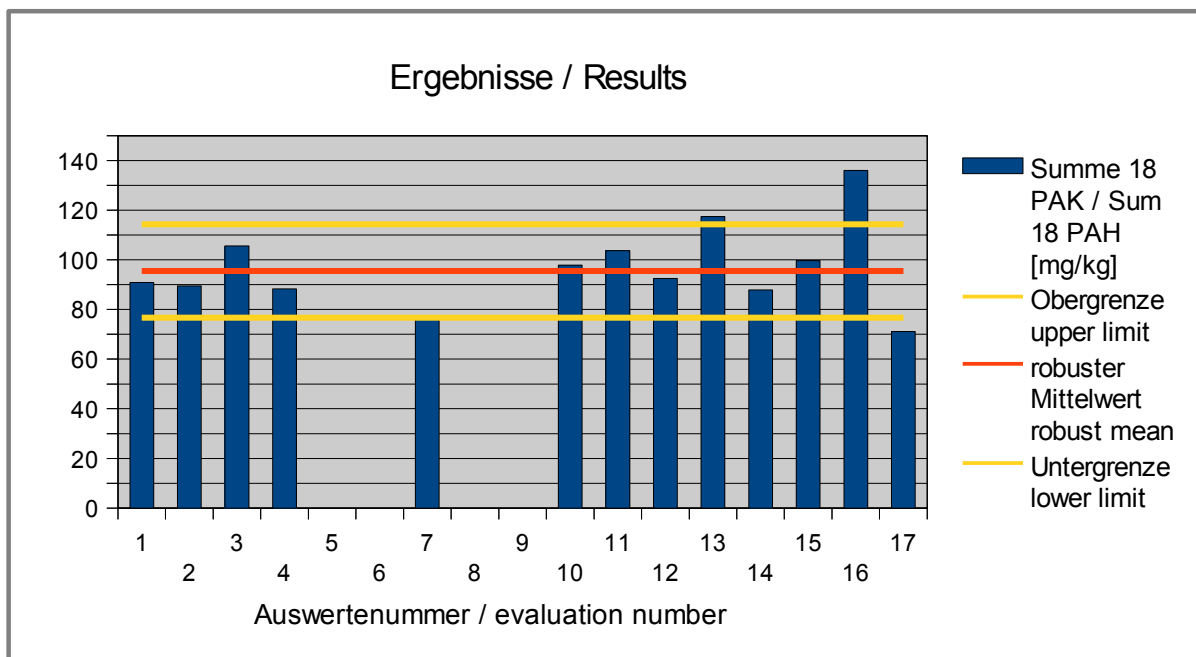


Abb. / Fig. 36: z'-Scores Benzo[ghi]perylene / Benzo[ghi]perylene

**4.19 Summe 18 PAK / Sum 18 PAH in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

<b>Statistic Data</b>	
Number of results	13
Number of outliers	-
Mean	96,7
Median	92,5
<b>Robust Mean (X)</b>	<b>95,5</b>
<b>Robust standard deviation (S*)</b>	<b>15,7</b>
<i>Target range:</i>	
<b>Target standard deviation <math>\sigma_{pt}</math></b>	<b>9,42</b>
Target standard deviation (for Information)	7,69
<b>lower limit of target range</b>	<b>76,6</b>
<b>upper limit of target range</b>	<b>114</b>
<i>Quotient <math>S^*/\sigma_{pt}</math></i>	<i>1,7</i>
<i>Standard uncertainty <math>U(x_{pt})</math></i>	<i>5,44</i>
<i>Results in the target range</i>	<i>10</i>
<i>Percent in the target range</i>	<i>77%</i>

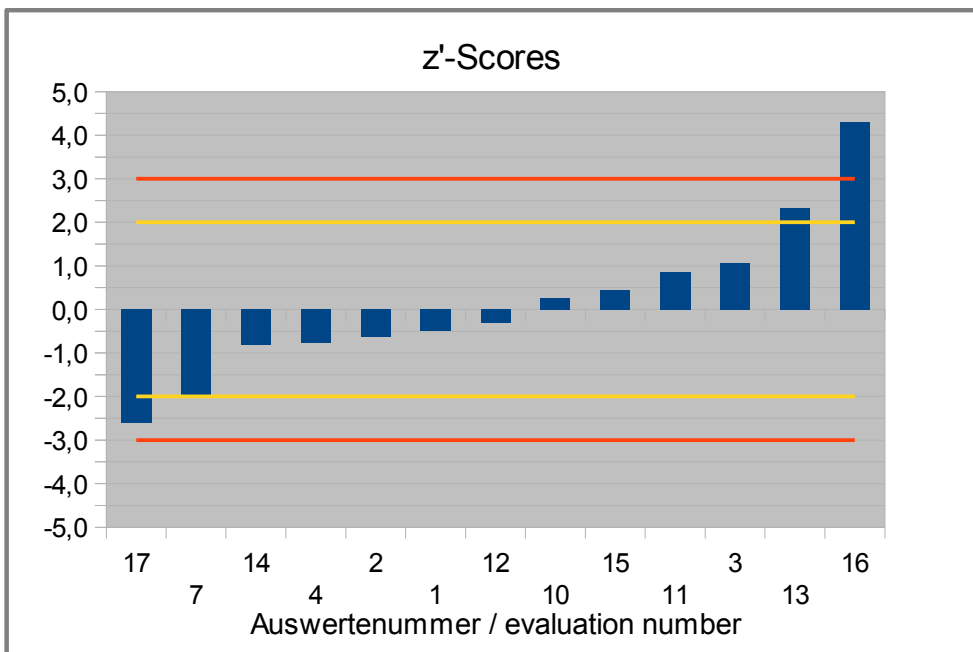


**Abb. / Fig. 37:** Ergebnisse Summe 18 PAK / Results Sum 18 PAH



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

Auswertenummer Evaluation number	Summe 18 PAK / Sum 18 PAH [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score ( $\sigma_{pt}$ )	z-Score (Info)	Hinweis Remark
1	90,9	-4,6	-0,49	-0,6	
2	89,5	-6,0	-0,64	-0,78	
3	106	10,1	1,1	1,3	
4	88,3	-7,2	-0,77	-0,94	
5					
6					
7	77,1	-18,4	-1,96	-2,4	
8					
9					
10	97,9	2,4	0,26	0,31	
11	104	8,2	0,87	1,1	
12	92,5	-3,0	-0,32	-0,39	
13	117	22,0	2,3	2,9	
14	87,9	-7,6	-0,81	-1,0	
15	99,7	4,2	0,44	0,54	
16	136	40,5	4,3	5,3	
17	71,0	-24,5	-2,6	-3,2	



**Abb. / Fig. 38:** Z'-Scores Summe 18 PAK / Sum 18 PAH

**4.20 Summe 7 PAK / Sum 7 PAH in mg/kg**

**Vergleichsuntersuchung / Proficiency Test**

Summe: Acenapthylen, Acenaphten, Fluoren, Phenanthren, Pyren, Anthracen, Fluoranthen

Statistic Data	
Number of results	14
Number of outliers	-
Mean	61,5
Median	62,8
<b>Robust Mean (X)</b>	<b>61,9</b>
<b>Robust standard deviation (S*)</b>	<b>12,0</b>
Target range:	
<b>Target standard deviation <math>\sigma_{pt}'</math></b>	<b>6,67</b>
Target standard deviation (for Information)	5,32
<b>lower limit of target range</b>	<b>48,5</b>
<b>upper limit of target range</b>	<b>75,2</b>
Quotient $S^*/\sigma_{pt}'$	1,8
Standard uncertainty $U(X_{pt})$	4,02
Results in the target range	10
Percent in the target range	71%

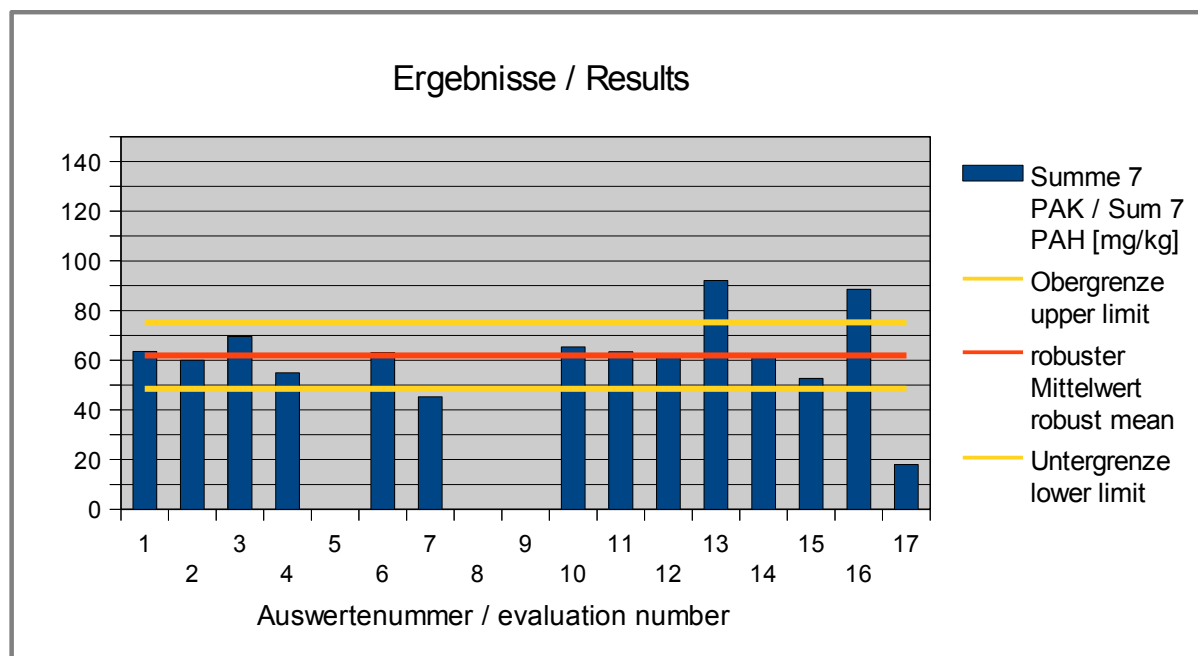
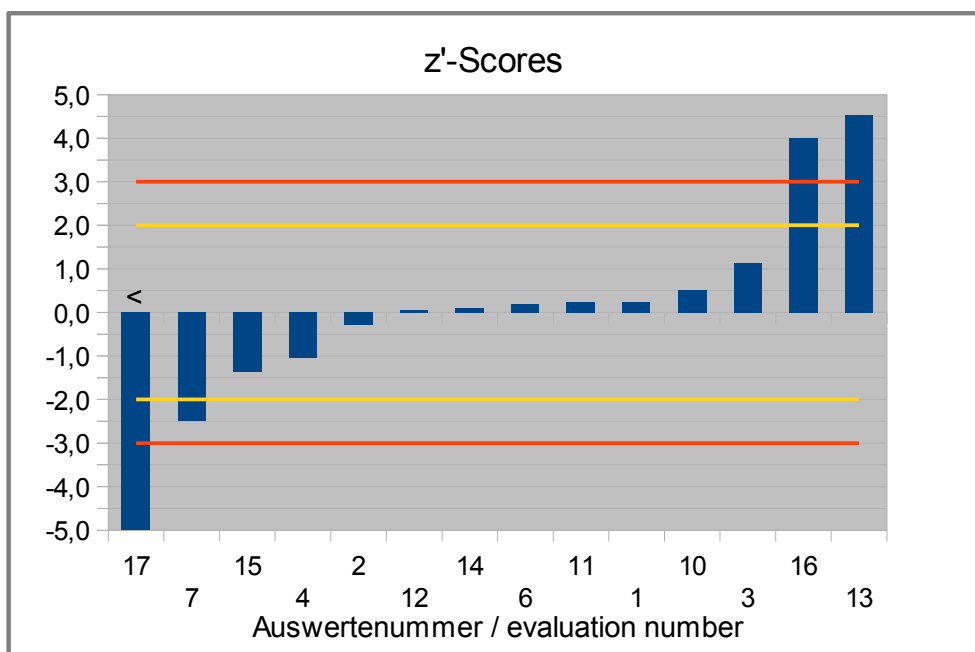


Abb. / Fig. 39: Ergebnisse Summe 7 PAK / Results Sum 7 PAH

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

Auswertenummer Evaluation number	Summe 7 PAK / Sum 7 PAH [mg/kg]	Abweichung [mg/kg] Deviation [mg/kg]	z'-Score (σ <sub>pt</sub> )	z-Score (Info)	Hinweis Remark
1	63,5	1,6	0,24	0,3	
2	60,0	-1,8	-0,27	-0,34	
3	69,5	7,6	1,1	1,4	
4	54,9	-6,9	-1,0	-1,3	
5					
6	63,1	1,2	0,2	0,23	
7	45,3	-16,6	-2,5	-3,1	
8					
9					
10	65,3	3,4	0,52	0,6	
11	63,4	1,5	0,23	0,3	
12	62,2	0,3	0,05	0,1	
13	92,1	30,3	4,5	5,7	
14	62,5	0,6	0,10	0,1	
15	52,7	-9,1	-1,37	-1,72	
16	88,6	26,7	4,0	5,0	
17	18,0	-43,8	-6,6	-8,2	



**Abb. / Fig. 40:** z'-Scores Summe 7 PAK / Sum 7 PAH

## 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

\* For application of the same method notes to the method could be given for naphthalene only.

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate in %	Method specification, as in test re- port / standard / literature *
Naphthalin / Naphthalene	1	mg/kg	0,242	0,2	no		AfPS GS 2014:01 PAH
	2	mg/kg	<0,2	0,2	no		AfPS GS 2014:01 PAH
	3	mg/kg	0,16	0,1			AfPS GS 2014:01 PAH
	4	mg/kg	<0,2	0,2	no	no	GC-MS/MS after extraction extraction (AfPS)
	5	mg/kg	0,22	0,2	no		AfPS GS PAH
	6	mg/kg	nd	0,002	no	-	in house method (AM-067:2015)
	7	mg/kg	< 0,20		no		AfPS GS 2014:01 PAH
	8	mg/kg					other measurement (GC_MS/MS and other internal standards)
	9	mg/kg					
	10	mg/kg	0,4	0,2	yes		AfPS GS 2014:01
	11	mg/kg	< 0,1	0,1	no		AfPS
	12	mg/kg	0,057	0,025	no	100	AfPS GS 2014:01 PAH
	13	mg/kg	<0,2	<0,2	no		AfPS
	14	mg/kg	<0,2	<0,2			AfPS GS 2014
	15	mg/kg	0,0904	0,2	no		AfPS GS 2014:01 PAH
	16	mg/kg	0,19	0,2	no		AfPS GS 2014:01 PAH
	17	mg/kg	0,14	<0.1	no		AfPS GS 2014:01 PAH

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Acenaphthylen(e)	1	mg/kg	0,121	0,2	no		
	2	mg/kg	<0,2	0,2	no		
	3	mg/kg	<0,1	0,1			
	4	mg/kg	<0,2	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	0,053	0,002	no	-	
	7	mg/kg	< 0,20		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	<0,2	0,2	yes		
	11	mg/kg	< 0,1	0,1	no		
	12	mg/kg	0,061	0,03	no	100	
	13	mg/kg	<0,2	<0,2	no		Specification accord. §21 par. 1
	14	mg/kg	<0,2	<0,2			
	15	mg/kg	0,0504	0,2	no		
	16	mg/kg	0,13	0,2	no		
	17	mg/kg	<0.1	<0.1	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Acenaphthen(e)	1	mg/kg	0,370	0,2	no		
	2	mg/kg	0,23	0,2	no		
	3	mg/kg	3,45	0,1			
	4	mg/kg	0,35	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	0,287	0,002	no	-	
	7	mg/kg	0,25		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	<0,2	0,2	yes		
	11	mg/kg	0,38	0,1	no		
	12	mg/kg	0,385	0,02	no	100	
	13	mg/kg	0,42	<0,2	no		No.3 ProdSG
	14	mg/kg	0,47	<0,2			
	15	mg/kg	0,3752	0,2	no		
	16	mg/kg	0,75	0,2	no		
	17	mg/kg	0,31	<0.1	no		

Parameter	Participant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test report / standard / literature *
					yes/no	in %	
Fluoren(e)	1	mg/kg	4,164	0,2	no		
	2	mg/kg	3,73	0,2	no		
	3	mg/kg	2,67	0,1			
	4	mg/kg	3,4	0,2	no	no	
	5	mg/kg	0,72	0,2	no		
	6	mg/kg	3,16	0,002	no	-	
	7	mg/kg	2,59		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	1,75	0,2	yes		
	11	mg/kg	3,04	0,1	no		
	12	mg/kg	3,42	0,01	no	100	
	13	mg/kg	3,53	<0,2	no		Status: 4.8.2014
	14	mg/kg	3,48	<0,2			
	15	mg/kg	3,641	0,2	no		
	16	mg/kg	4,6	0,2	no		
	17	mg/kg	2,99	<0.1	no		

Parameter	Participant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test report / standard / literature *
					yes/no	in %	
Phenanthren(e)	1	mg/kg	25,815	0,2	no		
	2	mg/kg	24,01	0,2	no		
	3	mg/kg	31,55	0,1			
	4	mg/kg	22	0,2	no	no	
	5	mg/kg	4,57	0,2	no		
	6	mg/kg	26,7	0,002	no	-	
	7	mg/kg	17,96		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	23,22	0,2	yes		
	11	mg/kg	27,38	0,1	no		
	12	mg/kg	25	0,05	no	100	
	13	mg/kg	31,81	<0,2	no		
	14	mg/kg	27,7	<0,2			
	15	mg/kg	27,174	0,2	no		
	16	mg/kg	37	0,2	no		
	17	mg/kg	22,36	<0.1	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Anthracen(e)	1	mg/kg	9,010	0,2	no		
	2	mg/kg	9,16	0,2	no		
	3	mg/kg	7,68	0,1			
	4	mg/kg	7,2	0,2	no	no	
	5	mg/kg	2,08	0,2	no		
	6	mg/kg	8,60	0,002	no	-	
	7	mg/kg	5,24		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	13,28	0,2	yes		
	11	mg/kg	8,45	0,1	no		
	12	mg/kg	11,05	0,16	no	100	
	13	mg/kg	10,8	<0,2	no		
	14	mg/kg	7,65	<0,2			
	15	mg/kg	8,235	0,2	no		
	16	mg/kg	13	0,2	no		
	17	mg/kg	7,44	<0.1	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Fluoranth(en)e	1	mg/kg	13,178	0,2	no		
	2	mg/kg	12,16	0,2	no		
	3	mg/kg	12,21	0,1			
	4	mg/kg	12	0,2	no	no	
	5	mg/kg	2,16	0,2	no		
	6	mg/kg	12,7	0,002	no	-	
	7	mg/kg	10,28		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	14,6	0,2	yes		
	11	mg/kg	12,9	0,1	no		
	12	mg/kg	11,9	0,04	no	100	
	13	mg/kg	16,6	<0,2	no		
	14	mg/kg	12,7	<0,2			
	15	mg/kg	13,252	0,2	no		
	16	mg/kg	17,8	0,2	no		
	17	mg/kg	9,56	<0.1	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Pyren(e)	1	mg/kg	10,826	0,2	no		
	2	mg/kg	10,74	0,2	no		
	3	mg/kg	11,93	0,1			
	4	mg/kg	10	0,2	no	no	
	5	mg/kg	1,75	0,2	no		
	6	mg/kg	11,6	0,002	no	-	
	7	mg/kg	8,93		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	12,46	0,2	yes		
	11	mg/kg	11,28	0,1	no		
	12	mg/kg	10,4	0,05	no	100	
	13	mg/kg	13,78	<0,2	no		
	14	mg/kg	10,5	<0,2			
	15	mg/kg	11,796	0,2	no		
	16	mg/kg	15,2	0,2	no		
	17	mg/kg	9,07	<0.1	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Chrysen(e)	1	mg/kg	7,565	0,2	no		
	2	mg/kg	8,8	0,2	no		
	3	mg/kg	12,23	0,1			
	4	mg/kg	12	0,2	no	no	
	5	mg/kg	0,5	0,2	no		
	6	mg/kg	11,5	0,002	no	-	
	7	mg/kg	9,8		no		
	8	mg/kg	8,25	0,003			
	9	mg/kg	100,1	0,03			
	10	mg/kg	8,36	0,2	yes		
	11	mg/kg	13,36	0,1	no		
	12	mg/kg	10,1	0,09	no	100	
	13	mg/kg	15,19	<0,2	no		
	14	mg/kg	8,02	<0,2			
	15	mg/kg	12,205	0,2	no		
	16	mg/kg	16,2	0,2	no		
	17	mg/kg	5,18	<0.1	no		



Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Benzo[a]anthracen(e)	1	mg/kg	6,690	0,2	no		
	2	mg/kg	8,77	0,2	no		
	3	mg/kg	7,14	0,1			
	4	mg/kg	10	0,2	no	no	
	5	mg/kg	0,43	0,2	no		
	6	mg/kg	8,47	0,002	no	-	
	7	mg/kg	9,8		no		
	8	mg/kg	6,42	0,003			
	9	mg/kg	58,9	0,077			
	10	mg/kg	7,92	0,2	yes		
	11	mg/kg	10,56	0,1	no		
	12	mg/kg	9,94	0,13	no	100	
	13	mg/kg	10,91	<0,2	no		
	14	mg/kg	6,59	<0,2			
	15	mg/kg	7,92	0,2	no		
	16	mg/kg	11,3	0,2	no		
	17	mg/kg	6,05	<0,2	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Benzo[b]fluoranthen(e)	1	mg/kg	1,988	0,2	no		
	2	mg/kg	1,92	0,2	no		
	3	mg/kg	0,74	0,1			
	4	mg/kg	1,8	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	3,33	0,002	no	-	
	7	mg/kg	0,81		no		
	8	mg/kg	2,29	0,003	yes	79	
	9	mg/kg	17,9	0,1			
	10	mg/kg	2,58	0,2	yes		
	11	mg/kg	3,95	0,3	no		
	12	mg/kg	1,76	0,15	no	100	
	13	mg/kg	1,97	<0,2	no		
	14	mg/kg	1,6	<0,2			
	15	mg/kg	2,447	0,2	no		
	16	mg/kg	2,62	0,2	no		
	17	mg/kg			no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Benzo[ <i>jj</i> ]fluoranthene(e)	1	mg/kg	0,730	0,2	no		
	2	mg/kg	0,6	0,2	no		
	3	mg/kg	0,47	0,1			
	4	mg/kg	1	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	not tested	not tested	no	-	
	7	mg/kg	0,81		no		
	8	mg/kg	0,75	0,003	yes	80	
	9	mg/kg	8,96	0,14			
	10	mg/kg	1,32	0,2	yes		
	11	mg/kg			no		
	12	mg/kg	0,82	0,15	no	100	
	13	mg/kg	<0,2	<0,2	no		
	14	mg/kg	0,53	<0,2			
	15	mg/kg	0,774	0,2	no		
	16	mg/kg	0,94	0,2	no		
	17	mg/kg			no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Benzo[ <i>k</i> ]fluoranthene(e)	1	mg/kg	0,816	0,2	no		
	2	mg/kg	0,93	0,2	no		
	3	mg/kg	3,25	0,1			
	4	mg/kg	0,69	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	0,803	0,002	no	-	
	7	mg/kg	0,83		no		
	8	mg/kg	0,81	0,003	yes	80	
	9	mg/kg	6,65	0,22			
	10	mg/kg	1,26	0,2	yes		
	11	mg/kg			no		
	12	mg/kg	0,89	0,15	no	100	
	13	mg/kg	1,35	<0,2	no		
	14	mg/kg	0,64	<0,2			
	15	mg/kg	0,904	0,2	no		
	16	mg/kg	1	0,2	no		
	17	mg/kg	0,71	<0,2	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Benzo[e]pyren(e)	1	mg/kg	3,426	0,2	no		
	2	mg/kg	2,58	0,2	no		
	3	mg/kg	3,09	0,1			
	4	mg/kg	3,8	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	4,24	0,002	no	-	
	7	mg/kg	3,55		no		
	8	mg/kg	3,75	0,003	yes	95	
	9	mg/kg	26,2				
	10	mg/kg	5,22	0,2	yes		
	11	mg/kg	4,38	0,1	no		
	12	mg/kg	2,4	0,1	no	100	
	13	mg/kg	3,67	<0,2	no		
	14	mg/kg	2,67	<0,2			
	15	mg/kg	3,228	0,2	no		
	16	mg/kg	5	0,2	no		
	17	mg/kg	2,74	<0,2	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Benzo[a]pyren(e)	1	mg/kg	3,391	0,2	no		
	2	mg/kg	3,49	0,2	no		
	3	mg/kg	4,02	0,1			
	4	mg/kg	3	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	4,30	0,002	no	-	
	7	mg/kg	3,55		no		
	8	mg/kg	3,59	0,003	yes	95	
	9	mg/kg	38,7	0,15			
	10	mg/kg	4,39	0,2	yes		
	11	mg/kg	4,27	0,1	no		
	12	mg/kg	3,19	0,07	no	100	
	13	mg/kg	4,07	<0,2	no		
	14	mg/kg	2,94	<0,2			
	15	mg/kg	4,302	0,2	no		
	16	mg/kg	6,4	0,2	no		
	17	mg/kg	2,68	<0,2	no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Dibenzo[ah]anthracen(e)	1	mg/kg	0,848	0,002	no		
	2	mg/kg	0,45		no		
	3	mg/kg	0,378	0,2			
	4	mg/kg	0,48	0,2	no	no	
	5	mg/kg	0,59	0,1	no		
	6	mg/kg	0,34	0,2	no	-	
	7	mg/kg	<0,2	0,2	no		
	8	mg/kg	0,596	0,003	yes	75	
	9	mg/kg	1,32	0,17			
	10	mg/kg	0,31	0,2	yes		
	11	mg/kg	0,68	0,1	no		
	12	mg/kg	0,2	0,14	no	100	
	13	mg/kg	0,72	<0,2	no		
	14	mg/kg	0,4	<0,2			
	15	mg/kg	0,8518	0,2	no		
	16	mg/kg	0,54	0,2	no		
	17	mg/kg			no		

Parameter	Partici- pant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test re- port / standard / literature *
					yes/no	in %	
Indeno[1,2,3-cd]pyren(e)	1	mg/kg	0,854	0,2	no		
	2	mg/kg	0,8	0,2	no		
	3	mg/kg	1,46	0,1			
	4	mg/kg	0,46	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	1,18	0,002	no	-	
	7	mg/kg	0,82		no		
	8	mg/kg	0,85	0,003	yes	78	
	9	mg/kg	5,103	0,39			
	10	mg/kg	0,45	0,2	yes		
	11	mg/kg	1,21	0,1	no		
	12	mg/kg	0,32	0,15	no	100	
	13	mg/kg	1,08	<0,2	no		
	14	mg/kg	0,82	<0,2			
	15	mg/kg	1,023	0,2	no		
	16	mg/kg	1,11	0,2	no		
	17	mg/kg	0,68	<0,2	no		

Parameter	Participant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test report / standard / literature *
					yes/no	in %	
Benzo[ghi]perylene(e)	1	mg/kg	1,225	0,2	no		
	2	mg/kg	1,33	0,2	no		
	3	mg/kg	1,26	0,1			
	4	mg/kg	0,99	0,2	no	no	
	5	mg/kg	<0,2	0,2	no		
	6	mg/kg	1,59	0,002	no	-	
	7	mg/kg	1,4		no		
	8	mg/kg	1,31	0,003	yes	75	
	9	mg/kg	11,3	0,29			
	10	mg/kg	0,75	0,2	yes		
	11	mg/kg	1,79	0,1	no		
	12	mg/kg	0,66	0,15	no	100	
	13	mg/kg	1,56	<0,2	no		
	14	mg/kg	1,2	<0,2			
	15	mg/kg	1,39	0,2	no		
	16	mg/kg	2,09	0,2	no		
	17	mg/kg	1,13	<0,2	no		

Parameter	Participant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test report / standard / literature *
					yes/no	in %	
Summe 18 PAK / Sum 18 PAH	1	mg/kg	90,897	0,2	nein		
	2	mg/kg	89,5				
	3	mg/kg	105,6				
	4	mg/kg	88,26				
	5	mg/kg					
	6	mg/kg	not tested	not tested		-	
	7	mg/kg	77,07		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	97,9		yes		
	11	mg/kg	103,7		no		
	12	mg/kg	92,5				
	13	mg/kg	117,46				
	14	mg/kg	87,9	<0,2			
	15	mg/kg	99,658		no		
	16	mg/kg	136	0,2	no		
	17	mg/kg	71,04				

Parameter	Participant	Unit	Result Batch 2	LOQ	Incl. RR	Recovery rate	Method specification, as in test report / standard / literature *
					yes/no	in %	
Summe 7 PAK / Sum 7 PAH (Acenaphylen(e), Acenaphten(e), Fluoren(e), Phenanathren(e), Pyren(e), Anthracen(e), Fluoranthen(e))	1	mg/kg	63,484	0,2	nein		
	2	mg/kg	60,03				
	3	mg/kg	69,5				
	4	mg/kg	54,94				
	5	mg/kg					
	6	mg/kg	63,1	-	-	-	
	7	mg/kg	45,25		no		
	8	mg/kg					
	9	mg/kg					
	10	mg/kg	65,3		yes		
	11	mg/kg	63,4		no		
	12	mg/kg	62,2				
	13	mg/kg	92,13				
	14	mg/kg	62,5	<0,2			
	15	mg/kg	52,73				
	16	mg/kg	88,6	0,2	no		
	17	mg/kg	18,04				

\* For application of the same method notes to the method could be given for naphthalene only.

**5.1.2 Analytical Methods**

\* When using the same method, instructions for the method should only be given in the first line of naphthalene. Specific details for certain parameters are given on the following pages.

Parameter	Participant	Remarks about sample preparation*	Method description*	Calibration and reference material	Recovery with same matrix yes / no	Method accredited to ISO / IEC 17025 yes / no	Further remarks
Naphthalin / Naphthalene	1					yes	
	2	extraction with toluene	GC-MSMS	0,0025 µg/ml to 0,1 µg/ml; AccuStandard: H-QME-01			sample I and II very inhomogenous!; high deviation of several preparations! Therefore only the results of batch 2 were submitted
	3	toluene-extract	GC/MS			yes	conspicuity in extracts (inhomogeneity)
	4		GC-MS/MS	ZCS	no	yes	
	5					yes	
	6	extraction with toluene	GC-MS	-	-	yes	nd-not detected
	7	AfPS GS 2014:01 PAH	GC-MS			no	
	8	additional sample was completely extracted as recommended by DLA. 3,1 g in 20 ml toluene dissolved; 1:20 diluted; 0,3 ml for analysis.				via 13C labeled internal standards directly in samples determined!	see email
	9						
	10	total sample amount extracted and partly diluted for measurement	calculated via internal standards	Reference material: DLA 73/2016		yes	
	11					yes	
	12	Homogenisation by shaking, no clean-up	GC/MS-SIM	ext. 7-point-calibration with recovery correction by 3 internal deuterated standards, reference material: 16 EPA-PAH + Benzo[e]pyrene + Benzo[j]fluoranthene		no	no

*Continuation next page*

Parameter	Participant	Remarks about sample preparation*	Method description*	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
					yes / no	yes / no	
Naphthalin / Naphthalene	13	Modifications: according to recommendation by DLA instead of 0,5 g of sample the total amount of 3,1533 g was extracted with 20 ml toluene (1 h at 60 °C ultrasonic bath). Dilution in 10 ml beaker plus 0,125 ml IS-solution: 1:5; 1:10 and 1:50	GC MS	Std from Ehrenstorfer	No, because of low sample amount of batch 2; samples 69 and 11 were too inhomogenous. Recovery could not valuated.	yes	
	14	AfPS GS 2014	GC-MS/MS			yes	
	15	solvent toluene, UB	GC/MS		no	yes	
	16	In general: sample weight 0,5g, extraction with 20ml toluene		7 Point Calibration		yes	In general: results of batch 2 were only the half of the first measurements. For batch 2 sample were extracted as the first samples. 5 days later the note for extraction came from DLA. It was too late for doing this. It would have been better to get this not along with the second batch.
	17	by SPE		IS: Naphthalene-d8	no	no	



Notes of the participants to specific parameters

Parameter	Participant	Remarks about sample preparation*	Method description*	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
	8		GC-MS/MS		yes / no	yes / no	
Chryen to Benzoperlyen	9	silica gel clean-up	ZB-35, GC-MSMS	0.05 - 2 mg/kg (for 0.5 g sample weight); PAH Mix EU 15+1 plus Benzo[e]pyrene	yes	yes	total amount each (3 g) extracted with 20 mL toluene, dilution 1:6, partly further diluted

Parameter	Participant	Remarks about sample preparation*	Method description*	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
					yes / no	yes / no	
all parameters: notes to internal standards	17			IS: Anthracene-d10: Acenaphthylene to Chrysene the same internal standard, IS: Triphenylbenzene: Benzoanthracene to Benzoperlyene the same internal standard			
Benzo[k]fluoranthene	17						The Benzofluoranthenes were not separated to the baseline, joint integration
Indeno[1,2,3-cd]pyrene/ Dibenzo[a,h]anthracene	17						Indeno[1,2,3-cd]pyrene/ Dibenzo[a,h]anthracene were not separated to the baseline, joint integration

Parameter	Participant	Remarks about sample preparation*	Method description*	Calibration and reference material	Recovery with same matrix	Method accredited to ISO / IEC 17025	Further remarks
					yes / no	yes / no	
Summe 18 PAK / Sum 18 PAH	11			5-Point calibration, 5 internal Standards			

## **5.2 Homogeneity**

### **5.2.1 Homogeneity of bottled PT samples**

Homogeneity test of batch 2 with determination as sum parameter by means of photometric measurement at 400 nm after toluene extraction:

Replicate measurements		rel. units
Sample No.	1	101,1
Sample No.	2	115,5
Sample No.	3	90,2
Sample No.	4	95,5
Sample No.	5	97,7

General average                      100,0  
Repeatability standard deviation      9,5      9,5%

**5.3 Kernel Density Plots of Results**

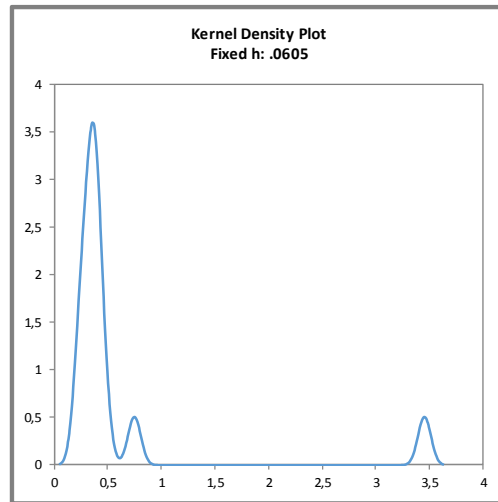
**Abbildungen:**

Kerndichte-Schätzungen der Teilnehmerergebnisse (mit  $h = 0,75 \times \sigma_{pt}$  von  $X_{pt}$ )

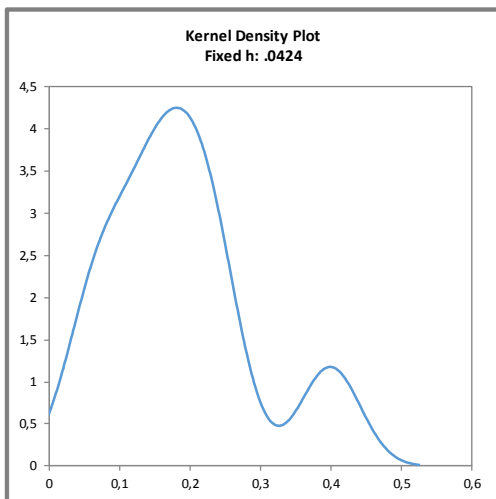
**Figures:**

Kernel density plots of participants' results (with  $h = 0,75 \times \sigma_{pt}$  of  $X_{pt}$ )

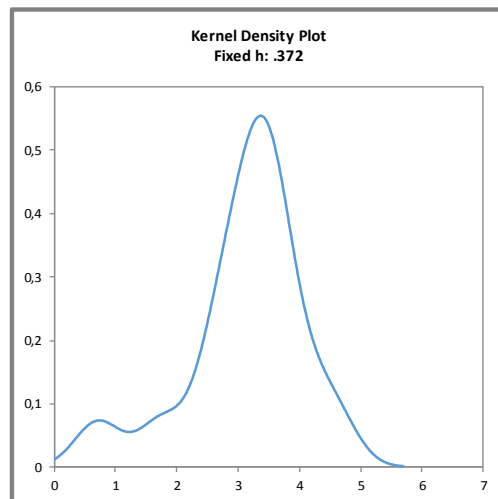
Acenaphthen (e)



Naphthalin (e)



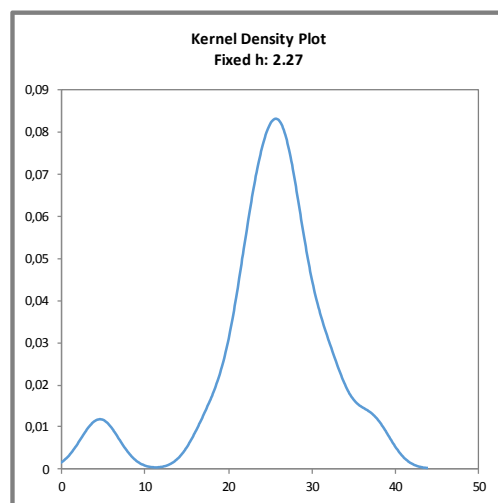
Fluoren (e)



Acenaphthylen (e)

< 8 Ergebnisse  
< 8 Results

Phenanthren (e)



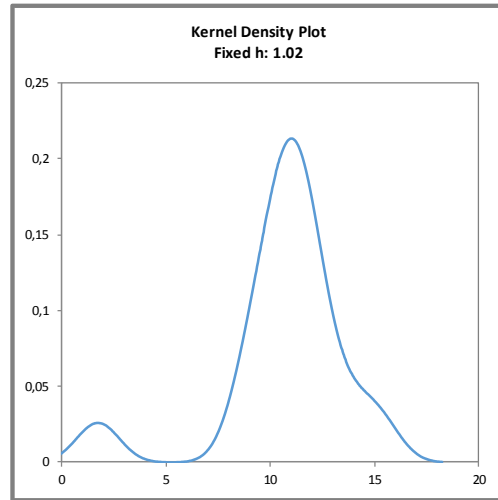
**Abbildungen:**

Kerndichte-Schätzungen der Teilnehmerergebnisse (mit  $h = 0,75 \times \sigma_{pt}$  von  $X_{pt}$ )

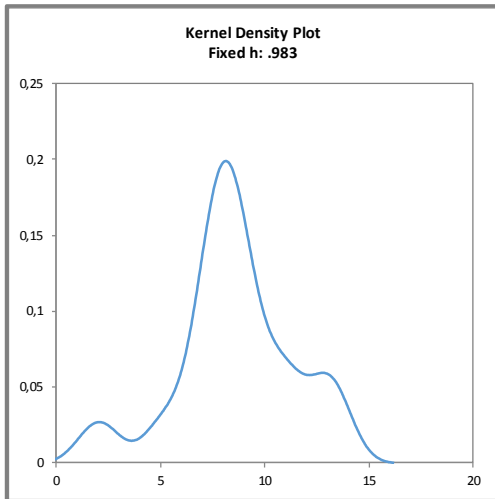
**Figures:**

Kernel density plots of participants' results (with  $h = 0,75 \times \sigma_{pt}$  of  $X_{pt}$ )

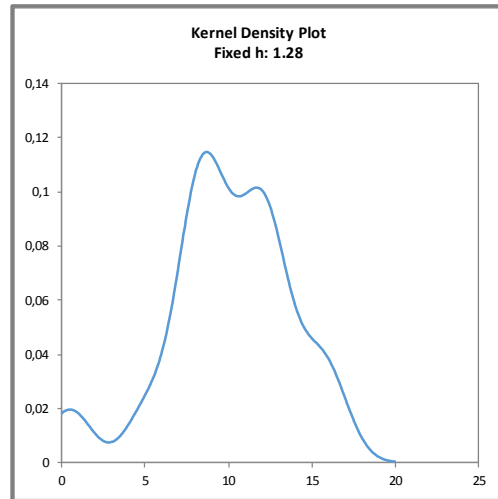
Pyren (e)



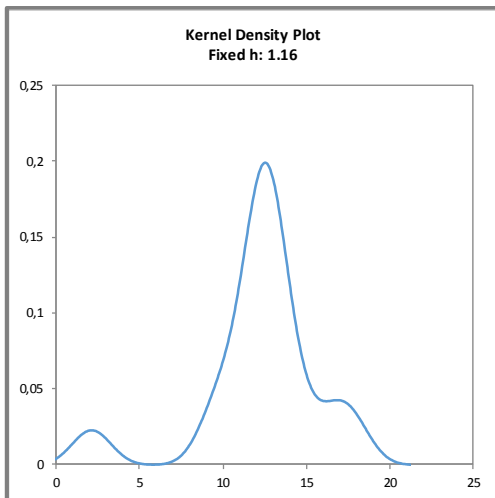
Anthracen (e)



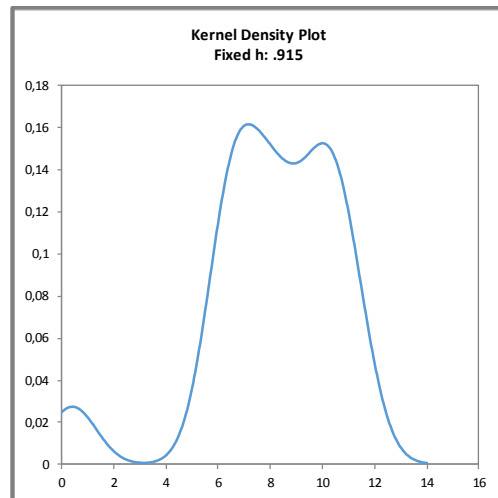
Chrysen (e)



Fluoranthen (e)



Benzo[a]anthracen (e)



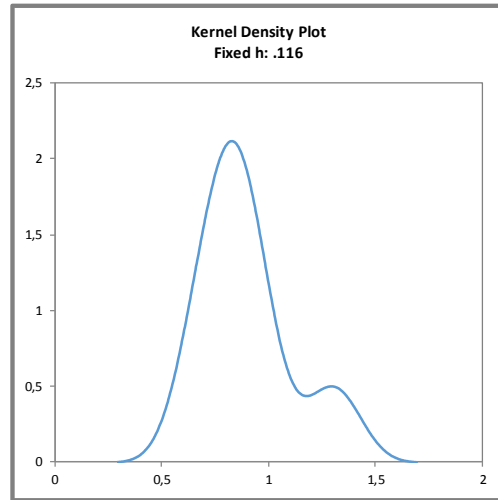
**Abbildungen:**

Kerndichte-Schätzungen der Teilnehmerergebnisse (mit  $h = 0,75 \times \sigma_{pt}$  von  $X_{pt}$ )

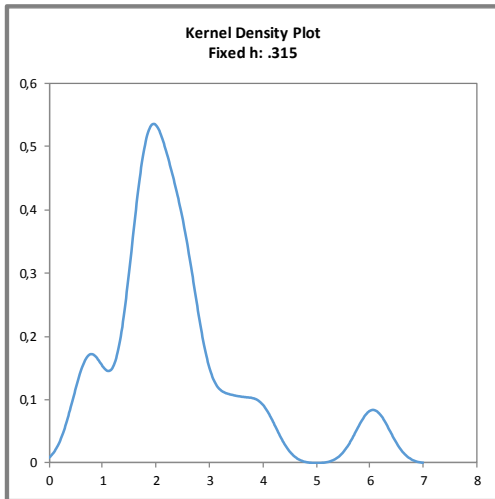
**Figures:**

Kernel density plots of participants' results (with  $h = 0,75 \times \sigma_{pt}$  of  $X_{pt}$ )

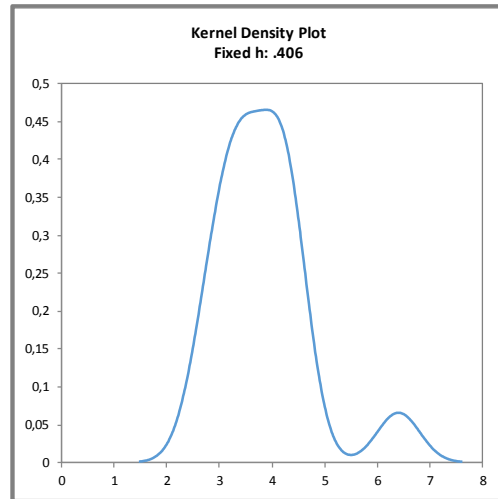
Benzo[k]fluoranthen (e)



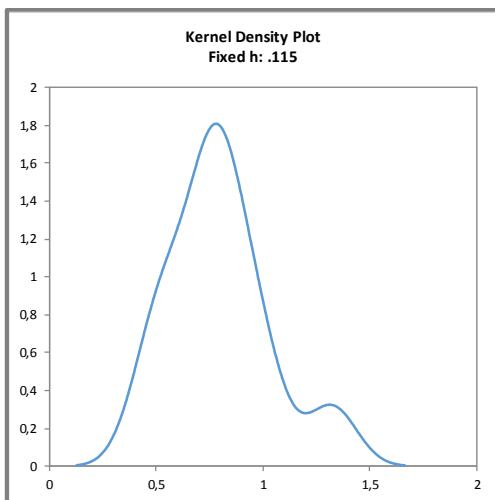
Benzo[b]fluoranthen (e)



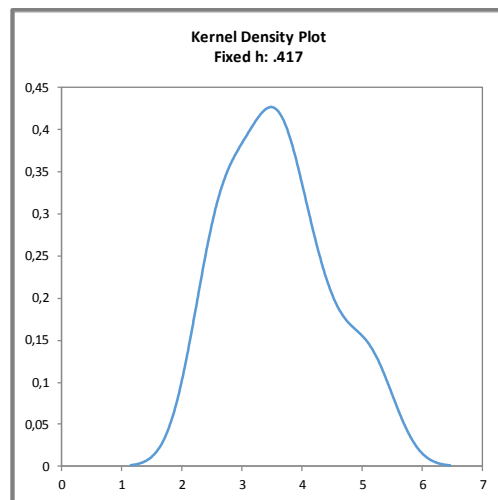
Benzo[a]pyren (e)



Benzo[j]fluoranthen (e)



Benzo[e]pyren (e)



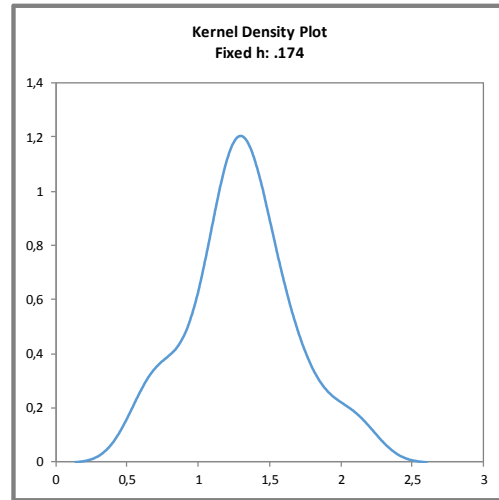
**Abbildungen:**

Kerndichte-Schätzungen der Teilnehmerergebnisse (mit  $h = 0,75 \times \sigma_{pt}$  von  $X_{pt}$ )

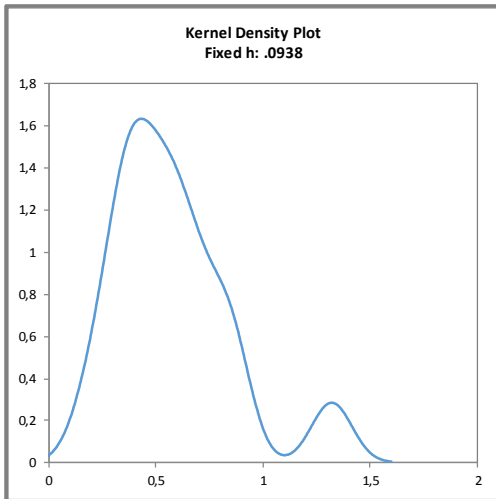
**Figures:**

Kernel density plots of participants' results (with  $h = 0,75 \times \sigma_{pt}$  of  $X_{pt}$ )

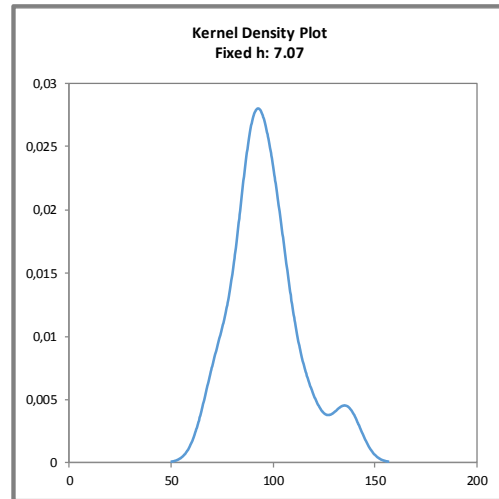
Benzo[ghi]perylen (e)



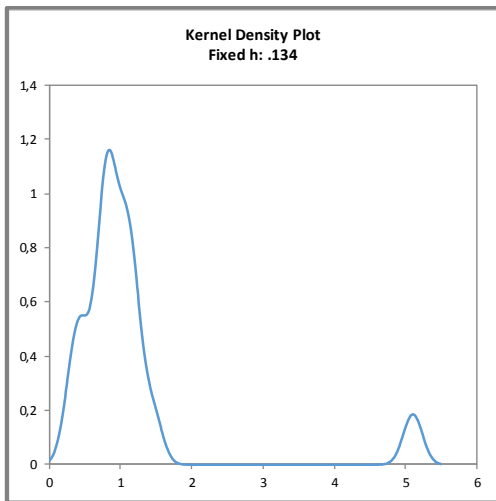
Dibenzo[ah]anthracen (e)



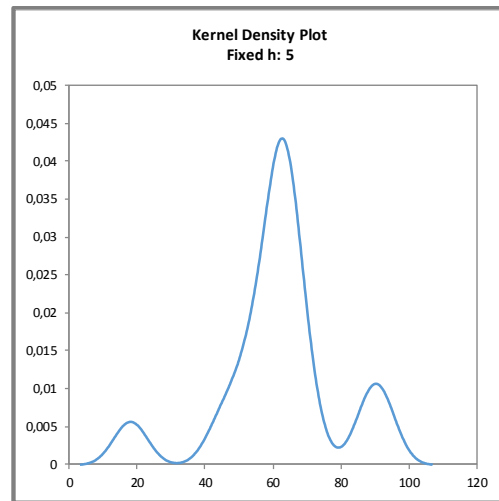
Summe 18 PAK / Sum 18 PAH



Indeno[1,2,3 cd]pyren (e)



Summe 7 PAK / Sum 7 PAH



**5.4 Information on the Proficiency Test (PT)**

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

<i>PT number</i>	<b>DLA 57-2018</b>
<i>PT name</i>	<b>Children's Product I: PAH in Plastic Children's Toy Product</b>
<i>Sample matrix*</i>	<i>Samples I + II: a mixture of plastic and rubber parts</i>
<i>Number of samples and sample amount</i>	<i>2 identical samples I + II, 3 g each.</i>
<b>Storage</b>	<i>Samples I + II: room temperature</i>
<i>Intentional use</i>	<i>Laboratory use only (quality control samples)</i>
<i>Parameter</i>	<i>quantitative: Polycyclic Aromatic Hydrocarbons (PAH) to be determined, as individual compounds as well as the sums of 18 PAH and 7 PAH, see result submission file</i>
<i>Methods of analysis</i>	<i>For determination of PAH the method of the Product Safety Commission of the Federal Institute for Occupational Safety and Health (AfPS 2014: 01 PAK) should be applied or an equivalent method may be used.</i>
<i>Notes to analysis</i>	<i>The analysis of PT samples should be performed like a routine laboratory analysis. In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights. For the present material we recommend to mix the whole sample amount.</i>
<i>Result sheet</i>	<i>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.</i>
<i>Units</i>	<i>mg/kg</i>
<i>Number of significant digits</i>	<i>at least 2</i>
<i>Further information</i>	<i>For information please specify:</i> <ul style="list-style-type: none"> <li>- <i>Date of analysis</i></li> <li>- <i>DLA-sample-numbers (for sample I and II)</i></li> <li>- <i>Limit of detection</i></li> <li>- <i>Assignment incl. Recovery</i></li> <li>- <i>Recovery with the same matrix</i></li> <li>- <i>Method is accredited</i></li> </ul>
<i>Result submission</i>	<i>The result submission file should be sent by e-mail to: <b>pt@dla-lvu.de</b></i>
<i>Deadline</i>	<b><i>the latest 26<sup>th</sup> October 2018</i></b>
<i>Evaluation report</i>	<i>The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.</i>
<i>Coordinator and contact person of PT</i>	<i>Matthias Besler-Scharf, PhD</i>

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

## 6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		SWITZERLAND
		Germany
		HUNGARY
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		Germany
		POLAND
		Germany
		Germany

*[Die Adressdaten der Teilnehmer wurden für die allgemeine Veröffentlichung des Auswertebereichs nicht angegeben.]*

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



## 7. Index of 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 Methodenvalidierung / DIN ISO 5725 series part 1, 2 and 6 Accuracy (trueness and precision) of measurement methods and results
5. Verordnung / Regulation 882/2004/EU; Verordnung über amtliche Kontrollen zur Überprüfung der Einhaltung des Lebensmittel- und Futtermittelrechts sowie der Bestimmungen über Tiergesundheit und Tierschutz / Regulation on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules
6. Evaluation of analytical methods used for regulation of food and drugs; W. Horwitz; Analytical Chemistry, 54, 67-76 (1982)
7. The International Harmonised Protocol for the Proficiency Testing of Analytical Laboratories ; J.AOAC Int., 76(4), 926 - 940 (1993)
8. A Horwitz-like funktion describes precision in proficiency test; M. Thompson, P.J. Lowthian; Analyst, 120, 271-272 (1995)
9. Protocol for the design, conduct and interpretation of method performance studies; W. Horwitz; Pure & Applied Chemistry, 67, 331-343 (1995)
10. Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing; M. Thompson; Analyst, 125, 385-386 (2000)
11. The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories; Pure Appl Chem, 78, 145 - 196 (2006)
12. AMC Kernel Density - Representing data distributions with kernel density estimates, amc technical brief, Editor M Thompson, Analytical Methods Committee, AMCTB No 4, Revised March 2006 and Excel Add-in Kernel.xla 1.0e by Royal Society of Chemistry
13. EURACHEM/CITAC Leitfaden, Ermittlung der Messunsicherheit bei analytischen Messungen (2003); Quantifying Uncertainty in Analytical Measurement (1999)
14. GMP+ Feed Certification scheme, Module: Feed Safety Assurance, chapter 5.7 Checking procedure for the process accuracy of compound feed with micro tracers in GMP+ BA2 Control of residues, Version: 1st of January 2015 GMP+ International B.V.
15. MTSE SOP No. 010.01 (2014): Quantitative measurement of mixing uniformity and carry-over in powder mixtures with the rotary detector technique, MTSE Micro Tracers Services Europe GmbH
16. Homogeneity and stability of reference materials; Linsinger et al.; Accred Qual Assur, 6, 20-25 (2001)
17. AOAC Official Methods of Analysis: Guidelines for Standard Method Performance Requirements, Appendix F, p. 2, AOAC Int (2016)
18. AfPS GS 2014:01 PAK: Prüfung und Bewertung von Polzyklischen Aromatischen Kohlenwasserstoffen (PAK) bei der Zuerkennung des GS-Zeichens, Ausschuss für Produktsicherheit (AfPS), GS-Spezifikation / Testing and assessment of polycyclic aromatic hydrocarbons (PAHs) in the course of awarding the GS mark, Product Safety Commission (AfPS), GS Specification
19. DIN EN 15527:2008: Charakterisierung von Abfällen - Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Abfall mittels Gaschromatographie-Massenspektrometrie (GC/MS) / Characterization of waste - Determination of polycyclic aromatic hydrocarbons (PAH) in waste using gas chromatography mass spectrometry (GC/MS)
20. Verordnung / Regulation 1272/2013/EU: zur Änderung von Anhang XVII der Verordnung (EG) Nr. 1907/2006 des Europäischen Parlament und des Rates zur Registrierung, Bewertung, Zulassung und Beschränkung chemischer Stoffe (REACH) hinsichtlich polyzyklischer aromatischer Kohlenwasserstoffe /

amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards polycyclic aromatic hydrocarbons