*Proficiency Tests*

# DLA

**food
cosmetics
consumer goods
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**Evaluation Report**
proficiency test

**DLA 69/2016**

## Contact Material I:

## Release of Elements
## from Food Contact Material

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

| | |
|---|---|
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| *EP-Koordinator*<br>*PT-Coordinator* | Dr. Matthias Besler |
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| *EP-Bericht Freigabe*<br>*PT-Report Authorization* | Dr. Matthias Besler (Technischer Leiter / Technical Manager)<br>*- gezeichnet / signed M. Besler*<br>Dr. Gerhard Wichmann (QM-Beauftragter / Quality Manager)<br>*- gezeichnet / signed G. Wichmann*<br>Datum / Date: 26 January 2017 |
| *Unteraufträge*<br>*Subcontractors* | Die Prüfung der Gehalte, Homogenität und Stabilität von EP-Parametern wird von DLA im Unterauftrag vergeben.<br>The analysis of the content, homogeneity and stability of PT-parameters are subcontracted by DLA. |

# Inhalt / Content

# 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 fillable food contact material made of metal: a small jug with handle, chromium steel 18/0 with a filling volume of 0.03 liters. The material was purchased in the trade by DLA as specimen from one production unit. The scope of determination based on preliminary investigations in accordance with the Resolution of the Council of Europe on metals and alloys in food contact materials and articles (CM / Res (2013) 9 (13)) was narrowed on 6 elements (Cr, Cu, Fe, Ni, Pb, Zn), with determinable levels in the migrate solution.

The jugs were packed into transparent LDPE plastic bags and then labeled.

### 2.1.1 Homogeneity

The suitability of the test material was checked by 5-fold determination of chromium and lead in the respective first eluate by ICP-MS. The repeatability standard deviations of 25 % for lead and 21 % for chromium were in the range of the target standard deviations according to Horwitz and Thompson, respectively. Therefore the homogeneity of the test material was considered acceptable. The results are given in the documentation.

Further, the calculation of the **repeatability standard deviation $S_r$ of the participants** was also used as an indicator of homogeneity. The results for iron (12.3%), chromium (17.3%) and nickel (21.7%) were in the range given by the Resolution of the Council of Europe. The repeatability standard deviations of zinc (35.7%), copper (46.3%), and lead (51.6%) were appreciably higher.

According to the Council of Europe Resolution the predicted within-laboratory standard deviation based on the Horwitz Equation is for concentrations of 10 mg/L 11,3 %, of 1 mg/L 16,0 % and of 100 µg/L 22,6 % [16].

The repeatability standard deviations of participants are given in the statistic data (see 4.1 to 4.6).

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

### 2.1.2 Stability

The test items made of metal (chromium steel) are known to be usually resistant to corrosion at room temperature and dry storage. The stability of the material can be considered given for the examination period of the PT.

## 2.2 Sample shipment and information to the test

Three samples (A, B, and C) of test material were sent to every participating laboratory in the 41$^{th}$ week of 2016. The tests should be finished at 25$^{th}$ November 2016 the latest.

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

*The material is a **fillable chromium steel jug**. Three samples are provided. The specific migration of the elements **Lead, Chromium, Iron, Copper, Nickel** and **Zinc** in part with low contents should be determined.*
*The **below conditions** according to Resolution of the Council of Europe on metals and alloys used in food contact materials (CM/Res(2013)9) for "hot fills" **should be followed**:*

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*1. filling volume: 20 mL,*
*2. simulant to be used: citric acid 5g/L (in water)*
*3. time and temperature: 2 h at 70°C, afterwards 24 h at 40°C*
*4. results given in mg/L.*

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*The results of the first eluate were evaluated. If there were enough results of the second and third eluate, the sum of eluates were evaluated too. For evaluation DLA uses the "final result". Please also indicate the single values for the DLA-sample A, B, and C.*

## 2.3 Submission of results

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

The concentrations of the parameters given in the column "final results" were used for the statistical evaluation. For the calculation of the repeatability– and reproducibility standard deviation the single values were used.

Queried and documented were single results, recovery and the used testing methods.

In case participants submitted several results for the same parameter obtained by different methods these results were evaluated with the same evaluation number with a letter as a suffix and indication of the related method.

All participants submitted the result in time.

# 3. Evaluation

## 3.1  Consensus value from participants (assigned value)

The robust mean of the submitted results was used as assigned value ($X_{pt}$) („consensus value from participants") providing a normal distribution. The calculation was done according to algorithm A as described in annex C of ISO 13528 [3].

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

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

The statistical evaluation is carried out for all the parameters for which a minimum of 7 values are present.

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

## 3.2 Robust standard deviation

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

## 3.3 Repeatability standard deviation

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

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

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

## 3.4 Reproducibility standard deviation

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

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

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

The relative reproducibility standard deviation as a percentage of the mean value is indicated as coefficient of variation $CV_R$ in the table of statistical characteristics in the results section in case single results from participants are available. Its meaning is explained in more detail in 3.9.

## 3.5 Exclusion of results and outliers

Before statistical evaluation obvious blunders, such as those with incorrect units, decimal point errors, and results for a another proficiency test item can be removed from the data set [2]. All results should be given at least with 2 significant digits. Specifying 3 significant digits is usually sufficient.

Results obtained by different analytical methods causing an increased variability and/or a bi- or multimodal distribution of results, are treated separately or could be excluded in case of too few numbers of results. For this results are checked by kernel density estimation [3, 12].

Results are identified as outliers by the use of robust statistics. If a value deviates from the robust mean by more than 3 times the robust standard deviation, it is classified as an outlier [3]. Detected outliers are stated for information only, when z-score are < -2 or > 2. Due to the use of robust statistics outliers are not excluded, provided that no other reasons are present [3].

## 3.6 Target standard deviation (for proficiency assessment)

The target standard deviation of the assigned value $\sigma_{pt}$ (= 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 respectively Horwitz/Thompson (concentration < 120 ppb) is preferably used for the proficiency assessment. It is usually suitable for  for evaluation of interlaboratory studies, where different analytical 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.


*In the present PT for valuation of  Chromium and Iron the target stand-ard deviation according to the general model of Horwitz was applied. For Lead, Copper, Nickel, and Zinc the target standard deviation according to the general model of Horwitz/Thompson was used.(see 3.6.1).*


*Further for Copper the standard uncertainty was considered and the res-ults were evaluated using the z'-Score (s. 3.8).*


*Due to the low number of < 7 the results of eluate 2 and 3 for Lead, Copper, Nickel, and Zinc were not evaluated by means of z-scores.*

### 3.6.1 General model of Horwitz/Thompson

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.

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

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

In the following evaluation the standard target deviation for concentrations <120 µg/kg (or µg/L) is indicated as "standard target deviation using the general model of Thompson" [10].

### 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]:

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

The values given in Table 1 relative repeatability standard deviation ($RSD_r$) and relative reproducibility standard deviation ($RSD_R$) were determined in collaborative trials using the specified methods. As there were no appropriate precision data given in the Resolution of the Council of Europe, precision data for the determination of water were given in the table for comparison [16, 17, 18].

<u>Table 1:</u> Relative repeatability standard deviations (RSD$_r$) and relative reproducibility standard deviations (RSD$_R$) from selected precision experiments and resulting target standard deviations $\sigma_{pt}$ [17, 18].

| Parameter | Matrix | Mean [mg/L] | RSD$_r$ | RSD$_R$ | $\sigma_{pt}$ | Method / Literature |
|---|---|---|---|---|---|---|
| Lead | Waste water | 0.147 | 2.9% | 7.2% | 6.8% | ICP-OES [18] |
| | Drinking water | 0.0184 | 8.2% | 15.8% | 14.3% | ICP-OES [18] |
| | Surface water | 0.0576 | 3.4% | 9.2% | 8.7% | ICP-OES [18] |
| Chromium | Waste water | 0.0983 | 3.3% | 5.6% | 4.9% | ICP-OES [18] |
| | Drinking water | 0.0162 | 3.1% | 9.0% | 8.6% | ICP-OES [18] |
| | Surface water | 0.0302 | 2.1% | 5.8% | 5.4% | ICP-OES [18] |
| Iron | Waste water | 0.817 | 1.8% | 5.9% | 5.7% | ICP-OES [18] |
| | Drinking water | 0.196 | 1.7% | 4.7% | 4.5% | ICP-OES [18] |
| | Surface water | 0.302 | 1.9% | 4.8% | 4.5% | ICP-OES [18] |
| | Mineral water | 13.8 | 2.6% | 4.8% | 4.4% | ICP-OES [17] |
| Copper | Waste water | 1.96 | 1.4% | 4.4% | 4.3% | ICP-OES [18] |
| | Drinking water | 0.634 | 1.2% | 3.7% | 3.6% | ICP-OES [18] |
| | Surface water | 0.802 | 3.9% | 4.8% | 3.6% | ICP-OES [18] |
| Nickel | Waste water | 0.192 | 1.6% | 5.1% | 4.9% | ICP-OES [18] |
| | Drinking water | 0.0259 | 3.8% | 7.4% | 6.7% | ICP-OES [18] |
| | Surface water | 0.0523 | 2.8% | 6.4% | 6.0% | ICP-OES [18] |
| Zinc | Waste water | 1.21 | 2.4% | 5.9% | 5.6% | ICP-OES [18] |
| | Drinking water | 0.124 | 1.9% | 4.9% | 4.6% | ICP-OES [18] |
| | Surface Water | 0.187 | 1.5% | 4.9% | 4.7% | ICP-OES [18] |

*3.6.3 Value by perception*

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

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

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

## 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:

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

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

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

*The z-score valid for the PT evaluation is designated z-score ($\sigma_{pt}$), while the value of z-score (Info) is for information only. The two z-scores are calculated using the different target standard deviations according to 3.6.*

## 3.7.1 Warning and action signals

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

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

Table 2: Characteristics of the present PT (on dark gray) in comparison to previous PTs since 2015 (SD = standard deviation, CV = coefficient of variation)

| Parameter | Matrix | rob. Mean [mg/L] | rob. SD (S*) [mg/L] | rel. SD (VK$_{S*}$) [%] | Quotient S*/$\sigma_{pt}$ | DLA-Report |
|---|---|---|---|---|---|---|
| Chromium | Mug stainless steel | 0.116 | 0.0226 | 19.5 | 0.88 | DLA 48/2015 |
| Chromium | Jug chromium steel | 0.262 | 0.0404 | 15.4 | 0.79 | DLA 69/2016 |
| Iron | Mug stainless steel | 5.13 | 1.55 | 30.2 | 2.0 | DLA 48/2015 |
| Iron | Jug chromium steel | 7.84 | 1.30 | 16.6 | 1.4 | DLA 69/2016 |
| Copper | Mug stainless steel | 0.0324 | 0.0169 | 52.2 | 1.9 | DLA 48/2015 |
| Copper | Jug chromium steel | 0.0582 | 0.0324 | 55.7 | 1.9 | DLA 69/2016 |

## 3.8 z'-Score

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

The calculation is performed by:

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

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

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$_R$)

The coefficient of variation (CV$_R$) of the reproducibility (= relative re-producibility 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$_K$ gives the relative variability within a data region. While a low CV$_R$, e.g. < 5-10% can be taken as evidence for a homogeneous set of results, a CV$_R$ 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 values or the performance evaluation of the participants possibly can not be done [3].

## 3.10 Quotient S*/σ$_{pt}$

Following the HorRat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation S* and target standard deviation σ$_{pt}$ does not exceed the value of 2.
A value > 2 means an insufficient precision, i.e. the analytical method is too variable, or the variation between the test participants is higher than estimated. Thus the comparability of the results is not given [3].

## 3.11 Standard uncertainty

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

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

If U(X$_{pt}$) ≤ 0,3 σ$_{pt}$ the standard uncertainty of the consensus value needs not to be included in the interpretation of the results of the PT [3]. A clear exceeded the value of 0,3 is an indication that the target standard deviation was possibly set too low for the standard uncertainty of the assigned value.

The quotient U(X$_{pt}$)/σ$_{pt}$ is reported in the characteristics of the test.

## 4. Results

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

In the first table the characteristics are listed:

| Statistic Data |
| --- |
| *Number of results* |
| *Number of outliers* |
| Mean |
| Median |
| Robust mean($X_{pt}$) |
| Robust standard deviation (S$^x$) |
| *Number with m replicate measurements* |
| Repeatability standard deviation (S$_r$) |
| Coefficient of Variation (CV$_r$) in % |
| Reproducibility standard deviation (S$_R$) |
| Coefficient of Variation (CV$_R$) in % |
| *Target range:* |
| Target standard deviation $\sigma_{pt}$ 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 ($X_{pt} + 2\sigma_{pt}$') * |
| Variation coefficient V$_K$ in % |
| *Quotient  S\*/$\sigma_{pt}$ or S\*/$\sigma_{pt}$'* |
| *Standard uncertainty U($X_{pt}$)* |
| *Quotient U($X_{pt}$)/$\sigma_{pt}$ or U($X_{pt}$)/$\sigma_{pt}$'* |
| *Number of results in the target range* |
| *Percent in the target range* |

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

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

| Auswerte-nummer | Parameter | Abweichung | z-Score | z-Score | Hinweis |
| --- | --- | --- | --- | --- | --- |
| Evaluation number | [Einheit / Unit] | Deviation | $\sigma_{pt}$ | (Info) | Remark |

## 4.1 Lead in mg/L

### 1. Eluat /1st Eluate

### Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| Number of results | 13 |
| Number of outliers | 0 |
| Mean | 0,0153 |
| Median | 0,0130 |
| **Robust Mean (X)** | **0,0148** |
| **Robust standard deviation (S*)** | **0,00527** |
| Number with 3 replicates | 12 |
| Repeatability SD ($S_r$) | 0,00744 |
| Repeatability ($CV_r$) | 51,6% |
| Reproducibility SD ($S_R$) | – |
| Reproducibility ($CV_R$) | – |
| Target range: | |
| **Target standard deviation $\sigma_{pt}$** | **0,00326** |
| Target standard deviation (for Information) | 0,00483 |
| **lower limit of target range** | **0,00830** |
| **upper limit of target range** | **0,0213** |
| Quotient S*/$\sigma_{pt}$ | 1,6 |
| Standard uncertainty $U_{(Xpt)}$ | 0,00183 |
| Quotient $U_{(Xpt)}$/$\sigma_{pt}$ | 0,56 |
| Results in the target range | 10 |
| Percent in the target range | 77% |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Thompson. The distribution of results shows a normal variability. The quotient S*/$\sigma_{pt}$ is less than 2.0. The repeatability standard deviation is higher in comparison to established values obtained by determination methods in water (see 3.6.2). The comparability of results can be regarded as given for used methods and the present range of concentrations.

With 0.56 the quotient $U_{(Xpt)}$/$\sigma_{pt}$ is increased.

77% of results were located in the target range.
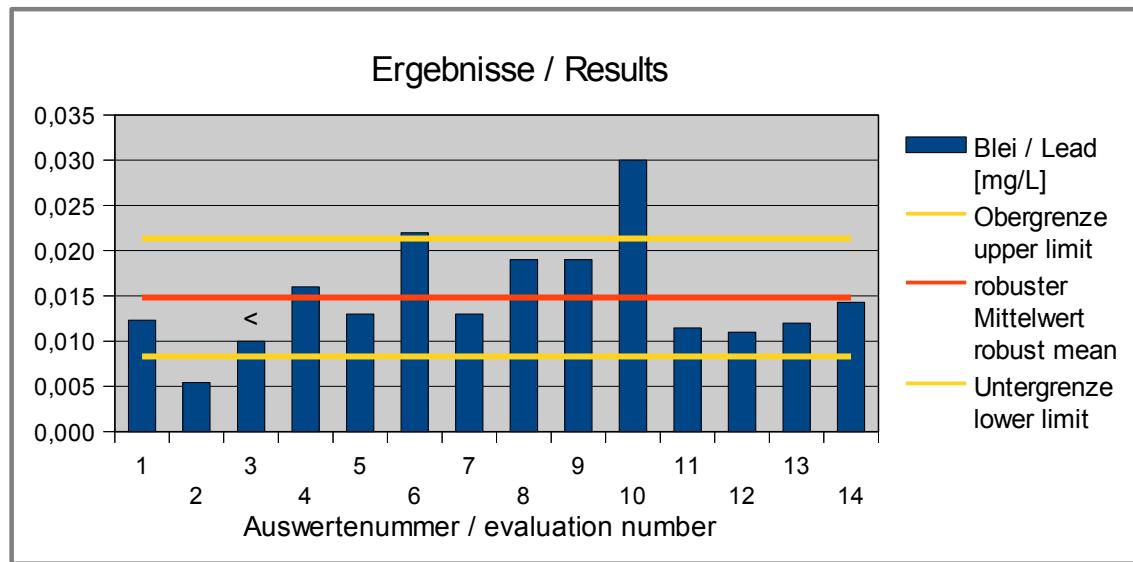
**Abb. / Fig. 1:** Ergebnisse Blei / Results Lead
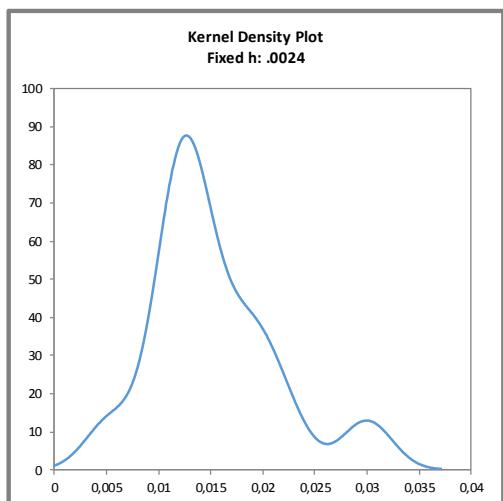


**Abb. / Fig. 2:**
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

Kernel density plot of results
(with h = 0,75 x $\sigma_{pt}$ of $X_{pt}$)

*Comment:*
The kernel density shows nearly a normal distribution of results, con-
taining a side-peak and two shoulders, due to the three results outside
the target range.

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

| Auswerte-nummer<br>Evaluation number | Blei / Lead [mg/L] | | Abweichung [mg/L]<br>Deviation [mg/L] | z-Score<br>($\sigma_{pt}$) | Hinweis<br>Remark |
|:---:|:---:|:---:|:---:|:---:|:---:|
| 1 | | 0,0123 | −0,00251 | −0,8 | |
| 2 | | 0,00541 | −0,00941 | −2,9 | |
| 3 | < | 0,0100 | | | |
| 4 | | 0,0160 | 0,00118 | 0,4 | |
| 5 | | 0,0130 | −0,00182 | −0,6 | |
| 6 | | 0,0220 | 0,00718 | 2,2 | |
| 7 | | 0,0130 | −0,00182 | −0,6 | |
| 8 | | 0,0190 | 0,00418 | 1,3 | |
| 9 | | 0,0190 | 0,00418 | 1,3 | |
| 10 | | 0,0300 | 0,0152 | 4,7 | |
| 11 | | 0,0115 | −0,00337 | −1,0 | |
| 12 | | 0,0110 | −0,00382 | −1,2 | |
| 13 | | 0,0120 | −0,00282 | −0,9 | |
| 14 | | 0,0143 | −0,000524 | −0,2 | |
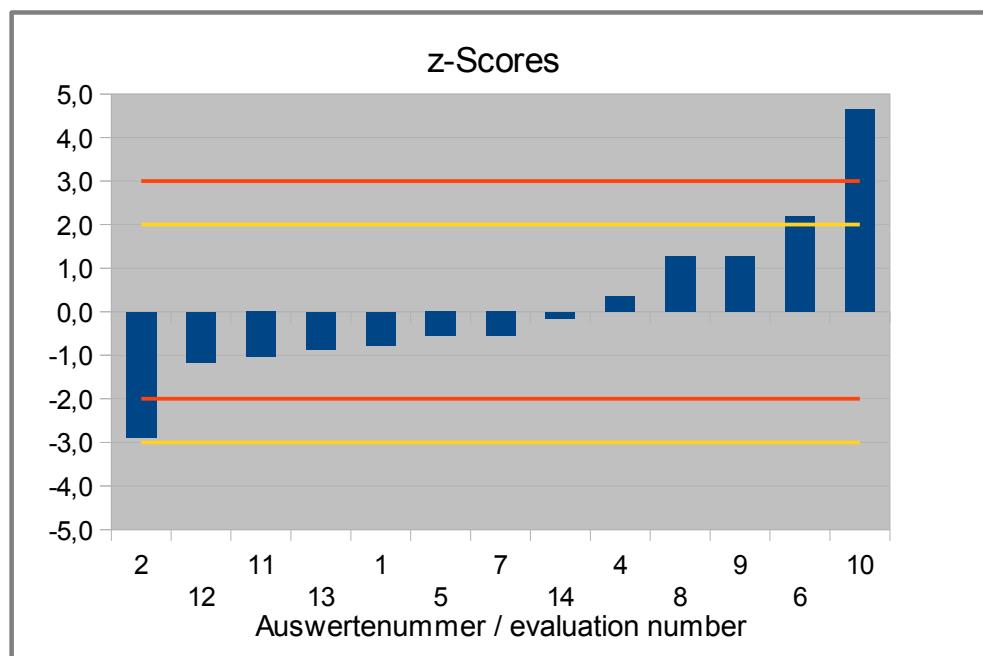


**Abb. / Fig. 3:**   Z-Scores Blei / Lead

## 4.2 Chromium in mg/L

### 1. Eluat /1$^{st}$ Eluate

### Vergleichsuntersuchung / Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 14 |
| *Number of outliers* | 0 |
| Mean | 0,260 |
| Median | 0,257 |
| **Robust Mean (X)** | **0,262** |
| **Robust standard deviation (S*)** | **0,0404** |
| *Number with 3 replicates* | 13 |
| Repeatability SD (S$_r$) | 0,0449 |
| Repeatability (CV$_r$) | 17,3% |
| Reproducibility SD (S$_R$) | 0,0481 |
| Reproducibility (CV$_R$) | 18,5% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,0513** |
| Target standard deviation (for Information) | 0,0530 |
| **lower limit of target range** | **0,160** |
| **upper limit of target range** | **0,365** |
| *Quotient S*/$\sigma_{pt}$* | *0,79* |
| *Standard uncertainty U$_{(Xpt)}$* | *0,0135* |
| *Quotient U$_{(Xpt)}$/$\sigma_{pt}$* | *0,26* |
| *Results in the target range* | *14* |
| *Percent in the target range* | *100%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Horwitz. The distribution of results shows a normal variability. The quotient S*/$\sigma_{pt}$ is less than 2.0. The robust standard deviation is comparable to those of prior PTs (see 3.6.3). The repeatability and reproducibility standard deviation were in the range of established values gained by determination methods in water (see 3.6.2). Thus the comparability of results is given for used methods and the present range of concentrations.

With 0.26 the quotient U$_{(Xpt)}$/$\sigma_{pt}$ is low.

All results were located in the target range.
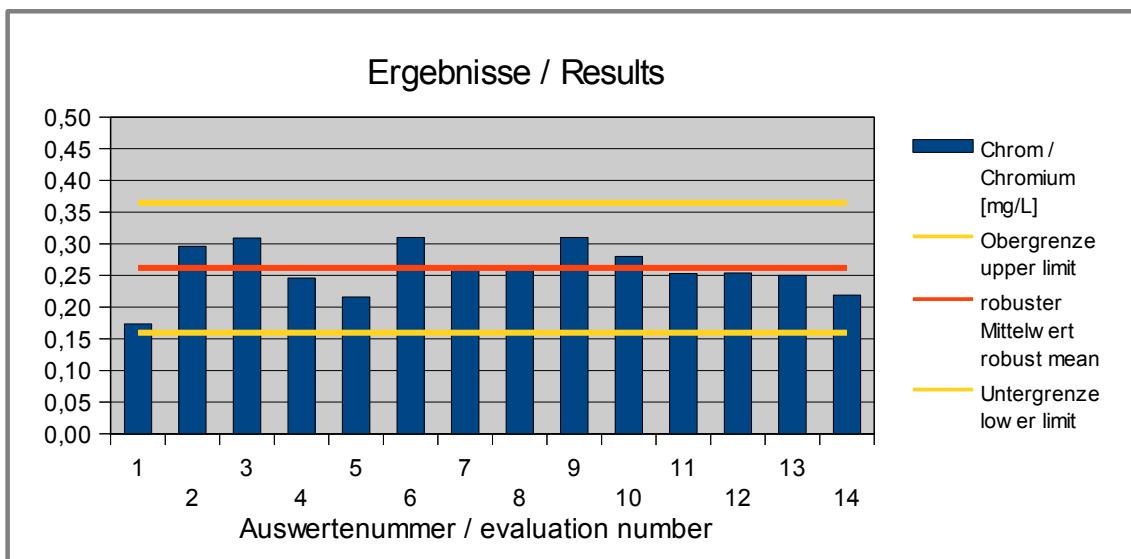
**Abb. / Fig. 4:** Ergebnisse Chrom **/** Results Chromium
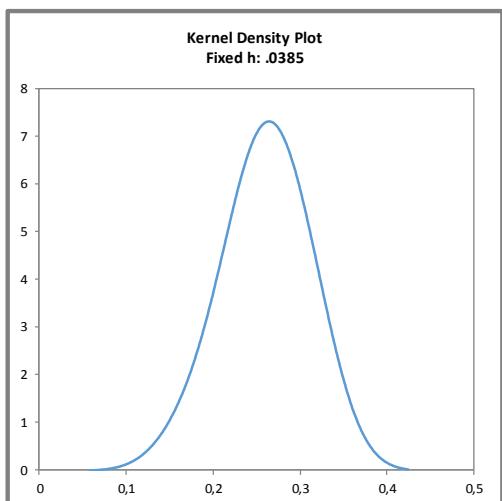


**Abb. / Fig. 5:**
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

Kernel density plot of results
(with h = 0,75 x $\sigma_{pt}$ of $X_{pt}$)

*Comment:*
The kernel density exhibit a normal distribution of results.

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

| Auswerte-nummer Evaluation number | Chrom / Chromium [mg/L] | Abweichung [mg/L] Deviation [mg/L] | z-Score ($\sigma_{pt}$) | Hinweis Remark |
|---|---|---|---|---|
| 1 | 0,173 | -0,0887 | -1,7 | |
| 2 | 0,296 | 0,0338 | 0,7 | |
| 3 | 0,309 | 0,0469 | 0,9 | |
| 4 | 0,246 | -0,0161 | -0,3 | |
| 5 | 0,216 | -0,0461 | -0,9 | |
| 6 | 0,310 | 0,0479 | 0,9 | |
| 7 | 0,260 | -0,00210 | 0,0 | |
| 8 | 0,265 | 0,00290 | 0,1 | |
| 9 | 0,310 | 0,0479 | 0,9 | |
| 10 | 0,280 | 0,0179 | 0,3 | |
| 11 | 0,253 | -0,00910 | -0,2 | |
| 12 | 0,254 | -0,00810 | -0,2 | |
| 13 | 0,250 | -0,0121 | -0,2 | |
| 14 | 0,219 | -0,0431 | -0,8 | |
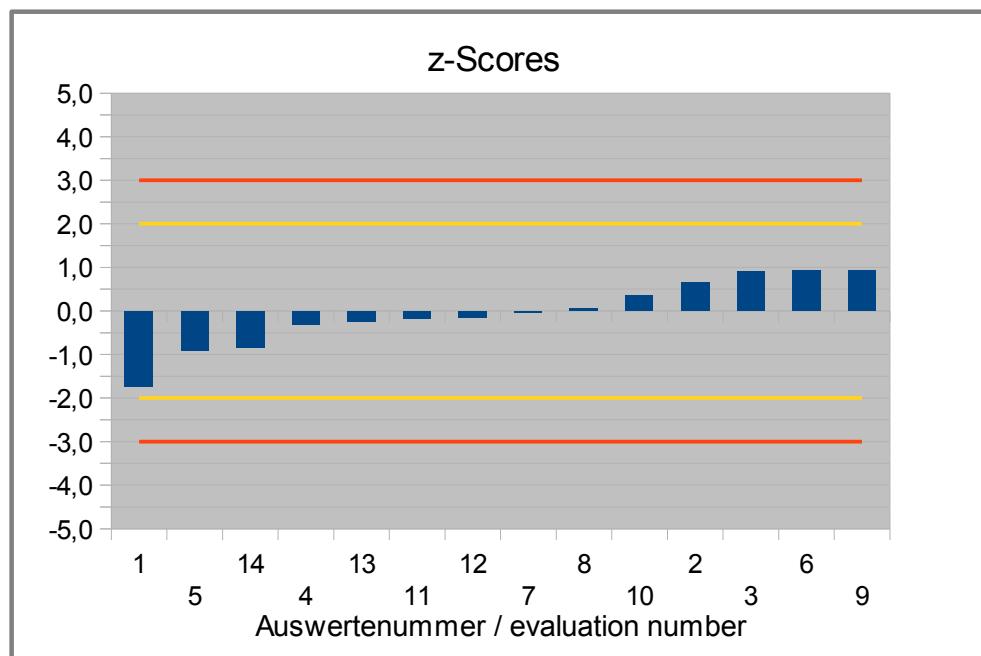


**Abb. / Fig. 6:**   Z-Scores Chrom / Chromium

**Summe der Eluate 1 + 2 / Sum of Eluates 1 + 2**

**Vergleichsuntersuchung / Proficiency Test**

| Statistic Data | |
|---|---|
| *Number of results* | 7 |
| *Number of outliers* | 0 |
| Mean | 0,346 |
| Median | 0,342 |
| **Robust Mean (X)** | **0,347** |
| **Robust standard deviation (S*)** | **0,0824** |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,0651** |
| Target standard deviation (for Information) | 0,0758 |
| **lower limit of target range** | **0,217** |
| **upper limit of target range** | **0,477** |
| *Quotient S*/$\sigma_{pt}$* | *1,3* |
| *Standard uncertainty U(Xpt)* | *0,0389* |
| *Quotient U(Xpt)/$\sigma_{pt}$* | *0,60* |
| *Results in the target range* | 7 |
| *Percent in the target range* | *100%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Horwitz. The distribution of results shows a normal variability. The quotient S*/$\sigma_{pt}$ is less than 2.0. The comparability of results is given for used methods and the present range of concentrations.

With 0.60 the quotient U(Xpt)/$\sigma_{pt}$ is higher than 0.3.

All results were located in the target range.
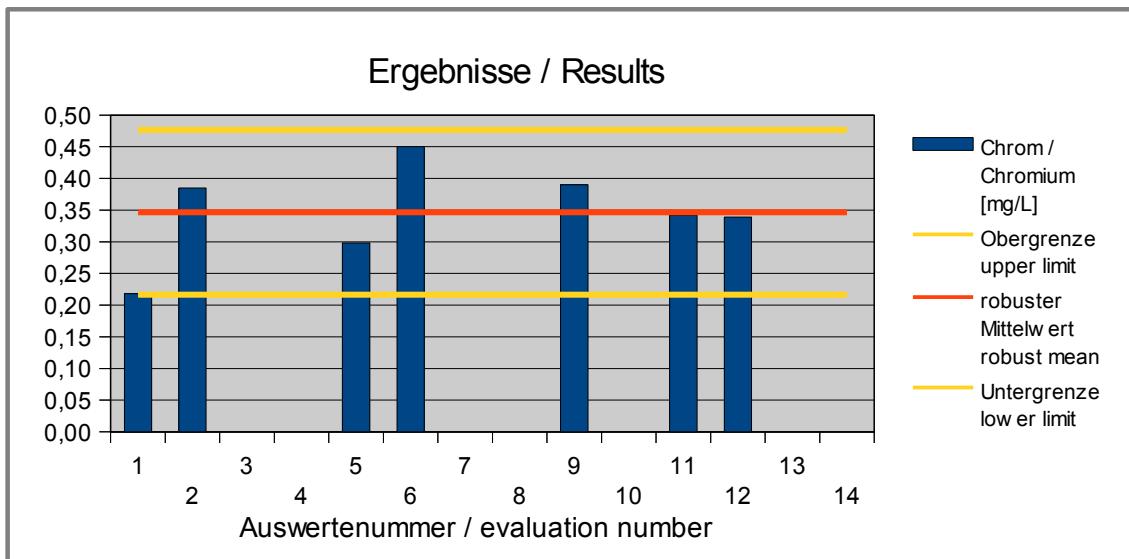
**Abb. / Fig. 7:** Ergebnisse Chrom (Summe der Eluate 1 + 2)/ Results Chromium (Sum of Eluates 1 + 2)

*Comment:*
Due to the low number < 8 of results a kernel density estimation was not done.

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

| Auswerte- nummer / Evaluation number | Chrom / Chromium [mg/L] | | Abweichung [mg/L] / Deviation [mg/L] | z-Score ($\sigma_{pt}$) | Hinweis / Remark |
|:---:|:---:|:---:|:---:|:---:|:---:|
| 1 | 0,218 | * | −0,129 | −2,0 | |
| 2 | 0,385 | * | 0,0382 | 0,6 | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | 0,298 | * | −0,0488 | −0,7 | |
| 6 | 0,450 | * | 0,103 | 1,6 | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | 0,390 | * | 0,0432 | 0,7 | |
| 10 | | | | | |
| 11 | 0,342 | * | −0,00477 | −0,1 | |
| 12 | 0,339 | * | −0,00777 | −0,1 | |
| 13 | | | | | |
| 14 | | | | | |

\* sums of eluates were calculated by DLA
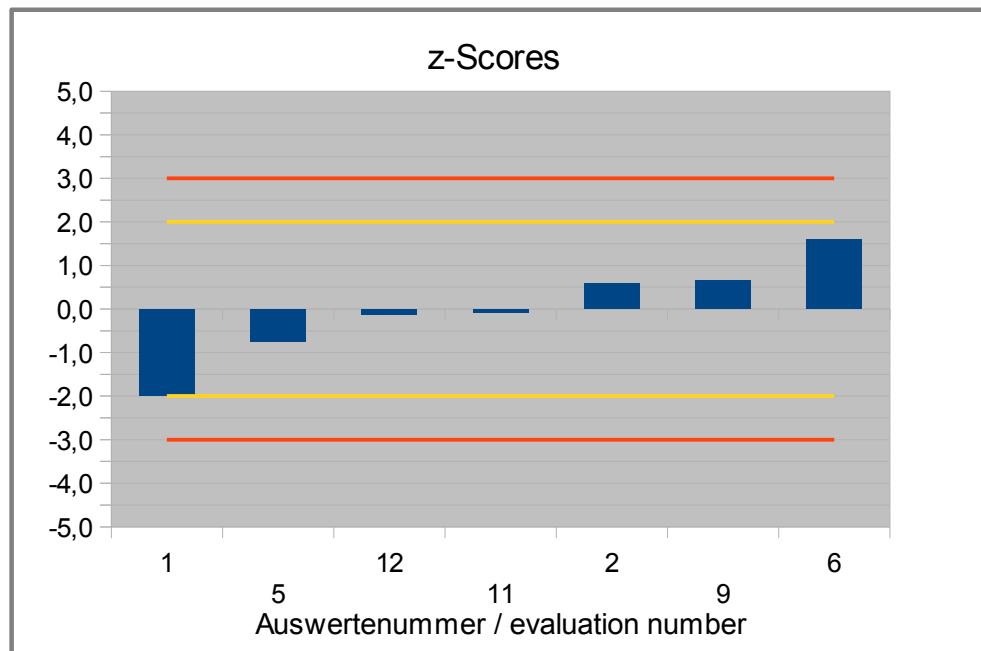


**Abb. / Fig. 8:** Z-Scores Chrom (Summe der Eluate 1 + 2)/ Chromium (Sum of Eluates 1 + 2)

## Summe der Eluate 1 + 2 + 3 / Sum of Eluates 1 + 2 + 3

## Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 7 |
| *Number of outliers* | 0 |
| Mean | 0,406 |
| Median | 0,406 |
| **Robust Mean (X)** | **0,409** |
| **Robust standard deviation (S\*)** | **0,0945** |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,0748** |
| Target standard deviation (for Information) | 0,0871 |
| **lower limit of target range** | **0,259** |
| **upper limit of target range** | **0,558** |
| *Quotient S\*/$\sigma_{pt}$* | *1,3* |
| *Standard uncertainty U$_{(Xpt)}$* | *0,0446* |
| *Quotient U$_{(Xpt)}$/$\sigma_{pt}$* | *0,60* |
| *Results in the target range* | *6* |
| *Percent in the target range* | *86%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Horwitz. The distribution of results shows a normal variability. The quotient S\*/$\sigma_{pt}$ is less than 2.0. The comparability of results is given for used methods and the present range of concentrations.

With 0.60 the quotient U$_{(Xpt)}$/$\sigma_{pt}$ is higher than 0.3.

86% of the results were located in the target range.

**Abb. / Fig. 9:** Ergebnisse Chrom (Summe der Eluate 1 + 2 + 3)/ Results Chromium (Sum of Eluates 1 + 2 + 3)


*Comment:*
Due to the low number < 8 of results the kernel density was not evaluated.

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

| Auswerte- nummer / Evaluation number | Chrom / Chromium [mg/L] | | Abweichung [mg/L] / Deviation [mg/L] | z-Score (σpt) | Hinweis / Remark |
|---|---|---|---|---|---|
| 1 | 0,246 | * | −0,163 | −2,2 | |
| 2 | 0,449 | * | 0,0402 | 0,5 | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | 0,355 | * | −0,0538 | −0,7 | |
| 6 | 0,533 | * | 0,124 | 1,7 | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | 0,450 | * | 0,0412 | 0,6 | |
| 10 | | | | | |
| 11 | 0,406 | * | −0,00280 | 0,0 | |
| 12 | 0,401 | * | −0,00780 | −0,1 | |
| 13 | | | | | |
| 14 | | | | | |

* sums of eluates were calculated by DLA
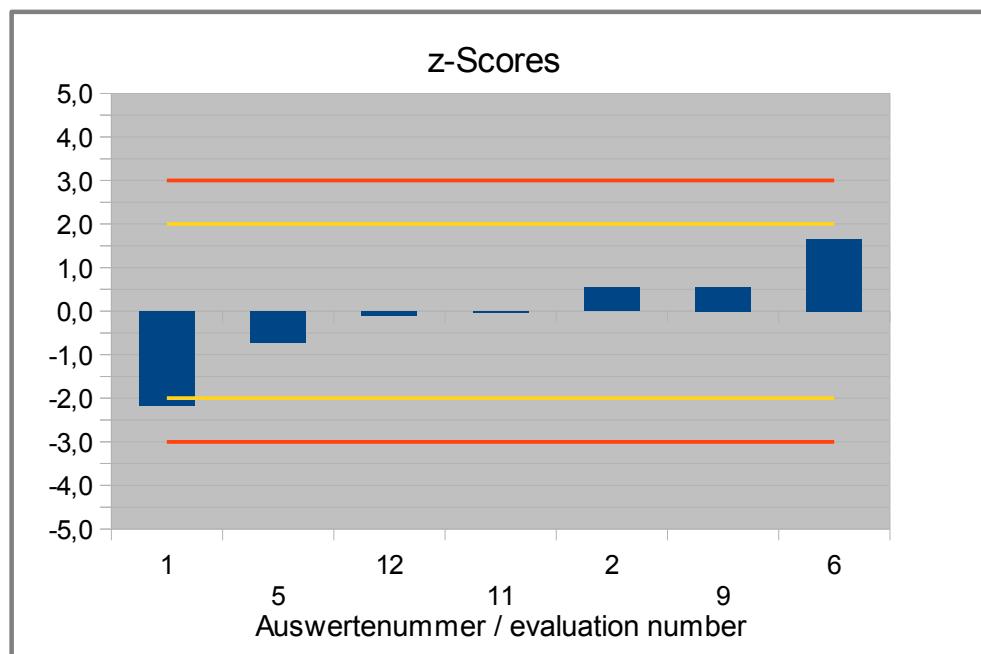


**Abb. / Fig. 10:** Z-Scores Chrom (Summe der Eluate 1 + 2 + 3)/ Chromium (Sum of Eluates 1 + 2 + 3)

## 4.3 Iron in mg/L

### 1. Eluat /1st Eluate

### Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 13 |
| *Number of outliers* | 0 |
| Mean | 7,73 |
| Median | 8,08 |
| **Robust Mean (X)** | **7,84** |
| **Robust standard deviation (S*)** | **1,30** |
| *Number with 3 replicates* | 12 |
| Repeatability SD ($S_r$) | 0,962 |
| Repeatability ($CV_r$) | 12,3% |
| Reproducibility SD ($S_R$) | 1,55 |
| Reproducibility ($CV_R$) | 19,9% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,920** |
| Target standard deviation (for Information) | 1,03 |
| **lower limit of target range** | **6,00** |
| **upper limit of target range** | **9,68** |
| *Quotient S*/$\sigma_{pt}$* | *1,4* |
| *Standard uncertainty U$_{(Xpt)}$* | *0,452* |
| *Quotient U$_{(Xpt)}$/$\sigma_{pt}$* | *0,49* |
| *Results in the target range* | *10* |
| *Percent in the target range* | *77%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Horwitz. The distribution of results shows a normal variability. The quotient S*/$\sigma_{pt}$ is less than 2.0. The robust standard deviation is comparable to those of prior PTs (see 3.6.3). The repeatability and reproducibility standard deviation were in the range of established values gained by determination methods in water (see 3.6.2). Thus the comparability of results is given for used methods and the present range of concentrations.

With 0.49 the quotient U$_{(Xpt)}$/$\sigma_{pt}$ is higher than 0.3.

77% of the results were located in the target range.
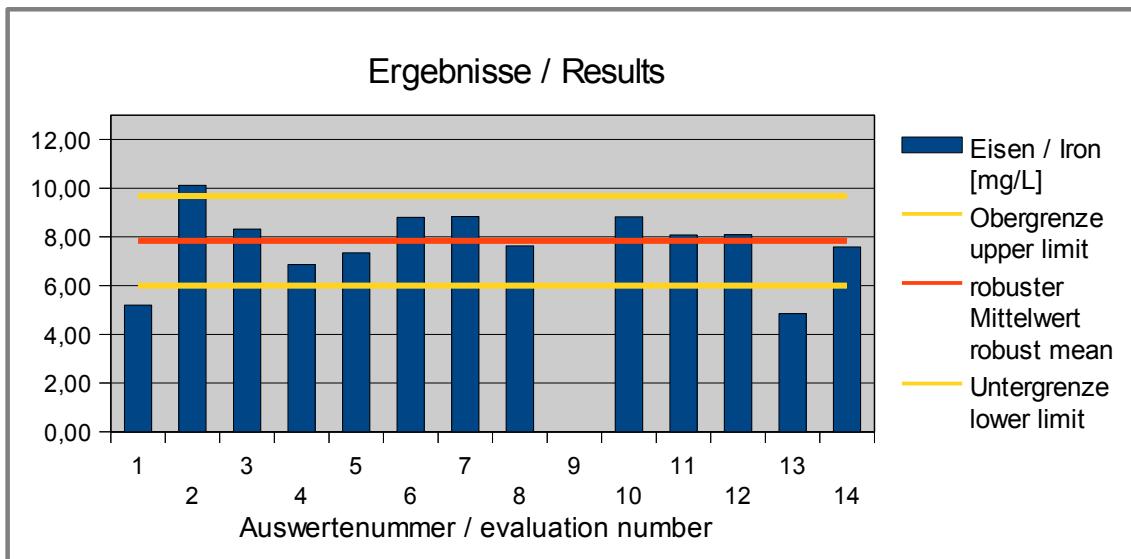
**Abb. / Fig. 11:** Ergebnisse Eisen **/** Results Iron
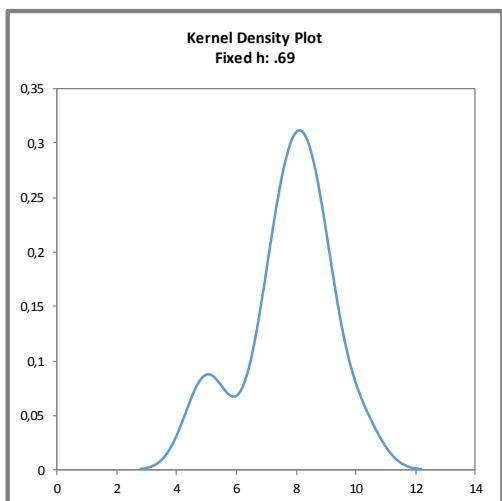


**Abb. / Fig. 12:**
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x $\sigma_{pt}$ von X$_{pt}$)

Kernel density plot of results
(with h = 0,75 x $\sigma_{pt}$ of X$_{pt}$)

*Comment:*
The kernel density exhibit a normal distribution of results, with a shoulder, due to two results below the target range.

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

| Auswerte-nummer / Evaluation number | Eisen / Iron [mg/L] | Abweichung [mg/L] / Deviation [mg/L] | z-Score ($\sigma_{pt}$) | Hinweis / Remark |
|:---:|:---:|:---:|:---:|:---:|
| 1 | 5,20 | −2,64 | −2,9 | |
| 2 | 10,1 | 2,28 | 2,5 | |
| 3 | 8,32 | 0,472 | 0,5 | |
| 4 | 6,86 | −0,983 | −1,1 | |
| 5 | 7,35 | −0,493 | −0,5 | |
| 6 | 8,80 | 0,957 | 1,0 | |
| 7 | 8,83 | 0,988 | 1,1 | |
| 8 | 7,63 | −0,215 | −0,2 | |
| 9 | | | | |
| 10 | 8,82 | 0,977 | 1,1 | |
| 11 | 8,08 | 0,237 | 0,3 | |
| 12 | 8,09 | 0,249 | 0,3 | |
| 13 | 4,85 | −2,99 | −3,3 | |
| 14 | 7,59 | −0,253 | −0,3 | |
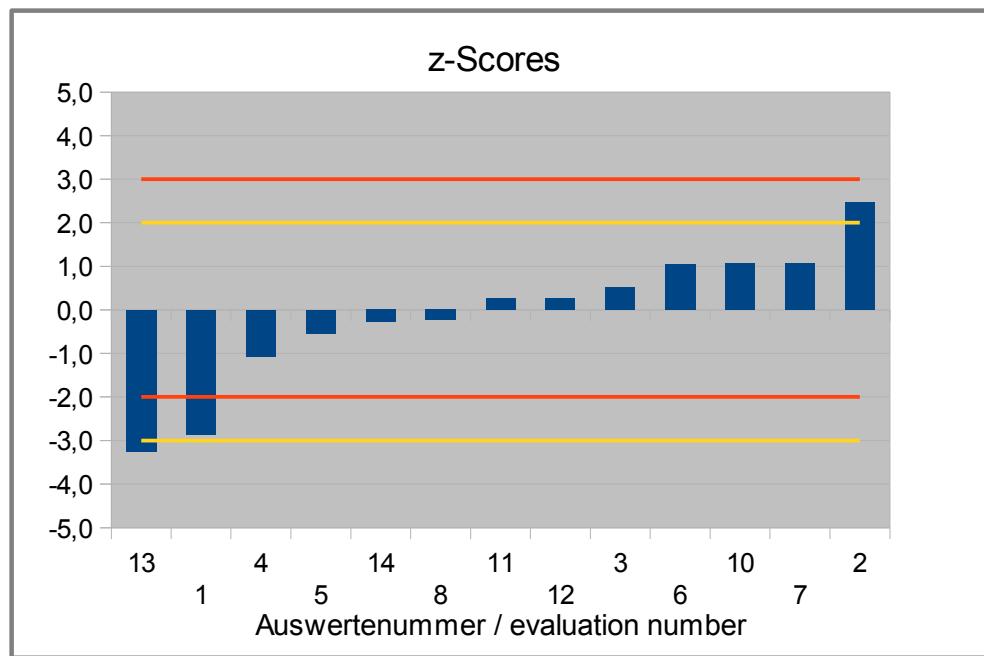


**Abb. / Fig. 13:**   Z-Scores Eisen / Iron

### Summe der Eluate 1 + 2 / Sum of Eluates 1 + 2

### Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 7 |
| *Number of outliers* | 0 |
| Mean | 9,05 |
| Median | 9,19 |
| **Robust Mean (X)** | **9,24** |
| **Robust standard deviation (S*)** | **1,46** |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **1,06** |
| Target standard deviation (for Information) | 1,26 |
| **lower limit of target range** | **7,12** |
| **upper limit of target range** | **11,4** |
| *Quotient S*/$\sigma_{pt}$* | *1,4* |
| *Standard uncertainty U$_{(Xpt)}$* | *0,689* |
| *Quotient U$_{(Xpt)}$/$\sigma_{pt}$* | *0,65* |
| *Results in the target range* | *6* |
| *Percent in the target range* | *86%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Horwitz. The distribution of results shows a normal variability. The quotient S*/$\sigma_{pt}$ is less than 2.0. The comparability of results is given for used methods and the present range of concentrations.

With 0.65 the quotient U$_{(Xpt)}$/$\sigma_{pt}$ is higher than 0.3.

86% of the results were located in the target range.
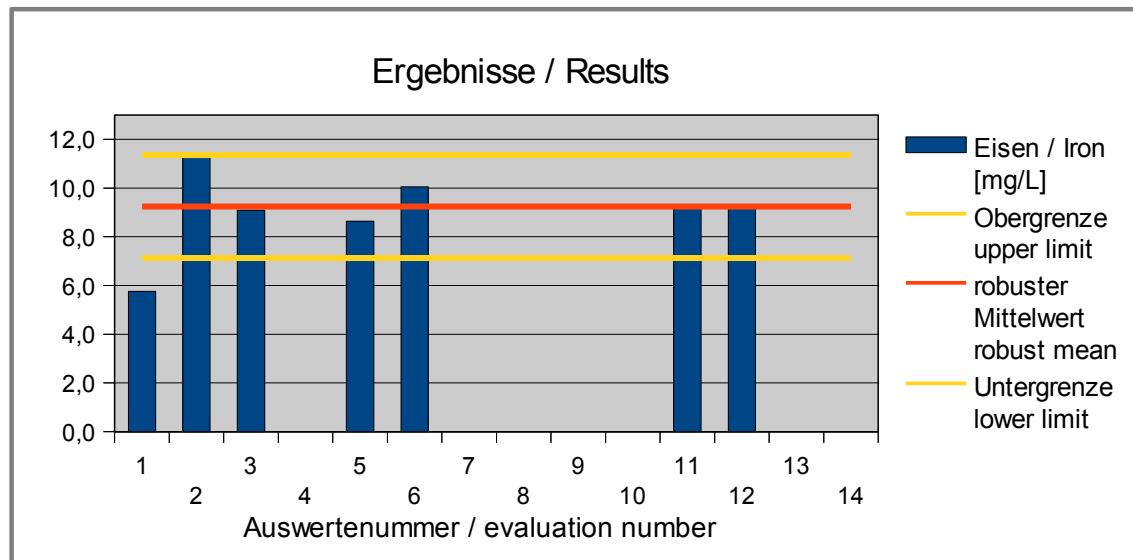
**Abb. / Fig. 14:** Ergebnisse Eisen **(Summe der Eluate 1 + 2)/** Results Iron (Sum of Eluates 1 + 2)

*Comment:*
Due to the low number < 8 of results a kernel density estimation was not done.

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

| Auswerte- nummer / Evaluation number | Eisen / Iron [mg/L] | | Abweichung [mg/L] / Deviation [mg/L] | z-Score ($\sigma_{pt}$) | Hinweis / Remark |
|---|---|---|---|---|---|
| 1 | 5,75 | * | -3,49 | -3,3 | |
| 2 | 11,3 | * | 2,07 | 2,0 | |
| 3 | 9,09 | * | -0,153 | -0,1 | |
| 4 | | | | | |
| 5 | 8,64 | * | -0,596 | -0,6 | |
| 6 | 10,1 | * | 0,811 | 0,8 | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |
| 11 | 9,29 | * | 0,0494 | 0,0 | |
| 12 | 9,19 | * | -0,0446 | 0,0 | |
| 13 | | | | | |
| 14 | | | | | |

* sums of eluates were calculated by DLA
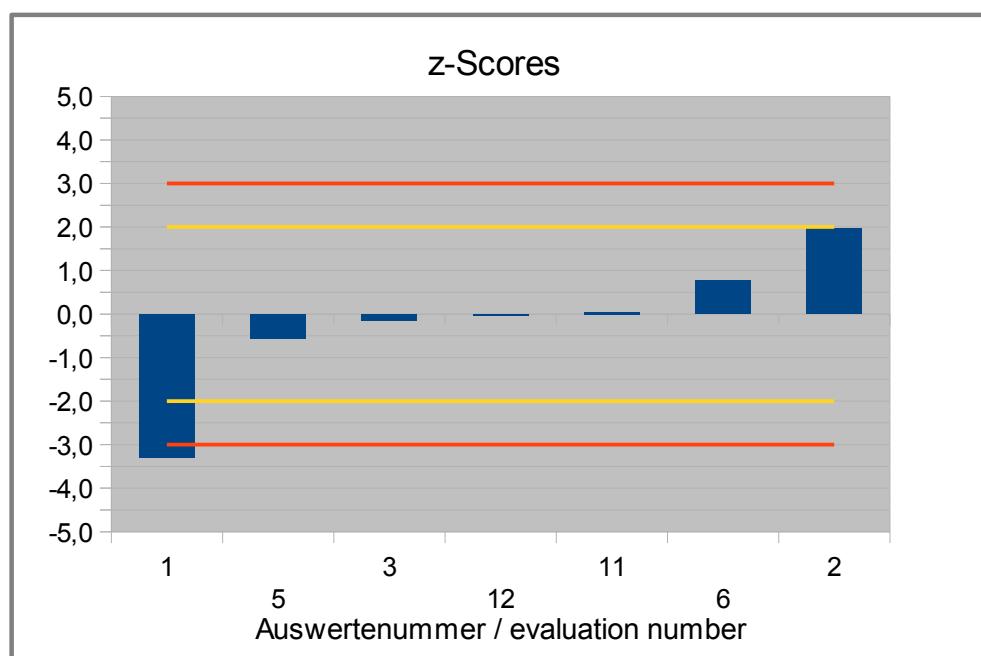


**Abb. / Fig. 15:**   Z-Scores Eisen (Summe der Eluate 1 + 2)/ Iron (Sum of Eluates 1 + 2)

## Summe der Eluate 1 + 2 + 3 / Sum of Eluates 1 + 2 + 3

## Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 7 |
| *Number of outliers* | 0 |
| Mean | 9,68 |
| Median | 9,84 |
| **Robust Mean (X)** | **9,94** |
| **Robust standard deviation (S\*)** | **1,43** |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **1,13** |
| Target standard deviation (for Information) | 1,31 |
| **lower limit of target range** | **7,69** |
| **upper limit of target range** | **12,2** |
| *Quotient S\*/$\sigma_{pt}$* | *1,3* |
| *Standard uncertainty U$_{(Xpt)}$* | *0,677* |
| *Quotient U$_{(Xpt)}$/$\sigma_{pt}$* | *0,60* |
| *Results in the target range* | *6* |
| *Percent in the target range* | *86%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Horwitz. The distribution of results shows a normal variability. The quotient S\*/$\sigma_{pt}$ is less than 2.0. The comparability of results is given for used methods and the present range of concentrations.

With 0.60 the quotient U$_{(Xpt)}$/$\sigma_{pt}$ is higher than 0.3.

86% of the results were located in the target range.

**Abb. / Fig. 16:** Ergebnisse Eisen (Summe der Eluate 1 + 2 + 3)/ Results Iron (Sum of Eluates 1 + 2 + 3)


*Comment:*
Due to the low number < 8 of results a kernel density estimation was not done.

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

| Auswerte-nummer / Evaluation number | Eisen / Iron [mg/L] | | Abweichung [mg/L] / Deviation [mg/L] | z-Score ($\sigma_{pt}$) | Hinweis / Remark |
|---|---|---|---|---|---|
| 1 | 6,03 | * | −3,90 | −3,5 | |
| 2 | 12,1 | * | 2,13 | 1,9 | |
| 3 | 9,67 | * | −0,269 | −0,2 | |
| 4 | | | | | |
| 5 | 9,47 | * | −0,466 | −0,4 | |
| 6 | 10,8 | * | 0,904 | 0,8 | |
| 7 | | | | | |
| 8 | | | | | |
| 9 | | | | | |
| 10 | | | | | |
| 11 | 9,84 | * | −0,0938 | −0,1 | |
| 12 | 9,86 | * | −0,0758 | −0,1 | |
| 13 | | | | | |
| 14 | | | | | |

* sums of eluates were calculated by DLA
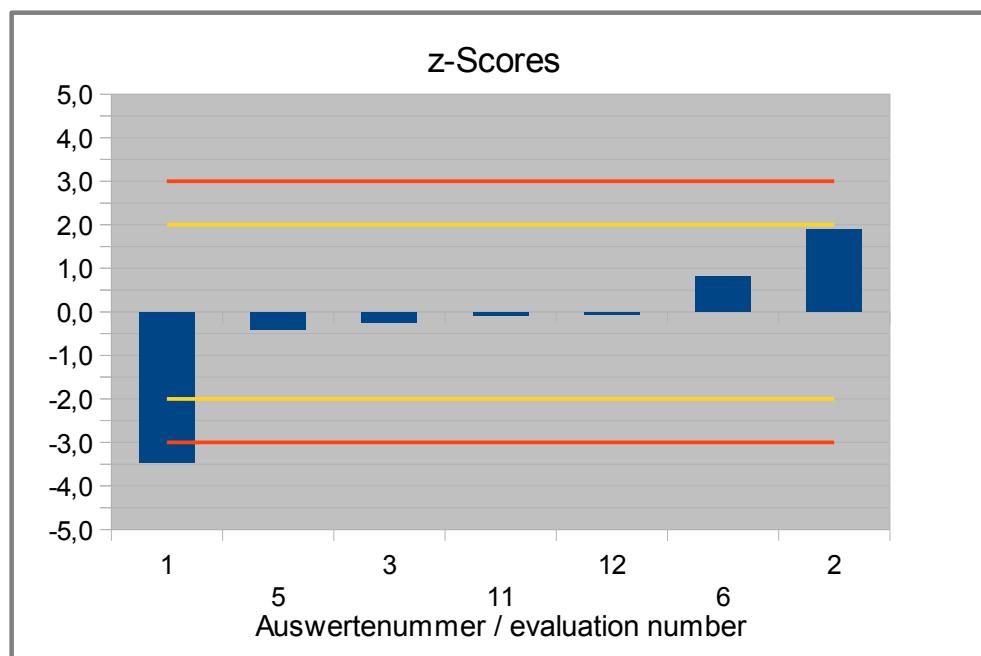


**Abb. / Fig. 17:** Z-Scores Eisen (Summe der Eluate 1 + 2 + 3)/ Iron (Sum of Eluates 1 + 2 + 3)

## 4.4 Copper in mg/L

### 1. Eluat /1st Eluate

### Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 12* |
| *Number of outliers* | 0 |
| Mean | 0,0649 |
| Median | 0,0585 |
| **Robust Mean (X)** | **0,0619** |
| **Robust standard deviation (S*)** | **0,0283** |
| *Number with 3 replicates* | 11 |
| Repeatability SD ($S_r$) | 0,0292 |
| Repeatability ($CV_r$) | 46,3% |
| Reproducibility SD ($S_R$) | 0,0384 |
| Reproducibility ($CV_R$) | 60,9% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt'}$** | **0,0170** |
| Target standard deviation (for Information) | 0,0136 |
| **lower limit of target range** | **0,0279** |
| **upper limit of target range** | **0,0959** |
| *Quotient S*/$\sigma_{pt'}$* | *1,7* |
| *Standard uncertainty $U_{(Xpt)}$* | *0,0102* |
| *Quotient $U_{(Xpt)}/\sigma_{pt'}$* | *0,60* |
| *Results in the target range* | *10* |
| *Percent in the target range* | *83%* |

 * without result from participant no. 13 (excluded before)

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Thompson considering the standard uncertainty. The distribution of results shows a slightly increased variability compared to the standard target deviation according to Thompson. Thus, the standard target deviation $\sigma_{pt'}$ and the z'-Score were used for evaluation.

The quotient  S*/$\sigma_{pt'}$ is less than 2.0. The robust standard deviation is comparable to those of prior PTs (see 3.6.3). The repeatability and re-producibility standard deviation were in the range of established values gained by determination methods in water (see 3.6.2). Thus the comparab-ility of results is given for used methods and the present range of con-centrations.

With 0.60 the quotient $U_{(Xpt)}/\sigma_{pt}$ is increased.

83% of the results were in the target range.
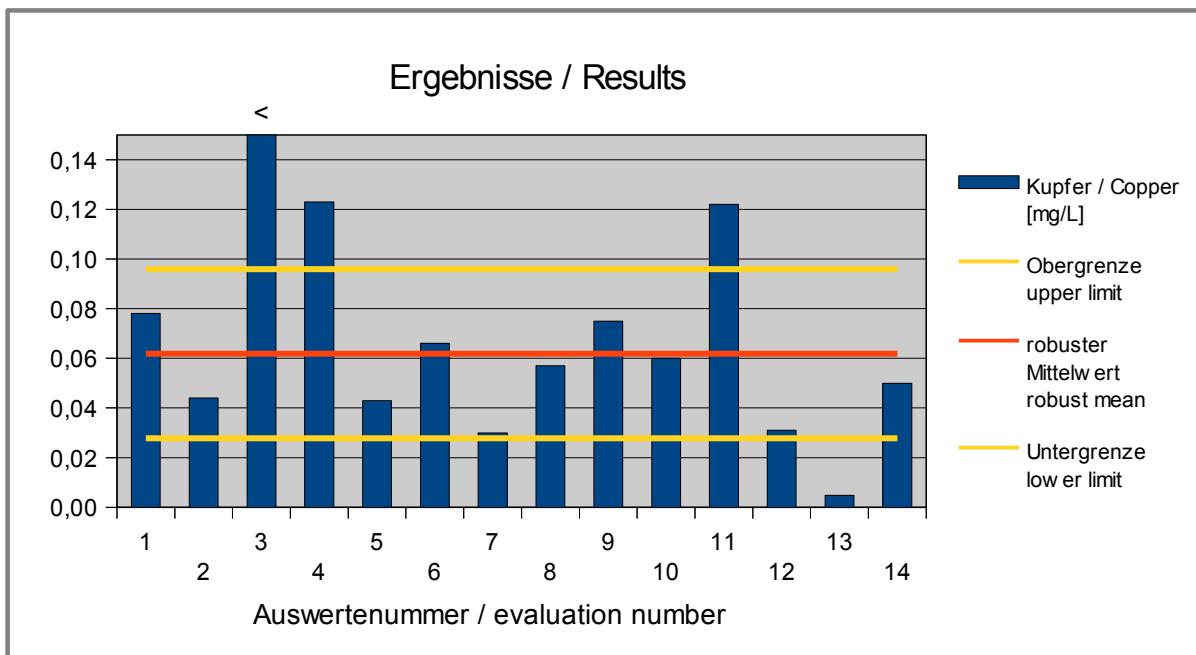
**Abb. / Fig. 18:** Ergebnisse Kupfer **/** Results Copper
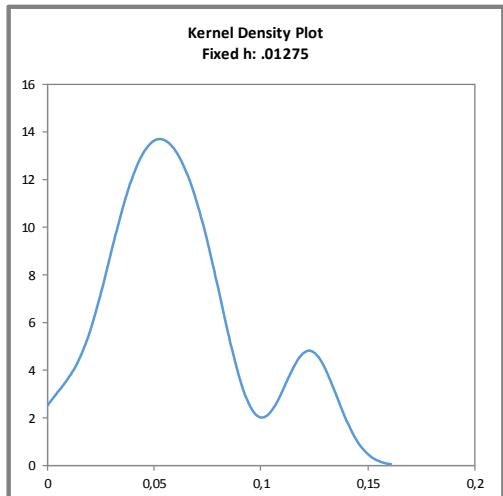


**Abb. / Fig. 19:**
Kerndichte-Schätzung der Ergebnisse
(mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

Kernel density plot of results
(with h = 0,75 x $\sigma_{pt}$ of $X_{pt}$)

*Comment:*
The kernel density shows a normal distribution of results with a shoulder, due to two results above the target range.

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

| Auswerte-nummer / Evaluation number | Kupfer / Copper [mg/L] | Abweichung [mg/L] / Deviation [mg/L] | z'-Score ($\sigma_{pt}$) | z-Score (Info) | Hinweis / Remark |
|---|---|---|---|---|---|
| 1 | 0,0781 | 0,0163 | 1,0 | 1,2 | |
| 2 | 0,0441 | −0,0178 | −1,0 | −1,3 | |
| 3 | < 0,570 | | | | |
| 4 | 0,123 | 0,0611 | 3,6 | 4,5 | |
| 5 | 0,0430 | −0,0189 | −1,1 | −1,4 | |
| 6 | 0,0660 | 0,00414 | 0,2 | 0,3 | |
| 7 | 0,0300 | −0,0319 | −1,9 | −2,3 | |
| 8 | 0,0570 | −0,00486 | −0,3 | −0,4 | |
| 9 | 0,0750 | 0,0131 | 0,8 | 1,0 | |
| 10 | 0,0600 | −0,00186 | −0,1 | −0,1 | |
| 11 | 0,122 | 0,0601 | 3,5 | 4,4 | |
| 12 | 0,0310 | −0,0309 | −1,8 | −2,3 | |
| 13 | 0,00480 | −0,0571 | −3,4 | −4,2 | Ergebnis ausgeschlossen (Faktor 10?) / Result excluded (factor 10?) |
| 14 | 0,0500 | −0,0119 | −0,7 | −0,9 | |
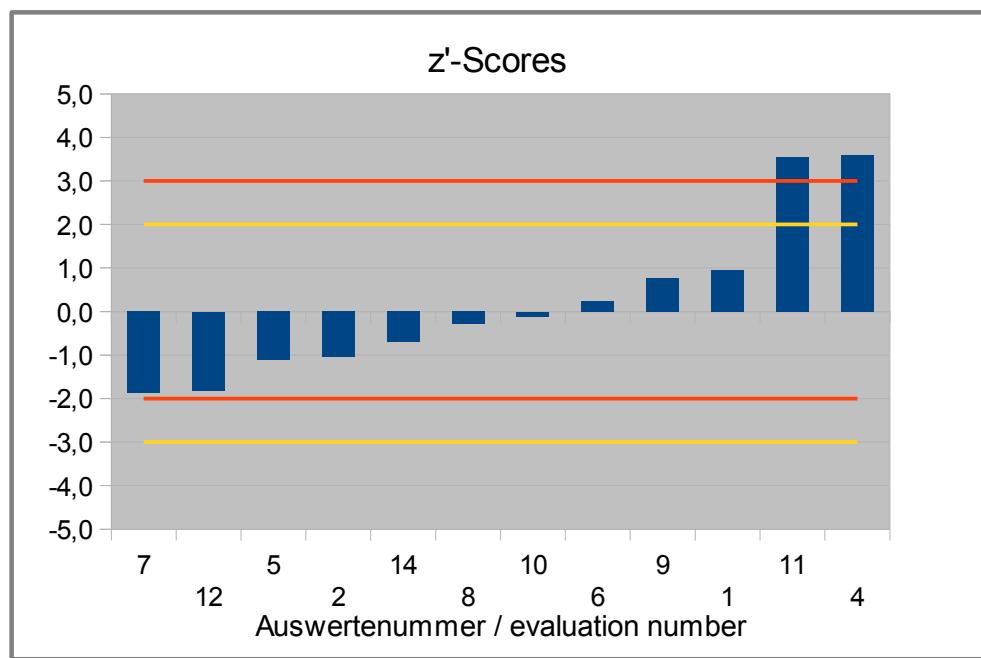


**Abb. / Fig. 20:**  Z`-Scores Kupfer / Copper

## 4.5 Nickel in mg/L

### 1. Eluat /1st Eluate

### Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 13 |
| *Number of outliers* | 0 |
| Mean | 0,0240 |
| Median | 0,0236 |
| **Robust Mean (X)** | **0,0240** |
| **Robust standard deviation (S\*)** | **0,00529** |
| *Number with 3 replicates* | 12 |
| Repeatability SD ($S_r$) | 0,00518 |
| Repeatability ($CV_r$) | 21,7% |
| Reproducibility SD ($S_R$) | 0,00545 |
| Reproducibility ($CV_R$) | 22,8% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,00527** |
| Target standard deviation (for Information) | 0,00558 |
| **lower limit of target range** | **0,0134** |
| **upper limit of target range** | **0,0345** |
| *Quotient S\*/$\sigma_{pt}$* | *1,0* |
| *Standard uncertainty $U_{(Xpt)}$* | *0,00183* |
| *Quotient $U_{(Xpt)}$/$\sigma_{pt}$* | *0,35* |
| *Results in the target range* | *13* |
| *Percent in the target range* | *100%* |

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Thompson. The distribution of results shows a normal variability. The quotient S\*/$\sigma_{pt}$ is less than 2.0.  The repeatability standard deviation is in the range of established values gained by determination methods in water (see 3.6.2). Thus the comparability of results is given for used methods and the present range of concentrations.

With 0.35 the quotient $U_{(Xpt)}$/$\sigma_{pt}$ is slightly increased.

All results were located in the target range.
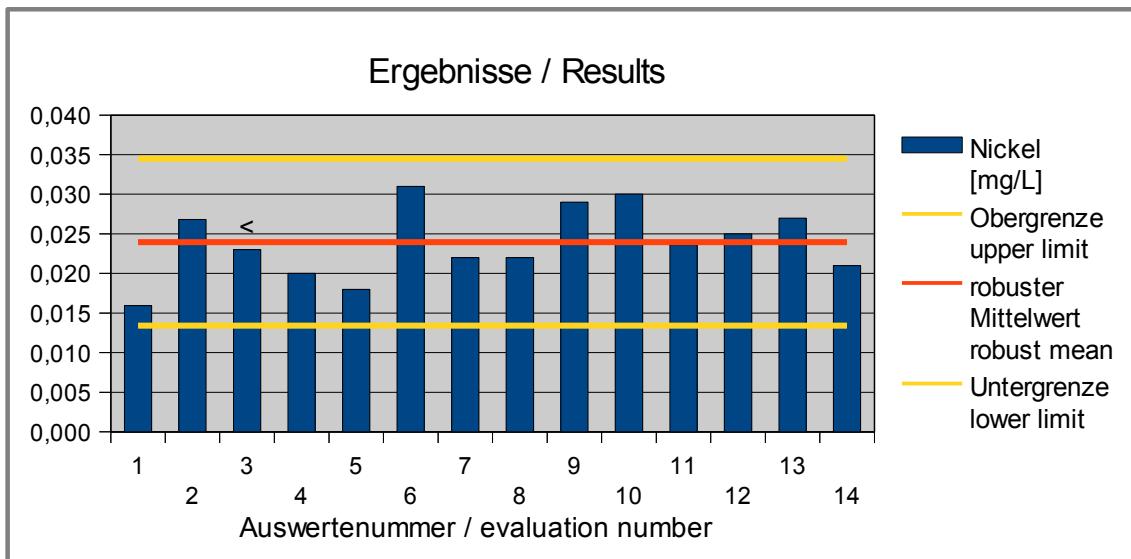
**Abb. / Fig. 21:** Ergebnisse Nickel **/** Results Nickel
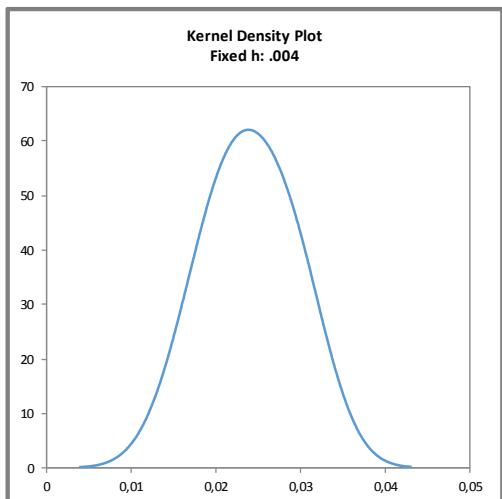


**Abb. / Fig. 22:**
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

Kernel density plot of results (with h = 0,75 x $\sigma_{pt}$ of $X_{pt}$)

*Comment:*
The kernel density exhibit a normal distribution of results.

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

| Auswerte-nummer | Nickel [mg/L] | | Abweichung [mg/L] | z-Score | Hinweis |
|---|---|---|---|---|---|
| Evaluation number | | | Deviation [mg/L] | $(\sigma_{pt})$ | Remark |
| 1 | | 0,0159 | −0,00803 | −1,5 | |
| 2 | | 0,0268 | 0,00287 | 0,5 | |
| 3 | < | 0,0230 | | | |
| 4 | | 0,0200 | −0,00396 | −0,8 | |
| 5 | | 0,0180 | −0,00596 | −1,1 | |
| 6 | | 0,0310 | 0,00704 | 1,3 | |
| 7 | | 0,0220 | −0,00196 | −0,4 | |
| 8 | | 0,0220 | −0,00196 | −0,4 | |
| 9 | | 0,0290 | 0,00504 | 1,0 | |
| 10 | | 0,0300 | 0,00604 | 1,1 | |
| 11 | | 0,0236 | −0,000359 | −0,1 | |
| 12 | | 0,0250 | 0,00104 | 0,2 | |
| 13 | | 0,0270 | 0,00304 | 0,6 | |
| 14 | | 0,0210 | −0,00296 | −0,6 | |
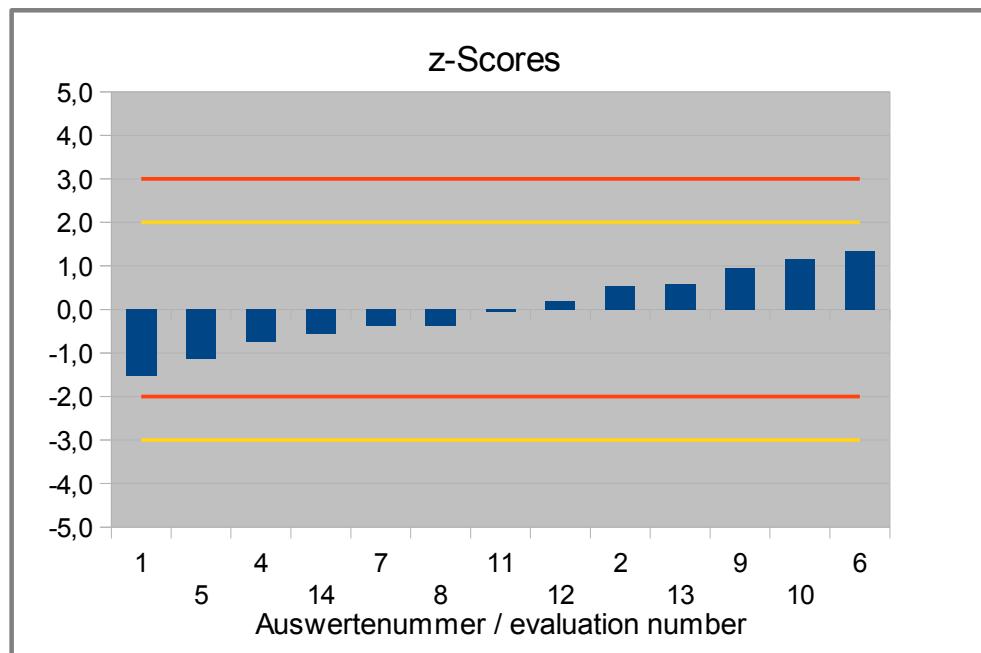


**Abb. / Fig. 23:**   Z-Scores Nickel

## 4.6 Zinc in mg/L

### 1. Eluat /1st Eluate

### Vergleichsuntersuchung  /  Proficiency Test

| Statistic Data | |
|---|---|
| *Number of results* | 10* |
| *Number of outliers* | 0 |
| Mean | 0,0296 |
| Median | 0,0282 |
| **Robust Mean (X)** | **0,0293** |
| **Robust standard deviation (S*)** | **0,00816** |
| *Number with 3 replicates* | 9 |
| Repeatability SD ($S_r$) | 0,0099 |
| Repeatability ($CV_r$) | 35,7% |
| Reproducibility SD ($S_R$) | 0,0102 |
| Reproducibility ($CV_R$) | 36,8% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **0,00646** |
| Target standard deviation (for Information) | 0,00861 |
| **lower limit of target range** | **0,0164** |
| **upper limit of target range** | **0,0423** |
| *Quotient S*/$\sigma_{pt}$* | *1,3* |
| *Standard uncertainty U($X_{pt}$)* | *0,00322* |
| *Quotient U($X_{pt}$)/$\sigma_{pt}$* | *0,50* |
| *Results in the target range* | *9* |
| *Percent in the target range* | *90%* |

*\* without result from participant no. 9 (excluded before)*

*Comments to the statistic data:*

The standard target deviation was evaluated using the model of Thompson. The distribution of results shows a normal variability. The quotient S*/$\sigma_{pt}$ is less than 2.0. The repeatability standard deviation is in the range of established values gained by determination methods in water (see 3.6.2). Thus the comparability of results is given for used methods and the present range of concentrations.

With 0.50 the quotient U($X_{pt}$)/$\sigma_{pt}$ is slightly increased.

90% of the results were located in the target range.
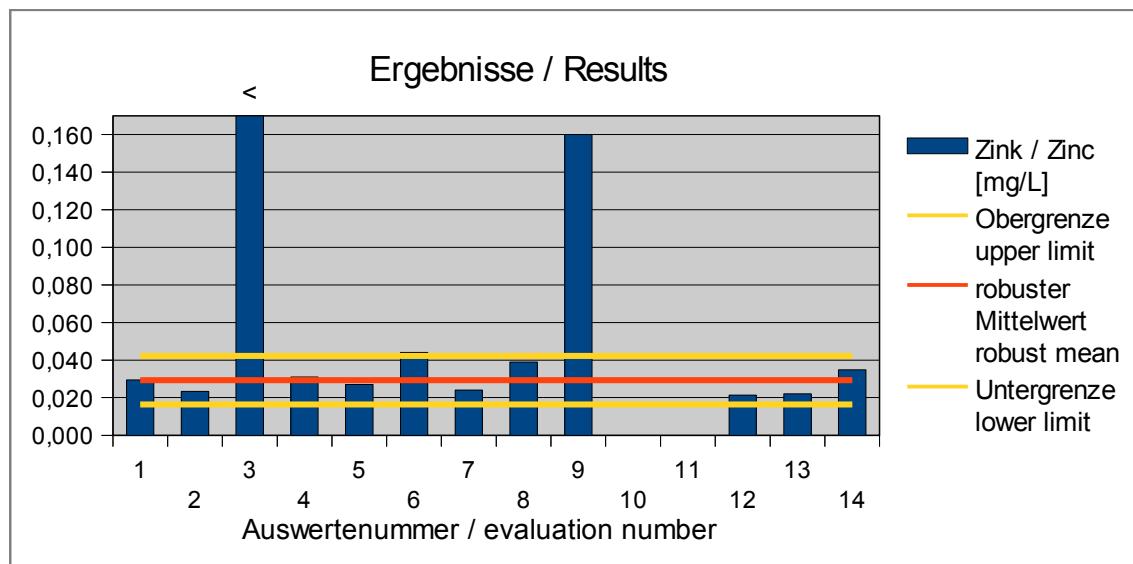
**Abb. / Fig. 24:** Ergebnisse Zink **/** Results Zinc
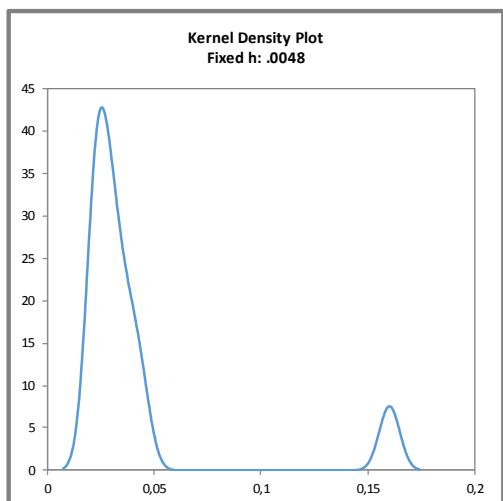


**Abb. / Fig. 25:**
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x $\sigma_{pt}$ von $X_{pt}$)

Kernel density plot of results (with h = 0,75 x $\sigma_{pt}$ of $X_{pt}$)

*Comment:*
The kernel density shows nearly a normal distribution of results, with a side-peak due to the excluded result (participant 9) above the target range.

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

| Auswerte-nummer Evaluation number | Zink / Zinc [mg/L] | Abweichung [mg/L] Deviation [mg/L] | z-Score ($\sigma_{pt}$) | Hinweis Remark |
|---|---|---|---|---|
| 1 | 0,0294 | 0,0000417 | 0,0 | |
| 2 | 0,0233 | −0,00604 | −0,9 | |
| 3 | < 0,920 | | | |
| 4 | 0,0310 | 0,00165 | 0,3 | |
| 5 | 0,0270 | −0,00235 | −0,4 | |
| 6 | 0,0440 | 0,0147 | 2,3 | |
| 7 | 0,0240 | −0,00535 | −0,8 | |
| 8 | 0,0390 | 0,00965 | 1,5 | |
| 9 | 0,160 | 0,1310 | 20 | Ergebnis ausgeschlossen / Result excluded |
| 10 | | | | |
| 11 | 0,000 | | | |
| 12 | 0,0213 | −0,00805 | −1,2 | |
| 13 | 0,0220 | −0,00735 | −1,1 | |
| 14 | 0,0349 | 0,00555 | 0,9 | |
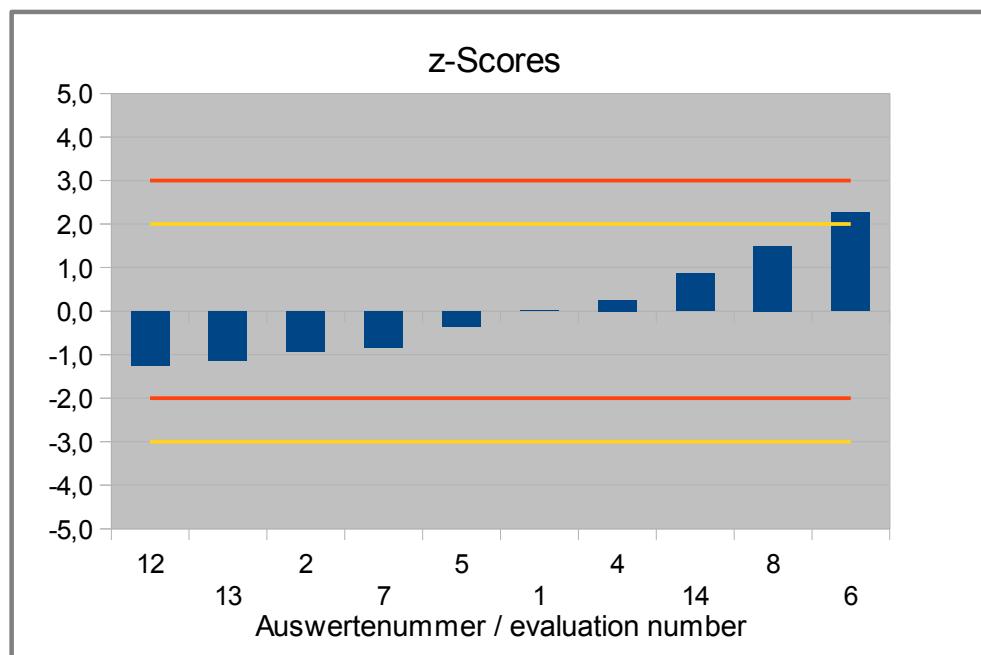


**Abb. / Fig. 26:**   Z-Scores Zink / Zinc

# 5. Documentation

## 5.1 Details by participants
## 5.1.1 Primary data

| Parameter | Auswerte-nummer | Einheit | Eluat | Summen der Eluate | Abschließen-des Ergebnis | Ergebnis A | Ergebnis B | Ergebnis C |
|-----------|-----------------|---------|-------|-------------------|--------------------------|------------|------------|------------|
| Analyte | Evaluation number | Unit | Eluate | Sums of Eluates | Final Result | Result A | Result B | Result C |
| Cr | 1 | mg/L | 1 | | **0,1734** | **0,1734** | **0,1733** | **0,2435** |
|  |  | mg/L | 2 | 0,218 | 0,04415 | 0,04415 | 0,0539 | 0,06952 |
|  |  | mg/L | 3 | 0,246 | 0,02851 | 0,02851 | 0,02974 | 0,03749 |
| Cr | 2 | mg/L | 1 | | **0,296** | **0,252** | **0,363** | **0,273** |
|  |  | mg/L | 2 | 0,385 | 0,0888 | 0,0876 | 0,1072 | 0,0714 |
|  |  | mg/L | 3 | 0,449 | 0,0641 | 0,0684 | 0,0678 | 0,0562 |
| Cr | 3 | mg/L | 1 | | **0,309** | **0,306** | **0,272** | **0,348** |
|  |  | mg/L | 2 | | <0,13 | <0,13 | <0,13 | <0,13 |
|  |  | mg/L | 3 | | <0,13 | <0,13 | <0,13 | <0,13 |
| Cr | 4 | mg/L | 1 | | **0,246** | **0,244** | **0,255** | **0,238** |
|  |  | mg/L | 2 | | | | | |
|  |  | mg/L | 3 | | | | | |
| Cr | 5 | mg/L | 1 | | **0,216** | **0,231** | **0,193** | **0,224** |
|  |  | mg/L | 2 | 0,298 | 0,082 | 0,076 | 0,089 | 0,080 |
|  |  | mg/L | 3 | 0,355 | 0,057 | 0,050 | 0,073 | 0,047 |
| Cr | 6 | mg/L | 1 | | **0,31** | **0,313** | **0,256** | **0,328** |
|  |  | mg/L | 2 | 0,450 | 0,14 | 0,141 | 0,111 | 0,143 |
|  |  | mg/L | 3 | 0,533 | 0,083 | 0,095 | 0,066 | 0,083 |
| Cr | 7 | mg/L | 1 | | **0,26** | **0,285** | **0,224** | **0,27** |
|  |  | mg/L | 2 | | | | | |
|  |  | mg/L | 3 | | | | | |
| Cr | 8 | mg/L | 1 | | **0,265** | **0,256** | **0,273** | |
|  |  | mg/L | 2 | | | | | |
|  |  | mg/L | 3 | | | | | |
| Cr | 9 | mg/L | 1 | | **0,31** | **0,27** | **0,41** | **0,24** |
|  |  | mg/L | 2 | 0,390 | 0,08 | 0,08 | 0,10 | 0,05 |
|  |  | mg/L | 3 | 0,450 | 0,06 | 0,06 | 0,08 | 0,04 |
| Cr | 10 | mg/L | 1 | | **0,28** | **0,22** | **0,31** | **0,3** |
|  |  | mg/L | 2 | | | | | |
|  |  | mg/L | 3 | | | | | |
| Cr | 11 | mg/L | 1 | | **0,253** | **0,263** | **0,2195** | **0,275** |
|  |  | mg/L | 2 | 0,342 | 0,089 | 0,089 | 0,0835 | 0,095 |
|  |  | mg/L | 3 | 0,406 | 0,065 | 0,055 | 0,073 | 0,066 |
| Cr | 12 | mg/L | 1 | | 0,254 | **0,205** | **0,319** | **0,238** |
|  |  | mg/L | 2 | 0,339 | 0,0846666667 | 0,068 | 0,1 | 0,086 |
|  |  | mg/L | 3 | 0,401 | 0,0626666667 | 0,053 | 0,071 | 0,064 |
| Cr | 13 | mg/L | 1 | | **0,25** | **0,27** | **0,23** | **0,25** |
|  |  | mg/L | 2 | | | | | |
|  |  | mg/L | 3 | | | | | |
| Cr | 14 | mg/L | 1 | | **0,219** | **0,257** | **0,217** | **0,182** |
|  |  | mg/L | 2 | | | | | |
|  |  | mg/L | 3 | | | | | |

\* sums of eluates were calculated by DLA

| Parameter | Auswerte nummer | Einheit | Eluat | Summen der Eluate | Abschließen-des Ergebnis | Ergebnis A | Ergebnis B | Ergebnis C |
|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Unit | Eluate | Sums of Eluates | Final Result | Result A | Result B | Result C |
| | | | | Summen | | | | |
| Cu | 1 | mg/L | 1 | | **0,07812** | **0,07812** | **0,03036** | **0,03851** |
| | | mg/L | 2 | 0,083 | 0,00499 | 0,00499 | 0,003927 | 0,005884 |
| | | mg/L | 3 | 0,086 | 0,002598 | 0,002598 | 0,001669 | 0,002724 |
| Cu | 2 | mg/L | 1 | | **0,044** | **0,026** | **0,035** | **0,072** |
| | | mg/L | 2 | 0,048 | 0,0035 | 0,0028 | 0,0040 | 0,0036 |
| | | mg/L | 3 | 0,050 | 0,0028 | 0,0029 | 0,0026 | 0,0030 |
| Cu | 3 | mg/L | 1 | | **<0,57** | **<0,57** | **<0,57** | **<0,57** |
| | | mg/L | 2 | | <0,57 | <0,57 | <0,57 | <0,57 |
| | | mg/L | 3 | | <0,57 | <0,57 | <0,57 | <0,57 |
| Cu | 4 | mg/L | 1 | | **0,123** | **0,137** | **0,051** | **0,181** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Cu | 5 | mg/L | 1 | | **0,043** | **0,047** | **0,032** | **0,051** |
| | | mg/L | 2 | | <0,010 | <0,010 | <0,010 | <0,010 |
| | | mg/L | 3 | | <0,010 | <0,010 | <0,010 | <0,010 |
| Cu | 6 | mg/L | 1 | | **0,066** | **0,075** | **0,045** | **0,066** |
| | | mg/L | 2 | 0,075 | 0,009 | 0,01 | 0,008 | 0,011 |
| | | mg/L | 3 | 0,082 | 0,007 | 0,008 | 0,006 | 0,007 |
| Cu | 7 | mg/L | 1 | | **0,03** | **0,063** | **0,007** | **0,021** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Cu | 8 | mg/L | 1 | | **0,057** | **0,057** | | |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Cu | 9 | mg/L | 1 | | **0,075** | **0,051** | **0,112** | **0,062** |
| | | mg/L | 2 | 0,093 | 0,018 | 0,018 | 0,02 | 0,016 |
| | | mg/L | 3 | 0,120 | 0,027 | 0,042 | 0,019 | 0,02 |
| Cu | 10 | mg/L | 1 | | **0,06** | **0,03** | **0,09** | **0,07** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Cu | 11 | mg/L | 1 | | **0,122** | **0,136** | **0,105** | **0,126** |
| | | mg/L | 2 | | 0,000 | < | < | < |
| | | mg/L | 3 | | 0,000 | < | < | < |
| Cu | 12 | mg/L | 1 | | 0,031 | **0,028** | **0,048** | **0,017** |
| | | mg/L | 2 | 0,067 | 0,0363333333 | 0,03 | 0,037 | 0,042 |
| | | mg/L | 3 | 0,097 | 0,03 | 0,016 | 0,032 | 0,042 |
| Cu | 13 | mg/L | 1 | | **0,0048** | **0,005** | **0,0051** | **0,0043** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Cu | 14 | mg/L | 1 | | **0,05** | **0,0557** | **0,0536** | **0,0406** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |

* sums of eluates were calculated by DLA

| Parameter | Auswerte nummer | Einheit | Eluat | Summen der Eluate | Abschließen-des Ergebnis | Ergebnis A | Ergebnis B | Ergebnis C |
|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Unit | Eluate | Sums of Eluates | Final Result | Result A | Result B | Result C |
| | | | | Summen | | | | |
| Fe | 1 | mg/L | 1 | | **5,204** | **5,204** | **5,437** | **7,524** |
| | | mg/L | 2 | 5,753 | 0,5489 | 0,5489 | 0,7836 | 0,9041 |
| | | mg/L | 3 | 6,033 | 0,2803 | 0,2803 | 0,2772 | 0,3709 |
| Fe | 2 | mg/L | 1 | | **10,120** | **9,377** | **11,424** | **9,561** |
| | | mg/L | 2 | 11,313 | 1,1926 | 1,2817 | 1,4017 | 0,8944 |
| | | mg/L | 3 | 12,069 | 0,7556 | 0,8995 | 0,6852 | 0,6820 |
| Fe | 3 | mg/L | 1 | | **8,315** | **8,435** | **7,028** | **9,481** |
| | | mg/L | 2 | 9,086 | 0,771 | 0,848 | 0,689 | 0,777 |
| | | mg/L | 3 | 9,667 | 0,581 | 0,631 | 0,543 | 0,57 |
| Fe | 4 | mg/L | 1 | | **6,86** | **6,822** | **6,78** | **6,977** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Fe | 5 | mg/L | 1 | | **7,35** | **7,34** | **6,99** | **7,72** |
| | | mg/L | 2 | 8,643 | 1,293 | 0,978 | 1,7 | 1,200 |
| | | mg/L | 3 | 9,470 | 0,827 | 0,748 | 1,12 | 0,613 |
| Fe | 6 | mg/L | 1 | | **8,8** | **8,92** | **7,78** | **8,91** |
| | | mg/L | 2 | 10,050 | 1,25 | 1,19 | 0,975 | 1,502 |
| | | mg/L | 3 | 10,840 | 0,79 | 0,801 | 0,666 | 0,883 |
| Fe | 7 | mg/L | 1 | | **8,831** | **8,845** | **7,842** | **9,806** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Fe | 8 | mg/L | 1 | | **7,628** | **7,522** | **7,733** | |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Fe | 9 | mg/L | 1 | | **-** | **-** | **-** | **-** |
| | | mg/L | 2 | | - | - | - | - |
| | | mg/L | 3 | | - | - | - | - |
| Fe | 10 | mg/L | 1 | | **8,82** | **6,79** | **10,05** | **9,61** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Fe | 11 | mg/L | 1 | | **8,080** | **8,295** | **7,285** | **8,66** |
| | | mg/L | 2 | 9,288 | 1,208 | 1,04 | 1,37 | 1,215 |
| | | mg/L | 3 | 9,842 | 0,554 | 0,5535 | 0,812 | 0,0793 |
| Fe | 12 | mg/L | 1 | | 8,0913333333 | **7,374** | **8,941** | **7,959** |
| | | mg/L | 2 | 9,194 | 1,1023333333 | 0,936 | 1,141 | 1,23 |
| | | mg/L | 3 | 9,860 | 0,666 | 0,605 | 0,666 | 0,727 |
| Fe | 13 | mg/L | 1 | | **4,85** | **5,37** | **4,23** | **4,94** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Fe | 14 | mg/L | 1 | | **7,59** | **8,42** | **7,33** | **7,01** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |

\* sums of eluates were calculated by DLA

| Parameter | Auswerte nummer | Einheit | Eluat | Summen der Eluate | Abschlie-ßendes Er-gebnis | Ergebnis A | Ergebnis B | Ergebnis C |
|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Unit | Eluate | Sums of Eluates | Final Result | Result A | Result B | Result C |
| | | | | Summen | | | | |
| Ni | 1 | mg/L | 1 | | **0,01593** | **0,01593** | **0,01488** | **0,02249** |
| | | mg/L | 2 | 0,018 | 0,001987 | 0,001987 | 0,001717 | 0,0026 |
| | | mg/L | 3 | 0,018 | 0,000572 | 0,000572 | 0,000168 | 0,000784 |
| Ni | 2 | mg/L | 1 | | **0,027** | **0,023** | **0,033** | **0,024** |
| | | mg/L | 2 | 0,030 | 0,0035 | 0,0031 | 0,0051 | 0,0023 |
| | | mg/L | 3 | 0,032 | 0,0018 | 0,0022 | 0,0020 | 0,0013 |
| Ni | 3 | mg/L | 1 | | **<0,023** | **<0,023** | **<0,023** | **<0,023** |
| | | mg/L | 2 | | <0,023 | <0,023 | <0,023 | <0,023 |
| | | mg/L | 3 | | <0,023 | <0,023 | <0,023 | <0,023 |
| Ni | 4 | mg/L | 1 | | **0,02** | **0,018** | **0,023** | **0,02** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Ni | 5 | mg/L | 1 | | **0,018** | **0,018** | **0,016** | **0,02** |
| | | mg/L | 2 | | <0,005 | <0,005 | 0,005 | <0,005 |
| | | mg/L | 3 | | <0,005 | <0,005 | <0,005 | <0,005 |
| Ni | 6 | mg/L | 1 | | **0,031** | **0,029** | **0,025** | **0,035** |
| | | mg/L | 2 | 0,036 | 0,005 | 0,005 | 0,003 | 0,009 |
| | | mg/L | 3 | 0,039 | 0,003 | 0,002 | 0,002 | 0,006 |
| Ni | 7 | mg/L | 1 | | **0,022** | **0,025** | **0,019** | **0,023** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Ni | 8 | mg/L | 1 | | **0,022** | **0,021** | **0,022** | |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Ni | 9 | mg/L | 1 | | **0,029** | **0,023** | **0,042** | **0,022** |
| | | mg/L | 2 | 0,032 | 0,003 | 0,002 | 0,00 | 0,001 |
| | | mg/L | 3 | 0,033 | 0,001 | nd | 0,001 | nd |
| Ni | 10 | mg/L | 1 | | **0,03** | **0,02** | **0,03** | **0,03** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Ni | 11 | mg/L | 1 | | **0,024** | **0,02336** | **0,02391** | **0,02339** |
| | | mg/L | 2 | 0,027 | 0,004 | 0,00307 | 0,00438 | 0,00352 |
| | | mg/L | 3 | 0,029 | 0,001 | 0,00134 | 0,0022089571 | 0,00188 |
| Ni | 12 | mg/L | 1 | | 0,025 | **0,018** | **0,034** | **0,023** |
| | | mg/L | 2 | 0,029 | 0,004 | 0,003 | 0,006 | 0,003 |
| | | mg/L | 3 | 0,032 | 0,0026666667 | 0,002 | 0,003 | 0,003 |
| Ni | 13 | mg/L | 1 | | **0,027** | **0,027** | **0,026** | **0,026** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Ni | 14 | mg/L | 1 | | **0,021** | **0,0219** | **0,0206** | **0,0205** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |

\* sums of eluates were calculated by DLA

| Parameter | Auswerte nummer | Einheit | Eluat | Summen der Eluate | Abschließen-des Ergebnis | Ergebnis A | Ergebnis B | Ergebnis C |
|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Unit | Eluate | Sums of Eluates | Final Result | Result A | Result B | Result C |
| | | | | Summen | | | | |
| Pb | 1 | mg/L | 1 | | **0,01231** | **0,01231** | **0,00613** | **0,01367** |
| | | mg/L | 2 | 0,013 | 0,00075 | 0,00075 | 0,00063 | 0,00062 |
| | | mg/L | 3 | 0,013 | 0,00035 | 0,00035 | 0,0001 | 0,00009 |
| Pb | 2 | mg/L | 1 | | **0,005** | **0,003** | **0,005** | **0,008** |
| | | mg/L | 2 | 0,006 | 0,0005 | 0,0004 | 0,0005 | 0,0006 |
| | | mg/L | 3 | 0,007 | 0,0010 | 0,0011 | 0,0010 | 0,0010 |
| Pb | 3 | mg/L | 1 | | **<0,01** | **< 0,01** | **<0,01** | **<0,01** |
| | | mg/L | 2 | | <0,01 | <0,01 | <0,01 | <0,01 |
| | | mg/L | 3 | | <0,01 | 0<0,01 | <0,01 | <0,01 |
| Pb | 4 | mg/L | 1 | | **0,016** | **0,018** | **0,009** | **0,02** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Pb | 5 | mg/L | 1 | | **0,013** | **0,018** | **0,009** | **0,011** |
| | | mg/L | 2 | | <0,005 | <0,005 | <0,005 | <0,005 |
| | | mg/L | 3 | | <0,005 | <0,005 | <0,005 | <0,005 |
| Pb | 6 | mg/L | 1 | | **0,022** | **0,029** | **0,022** | **0,011** |
| | | mg/L | 2 | 0,024 | 0,002 | 0,002 | 0,001 | 0,001 |
| | | mg/L | 3 | 0,025 | 0,001 | 0,001 | 0,001 | <0,001 |
| Pb | 7 | mg/L | 1 | | **0,013** | **0,029** | **0,01** | **0,011** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Pb | 8 | mg/L | 1 | | **0,019** | **0,018** | **0,019** | |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Pb | 9 | mg/L | 1 | | **0,019** | **0,012** | **0,028** | **0,018** |
| | | mg/L | 2 | 0,021 | 0,002 | 0,002 | 0,00 | 0,001 |
| | | mg/L | 3 | 0,022 | 0,001 | 0,001 | 0,001 | 0,001 |
| Pb | 10 | mg/L | 1 | | **0,03** | **0,01** | **0,04** | **0,02** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Pb | 11 | mg/L | 1 | | **0,011** | **0,0112** | **0,00895** | **0,01421** |
| | | mg/L | 2 | 0,012 | 0,001 | < | 0,00073 | 0,00086 |
| | | mg/L | 3 | 0,012 | < | < | 2,2089571178 | 0,00053 |
| Pb | 12 | mg/L | 1 | | 0,011 | **0,017** | **0,007** | **0,009** |
| | | mg/L | 2 | 0,012 | 0,0006666667 | 0,002 | 0 | 0 |
| | | mg/L | 3 | 0,012 | 0 | 0 | 0 | 0 |
| Pb | 13 | mg/L | 1 | | **0,012** | **0,019** | **0,012** | **0,0046** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Pb | 14 | mg/L | 1 | | **0,0143** | **0,015** | **0,0131** | **0,0148** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |

* sums of eluates were calculated by DLA

| Parameter | Auswerte nummer | Einheit | Eluat | Summen der Eluate | Abschließen-des Ergebnis | Ergebnis A | Ergebnis B | Ergebnis C |
|-----------|-----------------|---------|-------|-------------------|--------------------------|------------|------------|------------|
| Analyte | Evaluation number | Unit | Eluate | Sums of Eluates | Final Result | Result A | Result B | Result C |
| | | | | Summen | | | | |
| Zn | 1 | mg/L | 1 | | **0,02939** | **0,02939** | **0,01434** | **0,02446** |
| | | mg/L | 2 | 0,031 | 0,001807 | 0,001807 | 0,005984 | 0,001522 |
| | | mg/L | 3 | 0,032 | 0,000685 | 0,000685 | 0,002368 | 0,000205 |
| Zn | 2 | mg/L | 1 | | **0,023** | **0,006** | **0,020** | **0,044** |
| | | mg/L | 2 | 0,025 | 0,0016 | 0,0005 | 0,0013 | 0,0031 |
| | | mg/L | 3 | | < 0,001 | < 0,001 | < 0,001 | < 0,001 |
| Zn | 3 | mg/L | 1 | | **<0,92** | **<0,92** | **<0,92** | **<0,92** |
| | | mg/L | 2 | | <0,92 | <0,92 | <0,92 | <0,92 |
| | | mg/L | 3 | | <0,92 | <0,92 | <0,092 | <0,92 |
| Zn | 4 | mg/L | 1 | | **0,031** | **0,023** | **0,027** | **0,043** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Zn | 5 | mg/L | 1 | | **0,027** | **0,026** | **0,016** | **0,038** |
| | | mg/L | 2 | 0,041 | 0,014 | 0,012 | 0,018 | 0,011 |
| | | mg/L | 3 | 0,052 | 0,011 | 0,011 | <0,010 | 0,011 |
| Zn | 6 | mg/L | 1 | | **0,044** | **0,041** | **0,053** | **0,037** |
| | | mg/L | 2 | 0,048 | 0,004 | 0,004 | 0,004 | 0,004 |
| | | mg/L | 3 | 0,049 | 0,001 | 0,001 | 0,001 | 0,001 |
| Zn | 7 | mg/L | 1 | | **0,024** | **0,032** | **0,012** | **0,03** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Zn | 8 | mg/L | 1 | | **0,039** | **0,024** | **0,054** | |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Zn | 9 | mg/L | 1 | | **0,16** | **0,138** | **0,168** | **0,175** |
| | | mg/L | 2 | 0,172 | 0,012 | 0,018 | 0,01 | 0,01 |
| | | mg/L | 3 | 0,172 | nd | nd | nd | nd |
| Zn | 10 | mg/L | 1 | | | | | |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Zn | 11 | mg/L | 1 | | **0,000** | **<** | **<** | **<** |
| | | mg/L | 2 | | 0,000 | < | < | < |
| | | mg/L | 3 | | 0,000 | < | < | < |
| Zn | 12 | mg/L | 1 | | 0,0213333333 | **0,022** | **0,024** | **0,018** |
| | | mg/L | 2 | 0,036 | 0,0146666667 | 0,004 | 0,03 | 0,01 |
| | | mg/L | 3 | 0,036 | 0,0003333333 | 0,001 | 0 | 0 |
| Zn | 13 | mg/L | 1 | | **0,022** | **0,024** | **0,02** | **0,022** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |
| Zn | 14 | mg/L | 1 | | **0,0349** | **0,0347** | **0,0293** | **0,0407** |
| | | mg/L | 2 | | | | | |
| | | mg/L | 3 | | | | | |

\* sums of eluates were calculated by DLA

## 5.1.2 Analytical methods

| Parameter / Analyte | Auswertenummer / Evaluation number | Eluat / Eluate | Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben / Description of the methods like in a report analysis | Vorbehandlung des Gegenstands / Pre conditioning of material | Simulanzmittel Citronensäure 5 g/L / Simulant citric acid 5 g/L | Füllvolumen 20 mL / Filling volume 20 mL | Zeit und Temperatur: 2 h bei 70°C + 24 h bei 40°C / Time and temperature: 2 h at 70°C + 24 h at 40°C | Hinweise zur Analytik / Remarks to analysis | Methode ist akkreditiert / Method accredited | Sonstige Hinweise / Further Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 1 | 1 | ICP-OES citric acid | no | yes | yes | yes | LOQ = 0,020 mg/l | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 2 | ICP-OES citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 3 | ICP-OES citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| Cr | 2 | 1 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 2 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 3 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| Cr | 3 | 1 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | no | yes | yes | yes | | - | |
| | | 2 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| | | 3 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| Cr | 4 | 1 | ICP-MS | rinsed with water | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cr | 5 | 1 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 2 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) bzw. DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 3 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| Cr | 6 | 1 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 2 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 3 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| Cr | 7 | 1 | DIN EN ISO 11885 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cr | 8 | 1 | ICP-MS | | - | yes | yes | | np | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cr | 9 | 1 | Metal release using AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 2 | Metal release using AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 3 | Metal release using AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| Cr | 10 | 1 | DIN EN ISO 17294-2 2005-02 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cr | 11 | 1 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume 17,5 ml |
| | | 2 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume 17,5 ml |
| | | 3 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume for sample B =12 ml, thus no sum as final result is given |
| Cr | 12 | 1 | | | yes | yes | yes | 267,716 nm | yes | |
| | | 2 | | | yes | yes | yes | | yes | |
| | | 3 | | | yes | yes | yes | | yes | |
| Cr | 13 | 1 | DIN EN ISO 17294-2 | rinsed | yes | no* | no* | | yes | *Time-temperature- program: s. Lead |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cr | 14 | 1 | | wiped out using a lint free wipe | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |

| Parameter | Auswerte nummer | Eluat | Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben | Vorbehandlung des Gegenstands | Simulanzmittel Citronensäure 5 g/L | Füllvolumen 20 mL | Zeit und Temperatur: 2 h bei 70°C + 24 h bei 40°C | Hinweise zur Analytik | Methode ist akkreditiert | Sonstige Hinweise |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Eluate | Description of the methods like in a report analysis | Pre conditioning of material | Simulant citric acid 5 g/L | Filling volume 20 mL | Time and temperature: 2 h at 70°C + 24 h at 40°C | Remarks to analysis | Method accredited | Further Remarks |
| | | | | | ja / nein | ja / nein | ja / nein | | ja / nein | |
| Cu | 1 | 1 | ICP-OES citric acid | no | yes | yes | yes | LOQ = 0,050 mg/l | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 2 | ICP-OES citric acid | no | yes | yes | yes | | | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 3 | ICP-OES citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| Cu | 2 | 1 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 2 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 3 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| Cu | 3 | 1 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | no | yes | yes | yes | | - | |
| | | 2 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| | | 3 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| Cu | 4 | 1 | ICP-MS | rinsed with water | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cu | 5 | 1 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 2 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) bzw. DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 3 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| Cu | 6 | 1 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 2 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 3 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| Cu | 7 | 1 | DIN EN ISO 11885 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cu | 8 | 1 | ICP-MS | | - | yes | yes | | no | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cu | 9 | 1 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 2 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 3 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| Cu | 10 | 1 | DIN EN ISO 17294-2 2005-02 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cu | 11 | 1 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | final volume 17,5 ml |
| | | 2 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | final volume 17,5 ml, BG = 0,05 mg/L |
| | | 3 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | final volume 17,5 ml, BG = 0,05 mg/L |
| Cu | 12 | 1 | | | yes | yes | yes | 327,393 nm | yes | |
| | | 2 | | | yes | yes | yes | | yes | |
| | | 3 | | | yes | yes | yes | | yes | |
| Cu | 13 | 1 | DIN EN ISO 17294-2 | rinsed | yes | no* | no* | | yes | * Time-temperature- program: s. Lead |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Cu | 14 | 1 | | wiped out using a lint free wipe | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |

| Parameter | Auswerte nummer | Eluat | Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben | Vorbehandlung des Gegenstands | Simulanzmittel Citronensäure 5 g/L | Füllvolumen 20 mL | Zeit und Temperatur: 2 h bei 70°C + 24 h bei 40°C | Hinweise zur Analytik | Methode ist akkreditiert | Sonstige Hinweise |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Eluate | Description of the methods like in a report analysis | Pre conditioning of material | Simulant citric acid 5 g/L | Filling volume 20 mL | Time and temperature: 2 h at 70°C + 24 h at 40°C | Remarks to analysis | Method accredited | Further Remarks |
| | | | | | ja / nein | ja / nein | ja / nein | | ja / nein | |
| Fe | 1 | 1 | ICP-OES citric acid | no | yes | yes | yes | No LOQ estimated | no | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 2 | ICP-OES citric acid | no | yes | yes | yes | | no | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 3 | ICP-OES citric acid | no | yes | yes | yes | | no | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| Fe | 2 | 1 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 2 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 3 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| Fe | 3 | 1 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | no | yes | yes | yes | | - | |
| | | 2 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| | | 3 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| Fe | 4 | 1 | ICP-MS | rinsed with water | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | yes | |
| | | 3 | | | - | - | - | | - | |
| Fe | 5 | 1 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 2 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 3 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| Fe | 6 | 1 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 2 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 3 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| Fe | 7 | 1 | DIN EN ISO 11885 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Fe | 8 | 1 | ICP-MS | | - | yes | yes | | no | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Fe | 9 | 1 | - | | - | - | - | - | - | - |
| | | 2 | - | | - | - | - | | - | |
| | | 3 | - | | - | - | - | | - | |
| Fe | 10 | 1 | DIN EN ISO 17294-2 2005-02 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Fe | 11 | 1 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | final volume 17,5 ml |
| | | 2 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | final volume 17,5 ml |
| | | 3 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume for sample B =12 ml, thus no sum as final result is given |
| Fe | 12 | 1 | | | yes | yes | yes | 238,204 | yes | |
| | | 2 | | | yes | yes | yes | | yes | |
| | | 3 | | | yes | yes | yes | | yes | |
| Fe | 13 | 1 | § 64 LFGB L 00.00-19 | rinsed | yes | no* | no* | | yes | *Time-temperature- program: s. Lead |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Fe | 14 | 1 | | wiped out using a lint free wipe | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |

| Parameter | Auswerte nummer | Eluat | Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben | Vorbehandlung des Gegenstands | Simulanzmittel Citronensäure 5 g/L | Füllvolumen 20 mL | Zeit und Temperatur: 2 h bei 70°C + 24 h bei 40°C | Hinweise zur Analytik | Methode ist akkreditiert | Sonstige Hinweise |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Eluate | Description of the methods like in a report analysis | Pre conditioning of material | Simulant citric acid 5 g/L | Filling volume 20 mL | Time and temperature: 2 h at 70°C + 24 h at 40°C | Remarks to analysis | Method accredited | Further Remarks |
| | | | | | ja / nein | ja / nein | ja / nein | | ja / nein | |
| Ni | 1 | 1 | ICP-OES citric acid | no | yes | yes | yes | LOQ = 0,010 mg/l | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 2 | ICP-OES citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 3 | ICP-OES citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| Ni | 2 | 1 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 2 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 3 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| Ni | 3 | 1 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | no | yes | yes | yes | | - | |
| | | 2 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| | | 3 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| Ni | 4 | 1 | ICP-MS | rinsed with water | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Ni | 5 | 1 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 2 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 3 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| Ni | 6 | 1 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 2 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 3 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| Ni | 7 | 1 | DIN EN ISO 11885 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Ni | 8 | 1 | ICP-MS | | - | yes | yes | | no | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Ni | 9 | 1 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 2 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 3 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| Ni | 10 | 1 | DIN EN ISO 17294-2 2005-02 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Ni | 11 | 1 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-MS | - | Final volume 17,5 ml |
| | | 2 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-MS | - | Final volume 17,5 ml |
| | | 3 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-MS | - | Final volume for sample B =12 ml, thus no sum as final result is given |
| Ni | 12 | 1 | | | yes | yes | yes | 231,604 nm | yes | |
| | | 2 | | | yes | yes | yes | | yes | |
| | | 3 | | | yes | yes | yes | | yes | |
| Ni | 13 | 1 | § 64 LFGB L 00.00-19 | rinsed | yes | no* | no* | | yes | *Time-temperature- program: s. Lead |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Ni | 14 | 1 | | wiped out using a lint free wipe | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |

| Parameter / Analyte | Auswerte nummer / Evaluation number | Eluat / Eluate | Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben / Description of the methods like in a report analysis | Vorbehandlung des Gegenstands / Pre conditioning of material | Simulanzmittel Citronensäure 5 g/L / Simulant citric acid 5 g/L (ja / nein) | Füllvolumen 20 mL / Filling volume 20 mL (ja / nein) | Zeit und Temperatur: 2 h bei 70°C + 24 h bei 40°C / Time and temperature: 2 h at 70°C + 24 h at 40°C (ja / nein) | Hinweise zur Analytik / Remarks to analysis | Methode ist akkreditiert / Method accredited (ja / nein) | Sonstige Hinweise / Further Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| Pb | 1 | 1 | ICP-MS citric acid | no | yes | yes | yes | LOQ = 0,00050 mg/l | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 2 | ICP-MS citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 3 | ICP-MS citric acid | no | yes | yes | yes | | yes | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| Pb | 2 | 1 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 2 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 3 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| Pb | 3 | 1 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | no | yes | yes | yes | | - | |
| | | 2 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| | | 3 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| Pb | 4 | 1 | ICP-MS | rinsed with water | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Pb | 5 | 1 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | Priot treatment: rinsed out with demineralized water to remove adherent dust |
| | | 2 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 3 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| Pb | 6 | 1 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 2 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 3 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| Pb | 7 | 1 | DIN EN ISO 11885 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Pb | 8 | 1 | ICP-MS | | yes | yes | yes | | no | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Pb | 9 | 1 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 2 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| | | 3 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | GTA-AAS | yes | Final result is the mean of sample A, B and C |
| Pb | 10 | 1 | DIN EN ISO 17294-2 2005-02 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Pb | 11 | 1 | Extraction: 120 min/70°C followed by 24 h/40°C - simulant: 0.5 % citric acid; Determination of elements via ICP-OES | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-MS | - | Final volume 17,5 ml |
| | | 2 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-MS | - | Final volume 17,5 ml |
| | | 3 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-MS | - | Final volume for sample B =12 ml, thus no sum as final result is given |
| Pb | 12 | 1 | Sample rinsed and dried prior to analysis, filled with 20 ml citric acid (0.5%, 70 °C) incubated for 2h at 70 °C in a heating cabinet. Afterwards cooled down and hold at 40 °C for 24 h. Procedure was repeated twice. | | yes | yes | yes | 220,353 nm | yes | |
| | | 2 | | | yes | yes | yes | | yes | |
| | | 3 | | | yes | yes | yes | | yes | |
| Pb | 13 | 1 | DIN EN ISO 17294-2 | rinsed | yes | no* | no* | | yes | *Time-temperature- Program was missunerstood: first the sample was filled with 20 ml and leached for 2h at 70°C, afterwards the solution was removed and bottled. The sample was filled anew with 20 ml andleached for 24 h at 40°C. Both solution were analyzed seperated and the results were added |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Pb | 14 | 1 | | wiped out using a lint free wipe | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |

| Parameter | Auswerte nummer | Eluat | Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben | Vorbehandlung des Gegenstands | Simulanzmittel Citronensäure 5 g/L | Füllvolumen 20 mL | Zeit und Temperatur: 2 h bei 70°C + 24 h bei 40°C | Hinweise zur Analytik | Methode ist akkreditiert | Sonstige Hinweise |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | Evaluation number | Eluate | Description of the methods like in a report analysis | Pre conditioning of material | Simulant citric acid 5 g/L | Filling volume 20 mL | Time and temperature: 2 h at 70°C + 24 h at 40°C | Remarks to analysis | Method accredited | Further Remarks |
| | | | | | ja / nein | ja / nein | ja / nein | | ja / nein | |
| Zn | 1 | 1 | ICP-OES citric acid | no | yes | yes | yes | No LOQ estimated | no | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 2 | ICP-OES citric acid | no | yes | yes | yes | | no | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| | | 3 | ICP-OES citric acid | no | yes | yes | yes | | no | After the migration the simulant was reduced in volume, so we made up the volume to 20 ml with milli-q water |
| Zn | 2 | 1 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 2 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| | | 3 | TG Metals + Alloys 2013 | no | yes | yes | yes | | no | |
| Zn | 3 | 1 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | no | yes | yes | yes | | - | |
| | | 2 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| | | 3 | P3B00217 metal release of metal/alloy food contact material in relation to CM/Res (2013)9 | | yes | yes | yes | | - | |
| Zn | 4 | 1 | ICP-MS | rinsed with water | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Zn | 5 | 1 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 2 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| | | 3 | DIN EN 13130-1 (2004/08) / DIN EN ISO 11855 (E22) 2009-09 (ICP-OES) / DIN EN ISO 17294-2 (ICP-MS) | | yes | yes | yes | | yes | |
| Zn | 6 | 1 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 2 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| | | 3 | ICP-MS EN 17294-2 | | yes | yes | yes | | - | |
| Zn | 7 | 1 | DIN EN ISO 11885 | | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Zn | 8 | 1 | ICP-MS | | - | yes | yes | | no | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Zn | 9 | 1 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | Flame-AAS | yes | Final result is the mean of sample A, B and C |
| | | 2 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | Flame-AAS | yes | Final result is the mean of sample A, B and C |
| | | 3 | metal release with AAS | cleaned with dishwashing detergent | yes | yes | yes | Flame-AAS | yes | Final result is the mean of sample A, B and C |
| Zn | 10 | 1 | | | - | - | - | | - | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Zn | 11 | 1 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume 17,5 ml |
| | | 2 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume 17,5 ml |
| | | 3 | dto. | cleaned with diluted dishwashing detergent | yes | yes | yes | ICP-OES | - | Final volume for sample B =12 ml, thus no sum as final result is given |
| Zn | 12 | 1 | | | yes | yes | yes | 213,857 | yes | |
| | | 2 | | | yes | yes | yes | | yes | |
| | | 3 | | | yes | yes | yes | | yes | |
| Zn | 13 | 1 | DIN EN ISO 17294-2 | rinsed | yes | no* | no* | | yes | *Time-temperature- program: s. Lead |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |
| Zn | 14 | 1 | | wiped out using a lint free wipe | yes | yes | yes | | yes | |
| | | 2 | | | - | - | - | | - | |
| | | 3 | | | - | - | - | | - | |

## 5.2 Homogeneity

### 5.2.1 Homogeneity examination of sample material

The homogeneity of the first eluates of 5 sample materials was examined for Lead and Chromium by ICP-MS:

*Lead*

| repeated measurements | mg/L |
|---|---|
| 1 | 0,015 |
| 2 | 0,020 |
| 3 | 0,029 |
| 4 | 0,021 |
| 5 | 0,018 |

| | | |
|---|---|---|
| general mean | 0,0206 | |
| repeatability standard deviation | 0,00522 | 25% |

*Chromium*

| repeated measurements | mg/L |
|---|---|
| 1 | 0,21 |
| 2 | 0,36 |
| 3 | 0,30 |
| 4 | 0,35 |
| 5 | 0,27 |

| | | |
|---|---|---|
| general mean | 0,298 | |
| repeatability standard deviation | 0,0614 | 21% |

# 6. Index of participant laboratories in alphabetical order

| Teilnehmer / Participant | Ort / Town | Land / Country |
|---|---|---|
| | | Germany |
| | | Belgium |
| | | Germany |
| | | Germany |
| | | Germany |
| | | Switzerland |
| | | Switzerland |
| | | Germany |
| | | Germany |
| | | Germany |
| | | Germany |
| | | Germany |
| | | Germany |
| | | Germany |

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

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

# 7. Index of 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 interlaboratory comparisons
4. ASU §64 LFGB: Planung und statistische Auswertung von Ringversuchen zur Methodenvalidierung / DIN ISO 5725 series part 1, 2 and 6 Accuracy (trueness and precision) of measurement methods and results
5. Verordnung / Regulation 882/2004/EU; Verordnung über über amtliche Kontrollen zur Überprüfung der Einhaltung des Lebensmittel- und Futtermittelrechts sowie der Bestimmungen über Tiergesundheit und Tierschutz / Regulation on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules
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17. ASU §64 L 59.11-28: Bestimmung von Bor, Barium, Calcium, Eisen, Kalium, Magnesium, Mangan, Natrium und Strontium in Mineralwasser mittels optischer Emissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP-OES)
18. DIN EN ISO 11885:2009-09: Wasserbeschaffenheit - Bestimmung von ausgewählten Elementen durch induktiv gekoppelte Plasma-Atom-Emissionsspektrometrie (ICP-OES) / Water quality -Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)