Proficiency Tests

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Evaluation Report
proficiency test

DLA 70/2016

Contact Material II:

Nickel Release of Metal Contact Material (Costume Jewelry)

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

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Unteraufträge *Subcontractors*	Die Prüfung der Gehalte, Homogenität und Stabilität von EP-Parametern wird von DLA im Unterauftrag vergeben. The analysis of the content, homogeneity and stability of PT-parameters are subcontracted by DLA.
Vertraulichkeit *Confidentiality*	Die Teilnehmerergebnisse sind im EP-Bericht in anonymisierter Form mit Auswertenummern benannt. Daten einzelner Teilnehmer werden ausschließlich nach vorheriger Zustimmung des Teilnehmers an Dritte weitergegeben. Participant result are named anonymously with evalutation numbers in the PT report. Data of individual participants will be passed on to third parties only with prior consent of the participant.

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

Two different test materials were offered to be analysed. According to pre-tests the nickel release from the first material was clearly higher than the limit of migration of 0,5 µg/cm²/week (0,88 µg/cm²/week respectively) for articles intended to come into direct and prolonged contact with the skin according to EU-regulation 1907/2006 and EN 1811 (ASU §64 82.02-6) while the nickel release of the second material was below the migration limit [16].

Test item A (metal chain, nickel-plated):
The test material is a chain (necklace for dogs) made of nickel-plated iron (link length and width approx. 20 mm and 13 mm, thickness approx. 4 mm, see fig. 1a). The material was purchased in the trade by DLA as specimen from one production unit.

Test item B (metal chain):
The test material is a metal necklace (costume jewelry) (link length and width approx. 4 mm and 3 mm, thickness approx. 1 mm, see fig. 1b). The material was purchased in the trade by DLA as specimen from one production unit.

Fig. 1: a) left test item A and b) right test item B

The samples were packed in transparent plastic bags and labeled.

2.1.1 Homogeneity

The suitability of the test materials was checked by a nickel rapid test and by multiple determinations of nickel release according to ASU B 82.02-6 (corresponds to EN 1811-2012). Test material A was positive and test material B negative in the rapid test. Results of ICP-MS were for test material A in the range of 5-10 (mean 7,2) µg/cm²/week and for test material B 0,25 µg/cm²/week.
With 35% the repeatability standard deviation of test material A was considered acceptable in comparison to the combined measurement uncertainty of 46% (EN 1811, annex A). The results are given in the documentation [16].

The calculation of the **repeatability standard deviation S_r of the 3 results from participants** was also used as an indicator of homogeneity. It was 28% for test material A and 80% for test material B.
With respect to the respective mean of the test items the repeatability standard deviations of participants were in an usual range of the method [16]. The repeatability standard deviation of the participants' results is given in the table of statistic data (see 4.1 and 4.2).

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 are solid metal specimens, which can be considered stable when stored dry. Thus the stability of sample material is ensured under the given storage conditions.

2.2 Sample shipment and information to the test

Three samples of the test items A and B were sent to every participating laboratory in the 50th week of 2016. The tests should be finished at 27th January 2017 the latest.

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

*The test material are **tow different metal necklaces** samples A and B. Three test items per sample A and sample B are provided. The **nickel release** should be determined according to the conditions of EN 1811-2012 method:*

1. *test solution (EN 1811): 0,5% (m/m) NaCl, 0,1% (m/m) lactic acid, 0,1% (m/m) urea, adjust to pH 6,5*
2. *time and temperature (30°C, 168h)*
3. *results given in µg/cm²/week.*

*For statistical evaluation DLA will use the value you have filled in the column „**final result**" of the result file. Please report the results for samples A1 to A3 and samples B1 to B3 too, as well as the **volume of test solution** and **surface area** of the sample.*

DLA will exclude results from statistical evaluation, in case they have not been produced under the above mentioned conditions.

2.3 Submission of results

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

The finally calculated concentrations of the parameter as average of determinations of the samples were used for the statistical evaluation. For the calculation of the repeatability- and reproducibility standard deviation the single values of the triplet determinations were used.

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

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.

9 participants submitted their results in time. 2 participants submitted no results

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

3.3 Repeatability standard deviation

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

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

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

3.4 Reproducibility standard deviation

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

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

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

The relative reproducibility standard deviation 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 σ_{pt} (= standard deviation for proficiency assessment) can be determined according to the following methods.

If an acceptable quotient S^*/σ_{pt} is present, the target standard deviation of the general model by Horwitz is preferably used for the proficiency assessment. It is usually suitable for 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.

The valuation was done according to chapter 3.6.3 and followed the principle of "fitness for purpose" in order to ensure the suitability for decisions with respect to allowed maximum migration levels.

3.6.1 General model (Horwitz)

Based on statistical characteristics obtained in numerous PTs for different parameters and methods Horwitz has derived a general model for estimating the reproducibility standard deviation σ_R [6]. Later the model was modified by Thompson for certain concentration ranges [10]. The reproducibility standard deviation σ_R can be applied as the relative target standard deviation σ_{pt} in % of the assigned values and calculated according to the following equations [3]. For this the assigned value X_{pt} is used for the concentration c.

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

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

3.6.2 Value by precision experiment

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

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

For the determination of nickel release the data of repeatability and reproducibility standard deviations are not sufficiently given in ASU §64 B 82.02-6 and EN 1811, respectively [16]. In a proficiency test of quality control material a nickel migration rate of 0,31±0,06 µg/cm2/week with a relative reproducibility precision of 33,3% was obtained (annex B).

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].

Because neither the general model (s. 3.6.1) nor the values of precision experiments (s. 3.6.2) were suitable for valuation of the results, we choose the following basis for evaluation of the results.

According to DIN EN 1811 annex A (ASU B 82.02-6) the combined measurement uncertainty of the method is 46%. The expanded measurement uncertainty is applied in order to identify significant exceeding of the maximum migration limit. For this purpose the combined uncertainty is multiplied with the coverage factor k (1,65) for significance niveau 0,05 [16].

For the present evaluation of results a suitable **target standard deviation** was set based on the combined uncertainty of EN 1811 considering the value of the respective robust mean:

1) *Target standard deviation for the range of the migration limit*

The nickel release of the material is in the range of the migration limit of 0,5 µg/cm²/week (and 0,88 µg/cm²/week respectively) [16]. Half of the value for the expanded measurement uncertainty is considered for the target standard deviation. Consequently the relative standard target deviation is: 1,65 x 46% / 2 = 38%.
This target standard deviation was used for the evaluation of both test materials A and B.
Hereby it is ensured, that the valuation of results by z-scores is comparable to the criterium for exceeding of the maximum migration limit. The limit of the z-score ≥ -2 and ≤ 2 correspond to the decision limits of the expanded uncertainty.

2) *Target standard deviation for the range clearly higher than the migration limit*

The nickel release of the material is clearly above the migration limit of 0,5 µg/cm²/week (and 0,88 µg/cm²/week respectively) [16]. Therefore a lower target standard deviation is considered: half of the value for the combined measurement uncertainty. Hereby the uncertainty is not expanded. Consequently the relative standard target deviation is: 1/2 x 46% = 23%.

Table 1 shows selected characteristics of participants results of the present PT in comparison to the previous year.

Table 1: Characteristics of the present PT (on dark gray) in comparison to previous PTs since 2015 (SD = standard deviation, CV = coefficient of variation)

Parameter	**Material**	**robust Mean** µg/cm²/week	**rob. SD (S*)** µg/cm²/week	**rel. SD (CV_{S*})** [%]	**Quotient S^*/σ_{pt}**	**DLA-Report**
Nickel	Bracelet	0,037	0,019	51 %	1,3	DLA 49/2015
Nickel	Coin	24,9	13,2	53 %	1,7	DLA 49/2015
Nickel	Chain, nickel-plated	0,679	0,529	78 %	2,0	DLA 70/2016
Nickel	Necklace	0,478	0,426	89 %	2,3	DLA 70/2016

3.7 z-Score

To assess the results of the participants the z-score is used. It indicates about which multiple of the target standard deviation (σ_{pt}) the result (x_i) of the participant is deviating from the assigned value (X_{pt}) [3].
Participants' z-scores are derived from:

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

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

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

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

3.7.1 Warning and action signals

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

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

3.8 z'-Score

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

The calculation is performed by:

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

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

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

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

For warning and action signals see 3.7.1.

3.9 Reproducibility coefficient of variation (CV_R)

The coefficient of variation (CV_R) of the reproducibility (= relative reproducibility standard deviation) is calculated from the standard deviation and the mean as follows [4, 13]:

$$CV_R = \frac{S_R * 100}{X}$$

In contrast to the standard deviation as a measure of the absolute variability the CV_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 ($U(X_{pt})$) for this PT is calculated as follows [3]:

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

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

The quotient $U(X_{pt})/\sigma_{pt}$ is reported in the characteristics of the test.

4. Results

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

In the first table the characteristics are listed:

Statistic Data
Number of results
Number of outliers
Mean
Median
Robust mean(X_{pt})
Robust standard deviation (S^*)
Number with m replicate measurements
Repeatability standard deviation (S_r)
Coefficient of Variation (CV_r) in %
Reproducibility standard deviation (S_R)
Coefficient of Variation (CV_R) in %
Target range:
Target standard deviation σ_{pt} or σ_{pt}'
Target standard deviation for information
lower limit of target range ($X_{pt} - 2\sigma_{pt}$)*
upper limit of target range ($X_{pt} + 2\sigma_{pt}$)*
Variation coefficient V_K in %
Quotient S/σ_{pt} or S*/σ_{pt}'*
Standard uncertainty $U(X_{pt})$
Quotient $U(X_{pt})/\sigma_{pt}$ or $U(X_{pt})/\sigma_{pt}$'
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 formatted to 3 digits**:

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

** In the documentation the results are given as submitted by the participants.

4.1 Test Item A: Nickel Release in µg/cm²/week

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8**
Number of outliers	0
Mean	0,679
Median	0,601
Robust Mean (X)	**0,679**
Robust standard deviation (S*)	**0,529**
Number with 3 replicates	6
Repeatability SD (S_r)	0,188
Repeatability (CV_r)	27,7%
Reproducibility SD (S_R)	0,448
Reproducibility (CV_R)	66,1%
Target range:	
Target standard deviation σ_{pt}	**0,258**
lower limit of target range	**0,163**
upper limit of target range	**1,20**
Quotient S/σ_{pt}*	*2,0*
Standard uncertainty $U_{(Xpt)}$	*0,234*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*0,90*
Results in the target range	*5*
Percent in the target range	*63%*

*** result of participant no. 1 was excluded*

Comments to the statistic data:

The target standard deviation based on the combined measurement uncertainty of EN 1811 annex A (ASU B 82.02-6) according to section "value by perception" (s. 3.6.3).

With respect to the applied analytical method the distribution of results exhibits a normal to slightly increased variability. The quotient S*/σ_{pt} was 2,0. The robust standard deviation as well as the repeatability and reproducibility standard deviations are up to one third higher than in prior PTs (s. 3.6.3). The comparability of results is given.

The quotient $U_{(Xpt)}/\sigma_{pt}$ was increased > 0,3 (0,9), but acceptable due to the low number of results and the expected precision of the analytical method.

63% of results were in the target range. It should be noted that the results above the target range (z-score > 2,0) are not in contradiction with the specification (nickel-plated) and the preliminary tests of test material A (see 2.1).

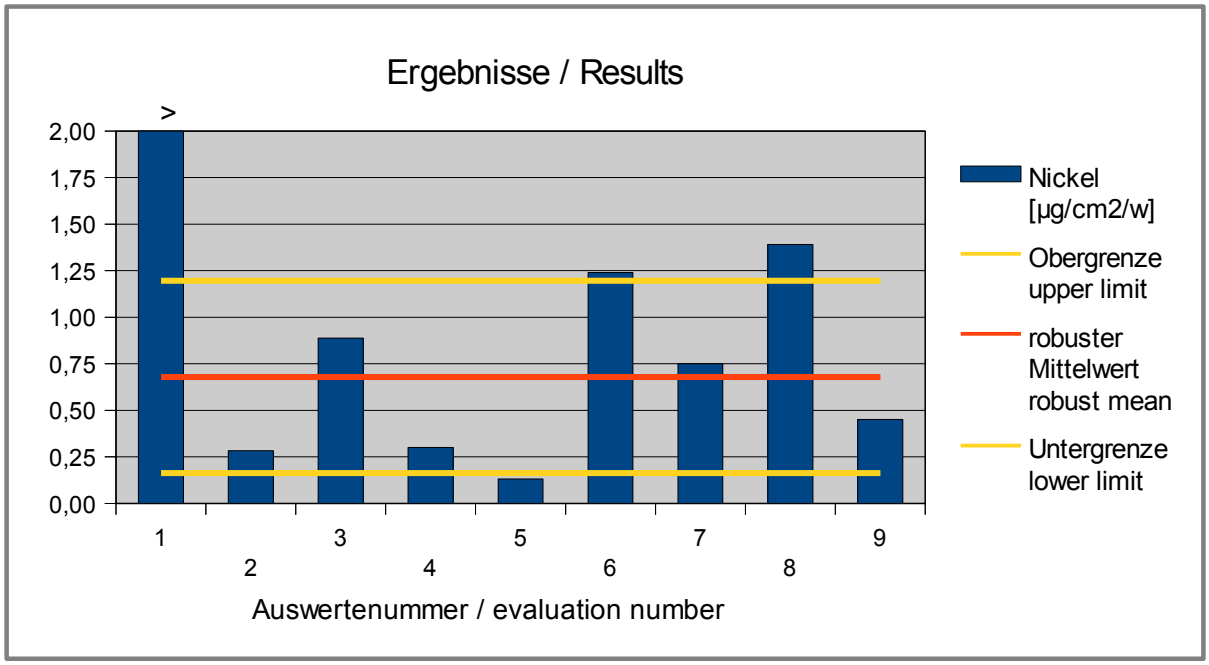

Abb. / Fig. 1: Ergebnisse Probe A / Results sample A

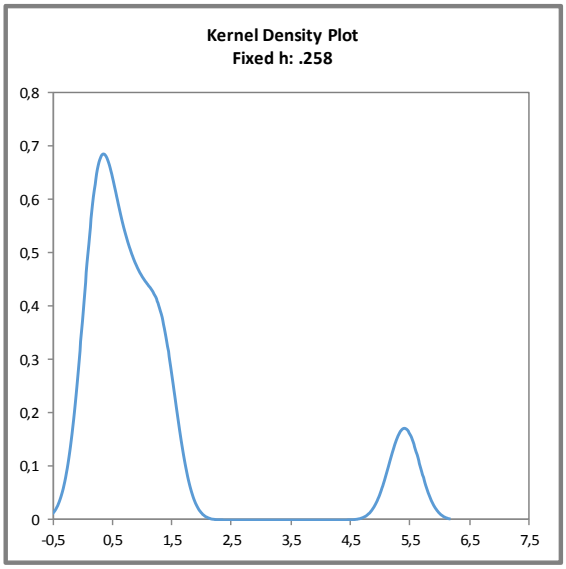

Abb. / Fig. 2:
Kerndichte-Schätzung der Ergebnisse (mit h = 1,0 x σ_{pt} von X_{pt})

Kernel density plot of results (with h = 1,0 x σ_{pt} of X_{pt})

Comment:
The kernel density plot shows nearly normal distribution of results with a shoulder at 1,2 - 1,3 µg/cm²/week and a second peak, due to the excluded result no. 1.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Nickel [µg/cm2/w]	Abweichung [µg/cm2/w] Deviation [µg/cm2/w]	z-Score (σ_{pt})	Hinweis Remark
1	5,40 **	4,72	18	
2	0,283 *	-0,396	-1,5	
3	0,888	0,209	0,8	
4	0,300	-0,379	-1,5	
5	0,132	-0,547	-2,1	
6	1,240	0,561	2,2	
7	0,750	0,071	0,3	
8	1,390	0,711	2,8	
9	0,451	-0,228	-0,9	

* mean calculated by DLA
** result excluded from statistical evaluation

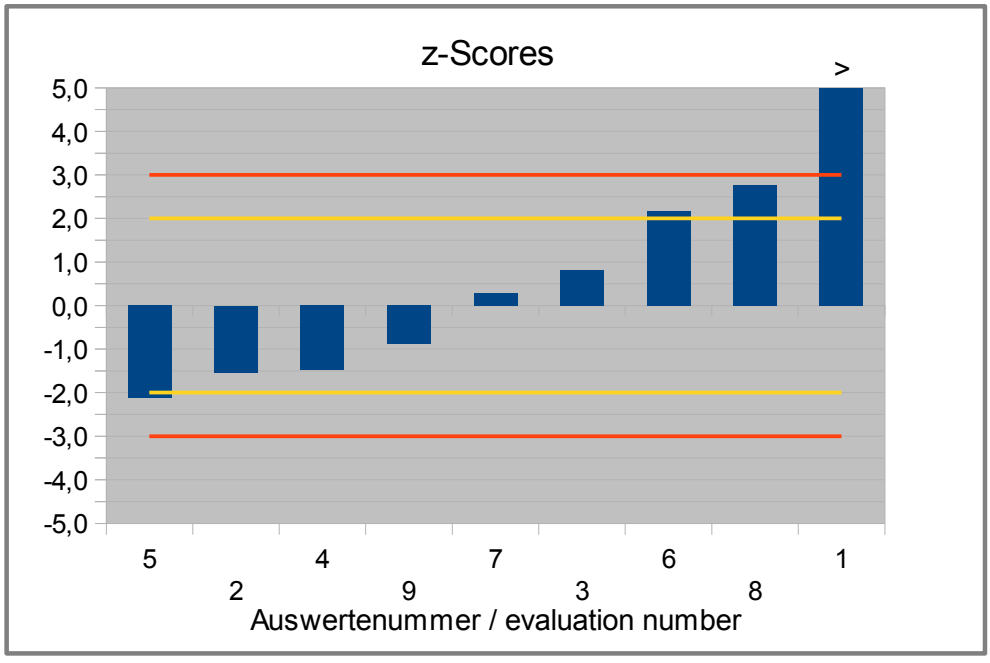

Abb. / Fig. 3: Z-Scores Probe A / sample A

4.2 Test Item B: Nickel Release in µg/cm²/week

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	7**
Number of outliers	0
Mean	0,478
Median	0,433
Robust Mean (X)	**0,478**
Robust standard deviation (S*)	**0,426**
Number with 3 replicates	7
Repeatability SD (S_r)	0,383
Repeatability (CV_r)	80,0%
Reproducibility SD (S_R)	0,464
Reproducibility (CV_R)	97,0%
Target range:	
Target standard deviation σ_{pt}	**0,182**
lower limit of target range	**0,115**
upper limit of target range	**0,842**
Quotient S/σ_{pt}*	*2,3*
Standard uncertainty $U_{(Xpt)}$	*0,201*
Quotient $U_{(Xpt)}/\sigma_{pt}$	*1,1*
Results in the target range	*3*
Percent in the target range	*43%*

*** result of participant no. 1 was excluded*

Comments to the statistic data:

The target standard deviation based on the combined measurement uncertainty of EN 1811 annex A (ASU B 82.02-6) according to section "value by perception" (s. 3.6.3).

With respect to the applied analytical method the distribution of results exhibits a slightly increased variability. The quotient S*/σ_{pt} was above 2,0. The robust standard deviation as well as the repeatability and reproducibility standard deviations are clearly higher than in prior PTs (s. 3.6.3). The comparability of results is limited.

The quotient $U_{(Xpt)}/\sigma_{pt}$ was increased > 0,3 (1,1), but acceptable due to the low number of results and the expected precision of the analytical method.

43% of results were in the target range. It should be noted that the results below the target range (z-score < 2,0) are not in contradiction with the specification and the preliminary tests of test material B (see 2.1).

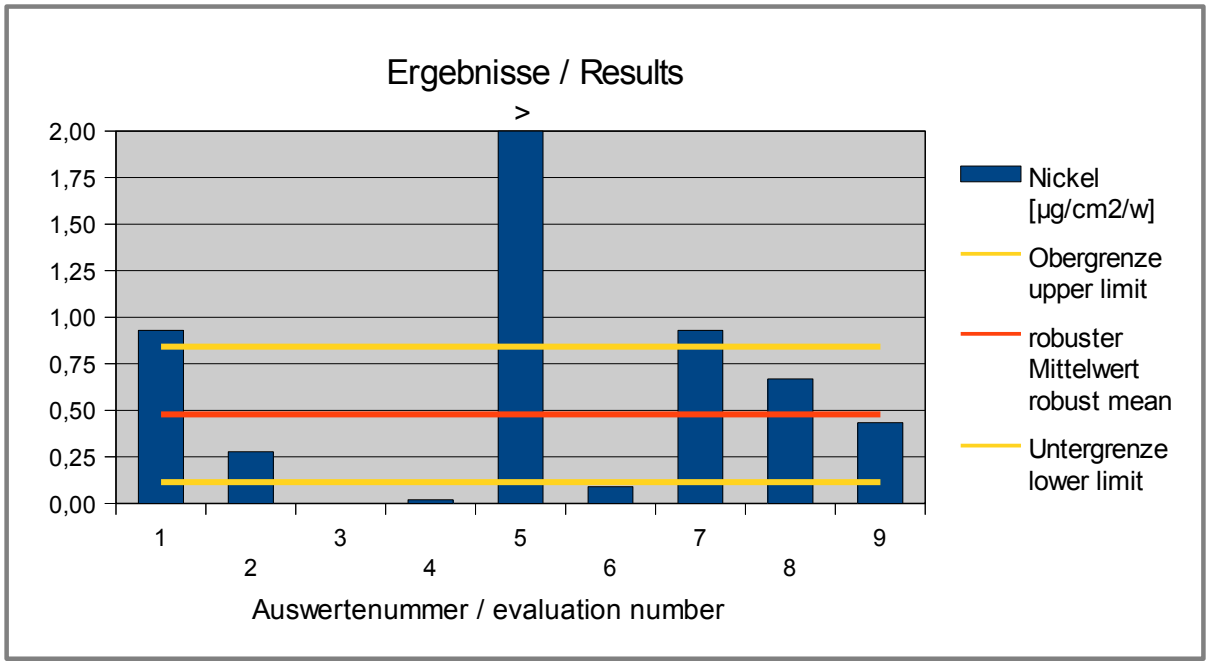

Abb. / Fig. 4: Ergebnisse Probe B / Results sample B

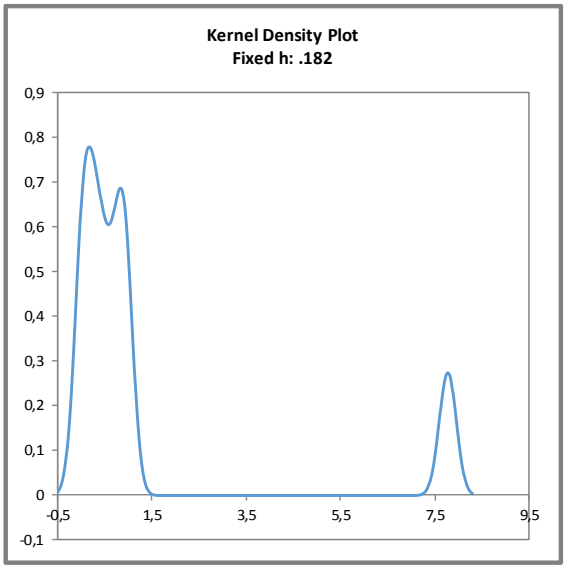

Abb. / Fig. 5:
Kerndichte-Schätzung der Ergebnisse
(mit h = 1,0 x σ_{pt} von X_{pt})

Kernel density plot of results
(with h = 1,0 x σ_{pt} of X_{pt})

Comment:
The kernel density plot a distribution of results with to peaks at < 1,0 µg/cm²/week and a second peak, due to the excluded result no. 5.

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Nickel [µg/cm2/w]	Abweichung [µg/cm2/w] Deviation [µg/cm2/w]	z-Score (σ_{pt})	Hinweis Remark
1	0,930	0,452	2,5	
2	0,277 *	-0,201	-1,1	
3				
4	0,020	-0,458	-2,5	
5	7,79 **	7,31	40	
6	0,090	-0,388	-2,1	
7	0,930	0,452	2,5	
8	0,669	0,191	1,0	
9	0,433	-0,045	-0,2	

* mean calculated by DLA

** result excluded from statistical evaluation

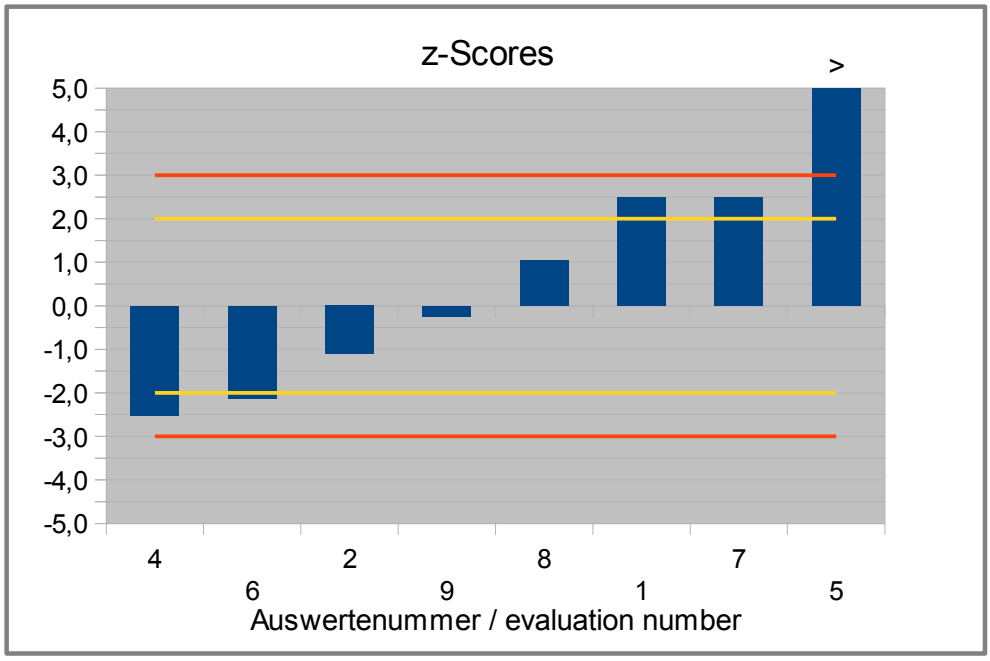

Abb. / Fig. 6: Z-Scores Probe B / sample B

5. Documentation

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

5.1 Details by participants

5.1.1 Primary data

Test material A

Parameter	Teil-nehmer	Einheit	Datum der Ana-lyse	Abschließen-des Ergebnis	Ergebnis 1	Ergebnis 2	Ergebnis 3	Methodenbeschreibung, wie in einem regulären Prüfbe-richt angegeben
Analyte	**Partici-pant**	**Unit**	**Date of analysis**	**Final Result**	**Result 1**	**Result 2**	**Result 3**	**Description of the methods like in a report analysis**
Nickel	1	µg/cm²/ week	24.01.17	5,4	5,06	5,78	5,35	determination of migration of nickel
Nickel	2	µg/cm²/ week	19.01.17		0,31	0,28	0,26	*
Nickel	3	µg/cm²/ week	13.01.17	0,888	0,772	0,873	1,018	Nickel release
Nickel	4	µg/cm²/ week		0,30	0,15	0,14	0,6	
Nickel	5	µg/cm²/ week	24.01.17	0,132	0,129	0,134		Nickel release according to EN1811:2015
Nickel	6	µg/cm²/ week	28.12.16	1,24	1,19	1,29	-	EN 1811-2012
Nickel	7	µg/cm²/ week	11.01.17	0,75	0,59	1,1	0,57	CH 12a 01 M
Nickel	8	µg/cm²/ week	30.12.16	1,39	1,472	1,313	1,402	
Nickel	9	µg/cm²/ week	27.01.17	0,451	0,43	0,633	0,29	DIN EN 1811

* details from participant no. 2:

DIN EN 1811 : 2015-10: Reference test method for release of nickel from all post assemblies which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin

Test material B

Parameter	Teil-nehmer	Einheit	Datum der Ana-lyse	Abschließen-des Ergebnis	Ergebnis 1	Ergebnis 2	Ergebnis 3	Methodenbeschreibung, wie in einem regulären Prüfbe-richt angegeben
Analyte	**Partici-pant**	**Unit**	**Date of analysis**	**Final Result**	**Result 1**	**Result 2**	**Result 3**	**Description of the methods like in a report analysis**
Nickel	1	µg/cm²/ Woche	24.01.17	0,93	0,89	0,92	0,98	determination of migration of nickel
Nickel	2	µg/cm²/ Woche	20.01.17		0,22	0,09	0,52	*
Nickel	3	µg/cm²/ Woche						Nickel release
Nickel	4	µg/cm²/ Woche		0,02	0,02	0,02	0,02	
Nickel	5	µg/cm²/ Woche	24.01.17	7,79	7,72	7,78	7,87	Nickel release according to EN1811:2015
Nickel	6	µg/cm²/ Woche	11.01.17	0,09	0,09	0,04	0,13	EN 1811-2012
Nickel	7	µg/cm²/ Woche	11.01.17	0,93	0,71	0,16	1,93	CH 12a 01 M
Nickel	8	µg/cm²/ Woche	30.12.16	0,669	0,606	0,732	0,671	
Nickel	9	µg/cm²/ Woche	27.01.17	0,433	0,444	0,042	0,812	DIN EN 1811

* details from participant no. 2:

DIN EN 1811 : 2015-10: Reference test method for release of nickel from all post assemblies which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin

5.1.2 Analytical methods

Test material A

Parameter	Teil-nehmer	Vorbehandlung des Gegenstands	Berechnete Oberfläche pro Muster	Volumen der Prüflösung pro Muster	Prüflösung nach EN 1811-2012	Zeit und Temperatur: 168 h bei370°C	Hinweise zur Analytik	Methode ist akkreditiert	Sonstige Hinweise
Analyte	Partici-pant	Pre conditioning of material	Calculated surface area per sample	Volume of test solution per sample	Test solution according EN 1811-2012	Time and temperature: 168 h at 30°C	Remarks to analysis	Method accredited	Further Remarks
			cm^2	yes / no	mL	yes / no		yes / no	
Nickel	1		12,64	yes	25	yes		yes	
Nickel	2	rinsed according to method	13,4	yes	25	yes		yes	
Nickel	3		10,7	yes	25	yes		no	
Nickel	4	defatted with SDBS solution	11,81	yes	12	yes		yes	
Nickel	5	none	12,97	yes	12,97	yes	Ni-Ions determined by ICP-OES	yes	strong corrosion s. photo
Nickel	6	defatted	9,3	yes	10	yes	result 3 not valid	yes	
Nickel	7	with paper towel and ethanol	12,03	yes	30	yes		yes	CH12a 01 M corresponds to EN1811-2012
Nickel	8		10,9/10,9/10,9	yes	30	yes		yes	
Nickel	9	defatted	9,23	9,23	9,23	yes	ICP-OES	yes	

Test material B

Parameter	Teil-nehmer	Vorbehandlung des Gegenstands	Berechnete Oberfläche pro Muster	Volumen der Prüflösung pro Muster	Prüflösung nach EN 1811-2012	Zeit und Temperatur: 168 h bei370°C	Hinweise zur Analytik	Methode ist akkreditiert	Sonstige Hinweise
Analyte	Partici-pant	Pre conditioning of material	Calculated surface area per sample	Volume of test solution per sample	Test solution according EN 1811-2012	Time and temperature: 168 h at 30°C	Remarks to analysis	Method accredited	Further Remarks
			cm^2	yes / no	mL	yes / no		yes / no	
Nickel	1		8,09	yes	10	yes		yes	
Nickel	2	rinsed according to method	10,15 sample 3 =10,52	yes	15	yes		yes	die B-Proben waren deutlich unterschiedlich korrodiert
Nickel	3			-		-		-	
Nickel	4	defatted with SDBS solution	7,99	yes	8	yes		yes	
Nickel	5	none	7,9	yes	7,9	yes	Ni-Ions determined by ICP-OES	yes	strong corrosion s. photo
Nickel	6	defatted	6,1	yes	6	yes		yes	
Nickel	7	with paper towel and ethanol	1) 8.00 (26 links) 2) 8.93 (29 links) 3) 8.62 (28 links)	yes	40	yes		yes	CH12a 01 M corresponds to EN1811-2012
Nickel	8		7,87/7,87/7,60	yes	30	yes		yes	
Nickel	9	defatted	7,37	7,37	7,37	yes	ICP-OES	yes	

5.2 Homogeneity

5.2.1 Homogeneity before bottling of test material

Analysis of items by determination of nickel release according to ASU B 82.02-6 (EN 1811) by ICP-MS [16]:

Test material A

independant samples	µg/cm²/week
1	4,9
2	10
3	6,8

Mean X	7,23	
Repeatability Standard Deviation	2,58	35,6%

6. Index of participant laboratories in alphabetical order

Teilnehmer / Participant	Ort / Town	Land / Country
		Germany
		Germany
		SERBIA
		SWITZERLAND
		Germany
		Germany
		SWITZERLAND
		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
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15. MTSE SOP No. 010.01 (2014): Quantitative measurement of mixing uniformity and carry-over in powder mixtures with the rotary detector technique, MTSE Micro Tracers Services Europe GmbH
16. ASU §64 L 82.02-6 (2016-07): Referenzprüfverfahren zur Bestimmung der Nickellässigkeit von sämtlichen Stäben, die in durchstochene Körperteile eingeführt werden, und Erzeugnissen, die unmittelbar und länger mit der Haut in Berührung kommen (nach DIN EN 1811) / EN 1811-2011 + A1-2015: Reference test method for release of nickel from all post assemblies which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin