Evaluation Report
proficiency test

DLA 49/2015

Contact Material II:

Nickel Release
of Metal Contact Material
(Costume Jewelry and Coin)

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1. Introduction

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

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 (6).

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 below 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 §6 82.02-6) while the nickel release of the second material was above the migration limit (13).

Test item I (jewelry):
The test material is a bracelet (costume jewelry) made of metal (diameter appr. 6.6 cm, height appr. 4 mm, see fig. 1a). The material was purchased in the trade by DLA as specimen from one production unit.

Test item II (coin):
The test material is a 2 Euro commemorative coin from the Federal Republic of Germany: material ring copper/nickel alloy CuNi25 and kernel brass (diameter 25.75 mm, height 2.20 mm, see fig. 1b). The material was purchased in the trade by DLA as specimen from one production unit (original rolls, 25 x 2 Euro commemorative coins 2010 “City Hall and Roland (Bremen)”, coining site A).

![Fig. 1: a) left bracelet test item I and b) right 2 Euro coins](image-url)
The samples were packed in transparent plastic bags and labeled.

2.1.1 Homogeneity

The suitability of the test material was checked by multiple determinations of nickel release according to ASU B 82.02-6 (corresponds to EN 1811-2012). The mean was 0.078 µg/cm²/week for test item I and 59.5 µg/cm²/week for test item II. With 19% and 8.1% respectively the repeatability standard deviations were considered acceptable in comparison to the combined measurement uncertainty of 46% (EN 1811, annex A). The results are given in the documentation (13).

The calculation of the repeatability standard deviation of the participants was also used as an indicator of homogeneity. The repeatability standard deviation between samples was calculated from the 3 results of each participant. For test item II the relative repeatability standard deviation was 6.2%.

For test item I the results of participants showed two groups of results for which the mean differed about 10 times. Therefore all subsequent calculations for test item I were exclusively done with results > 0.010 µg/cm²/week. For 2 samples each of 5 participants the repeatability standard deviation within the (remaining) samples was 28%.

With respect to the respective mean of test items I and II the repeatability standard deviations of participants were in an usual range of the method (13).

The repeatability standard deviations of the participants' results are given in the documentation.
2.2 Shipment of test items and information for analysis

Three samples A, B and C of the test item I were sent to every participating laboratory in the 48th week of 2015 and three samples A, B and C of test item II in the 5th week of 2016. The tests should be finished at 15th January 2016 and 11th March 2016, respectively.

With the cover letter the following conditions according to the German official methods ASU B 82.02-6 (corresponding to EN 1811-2012) for testing of nickel release of articles intended for skin contact were set to by applied (13):

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.

2.3 Submission of results

The participants submitted their results in provided standard forms by email.

The concentration of the parameters as given by the participants in the column "final result" was used for each statistical evaluation, in case at least 7 results were submitted. In case of test item I due to a bimodal distribution of results (all single results estimated by kernel density plot) exclusively results > 0.010 µg/cm²/week were considered for statistical evaluation.

Queried and documented were single results and the testing methods used. All participants submitted their results in time.
3. Evaluation

3.1 Assigned value

Because the analysed material was no certified reference material the robust mean of the submitted results was used as assigned value X (6).

For test item I the kernel density estimation of all single results (results given as “below” excluded) showed a distribution of results in two major groups for which the mean differed about 10 times. Therefore all subsequent calculations for test item I were exclusively done with results > 0.010 µg/cm²/week.

For test item II the distribution of submitted results showed no hint for bimodal distribution or other reasons for a higher variability. The statistical evaluation is performed when there are at least 7 results for a parameter.

Single results giving values outside the measuring range of the participating laboratory or given as ”0” are not considered for statistical evaluation (e.g. results given as > 25 mg/kg and < 2.5 mg/kg, respectively) (6).

3.2 Standard deviation

For comparison to the target standard deviation a robust standard deviation ($S^*$) was calculated (6).

3.3 Outliers

Statistical outliers were determined by Mandel’s-$H$-Statistic for 95% significance niveau (5). Detected outliers were stated for information only, when z-score was < -2 or > 2.

3.4 Target standard deviation

The target standard deviation of the assigned value is determined according to the following methods.

In general the Horwitz target standard deviation is suitable for the statistical evaluation of interlaboratory tests where different analytical methods are applied. The standard deviation from precision experiments are derived from proficiency tests where a specific analytical method is mandatory. For information the z-scores from both models were given in the result tables, if available.

For valuation of the present results neither the general model according to Horwitz (s. 3.4.1) nor the values by precision experiments (s. 3.4.2) were suitable.

The valuation was done according to chapter 3.4.3 and followed the prin-
ciple of "fitness for purpose" in order to ensure the suitability for decisions with respect to allowed maximum migration levels.

3.4.1 General model (Horwitz)

The relative target standard deviation in % of the assigned value is derived from following equation (Horwitz)

\[ \sigma_{(\%)} = 2^{1-0.5\log X} \]

From the result the target standard deviation is calculated

\[ \sigma = X \times \frac{\sigma_{(\%)}}{100}. \]

3.4.2 Value by precision experiment

Using the reproducibility standard deviation \( \sigma_R \) and the repeatability standard deviation \( \sigma_r \) of a precision experiment the between-laboratories standard deviation can be calculated \( \sigma_L \):

\[ \sigma_L = \sqrt{(\sigma_R^2 - \sigma_r^2)}. \]

And then, using the number of replicate measurements \( n \), each participant is to perform, the target standard deviation for proficiency assessment is calculated:

\[ \hat{\sigma} = \sqrt{(\sigma_L^2 + (\sigma_r^2/n))}. \]

The target standard deviations in table 1 were calculated from the precision data of the respective method.

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 (13). 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).
3.4.3 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 (6).

Because neither the general model (s. 3.4.1) nor the values of precision experiments (s. 3.4.2) 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 \( 0,05 \) (13).

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 test item I

The nickel release of the material is below the migration limit of 0,5 µg/cm²/week (and 0,88 µg/cm²/week respectively). Half of the value for the expanded measurement uncertainty was considered for the target standard deviation. Consequently the relative standard target deviation is: \( 1.65 \times 46\% / 2 = 38\% \).

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 \( \geq -2 \) and \( \leq 2 \) correspond to the decision limits of the expanded uncertainty.

2) Target standard deviation for test item II

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). Therefore a lower target standard deviation was considered: half of the value for the combined measurement uncertainty. Hereby the uncertainty is not expanded. Consequently the relative standard target deviation is: \( 1/2 \times 46\% = 23\% \).
3.5 z-Score

To assess the results of the participants the z-score is used. It indicates about which multiple of the target standard deviation (\( \hat{\sigma} \)) the result (x) of the participant is deviating from the assigned value (X) (6).

Participants’ z-scores were derived as:

\[
z = \frac{(x - X)}{\hat{\sigma}};
\]

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

\[-2 \leq z \leq 2.\]

3.6 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 assigned value (X) to the square root of quadrat sum of the target standard deviation (\( \hat{\sigma} \)) and the standard uncertainty (Ux) (6).

Participants’ z'-scores are derived as:

\[
z' = \frac{(x - X)}{\sqrt{\hat{\sigma}^2 + u_x^2}}.
\]

If applied, we define the denominator \( \sqrt{\hat{\sigma}^2 + u_x^2} \) as the target standard deviation \( \hat{\sigma}' \) in following sections.

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

\[-2 \leq z' \leq 2.\]

3.7 Quotient \( S'/\hat{\sigma} \)

Following the Horrat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation and target standard deviation 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 (11).

In the present proficiency tests the quotients \( S'/\hat{\sigma} \) for test item I was below 2,0 and for test item II above 2,0. Therefore for evaluation of
test item II the z'-Score (s. 3.6) considering the standard uncertainty of the assigned value was applied (s. 3.8).

3.8 Standard uncertainty

The assigned value $X$ has a standard uncertainty $u_X$ that depends on the analytical method, differences between the analytical methods used, the test material, the number of participant laboratories and perhaps on other factors. The standard uncertainty $u_X$ for this PT is calculated as follows (6).

$$u_X = 1.25 \times \frac{S_x}{\sqrt{p}}$$

If $u_X \leq 0.3 \times \hat{\sigma}$ the standard uncertainty of the assigned value needs not to be included in the interpretation of the results of the PT (6). Values exceeding 0.3 imply, that the target standard deviation could be too low with respect to the standard uncertainty of the assigned value.

In the present proficiency tests the quotients $U_x/\hat{\sigma}$ were 0.68 and 0.67, respectively. For test item II the quotients $U_x/\hat{\sigma}$ and $S_x/\hat{\sigma}$ were $> 0.3$ and $> 2.0$ at the same time, therefore the z'-Score considering the standard uncertainty of the assigned value was applied (s. 3.6).
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:

<table>
<thead>
<tr>
<th>Statistic Data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of results</td>
<td></td>
</tr>
<tr>
<td>Number of outliers</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td></td>
</tr>
<tr>
<td>Robust mean (X)</td>
<td></td>
</tr>
<tr>
<td>Robust standard deviation (S')</td>
<td></td>
</tr>
<tr>
<td>Target range:</td>
<td></td>
</tr>
<tr>
<td>Target standard deviation ̂σ or ̂σ'</td>
<td></td>
</tr>
<tr>
<td>Target standard deviation for information</td>
<td></td>
</tr>
<tr>
<td>lower limit of target range (X - 2 ̂σ) or (X - 2 ̂σ') *</td>
<td></td>
</tr>
<tr>
<td>upper limit of target range (X + 2 ̂σ) or (X + 2 ̂σ') *</td>
<td></td>
</tr>
<tr>
<td>Quotient S'/̂σ'</td>
<td></td>
</tr>
<tr>
<td>Standard uncertainty ux</td>
<td></td>
</tr>
<tr>
<td>Quotient u_x/̂σ'</td>
<td></td>
</tr>
<tr>
<td>Number of results in the target range</td>
<td></td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Evaluation number</th>
<th>Parameter [Einheit / Unit]</th>
<th>Abweichung [Einheit / Unit]</th>
<th>z-Score ̂σ</th>
<th>z-Score (Info)</th>
<th>Hinweis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auswerte-nummer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remark</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Vergleichsuntersuchung / Proficiency Test

<table>
<thead>
<tr>
<th>Statistic Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of results</td>
</tr>
<tr>
<td>Number of outliers</td>
</tr>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>Median</td>
</tr>
<tr>
<td>Robust Mean (X)</td>
</tr>
<tr>
<td>Robust standard deviation (S°)</td>
</tr>
<tr>
<td>Target range:</td>
</tr>
<tr>
<td>Target standard deviation (σ)</td>
</tr>
<tr>
<td>lower limit of target range</td>
</tr>
<tr>
<td>upper limit of target range</td>
</tr>
<tr>
<td>Quotient S°/σ</td>
</tr>
<tr>
<td>Standard uncertainty u_x</td>
</tr>
<tr>
<td>Quotient u_x/σ</td>
</tr>
<tr>
<td>Results in the target range</td>
</tr>
<tr>
<td>Percent in the target range</td>
</tr>
</tbody>
</table>

Abb. 2: Ergebnisse Probenmaterial I

Fig. 2: Results test item I
Ergebnisse der teilnehmenden Institute:  
Results of Participants:

<table>
<thead>
<tr>
<th>Auswertenummer</th>
<th>Nickel [µg/cm²/week]</th>
<th>Abweichung [µg/cm²/Woche]</th>
<th>z-Score</th>
<th>Hinweis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,0830 *</td>
<td>0,046</td>
<td>3,3</td>
<td>Ausreisser / Outlier</td>
</tr>
<tr>
<td>2</td>
<td>&lt; 0,01 **</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0,0235 *</td>
<td>-0,013</td>
<td>-0,9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0,0415</td>
<td>0,0048</td>
<td>0,3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0,0433</td>
<td>0,0066</td>
<td>0,5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0,0244 *</td>
<td>-0,012</td>
<td>-0,9</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>&lt; 0,01 **</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>&lt; 0,05 **</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>&lt; 0,01 **</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0,0230 *</td>
<td>-0,014</td>
<td>-1,0</td>
<td></td>
</tr>
</tbody>
</table>

* mean calculated by DLA from results >0,01  
** results indicated by < were not considered  
the original data are given in the documentation

Notes:  
All participants' results were below the maximum migration limit of 0,5 µg/cm²/week (after subtracting the expanded measurement uncertainty of 0,28 µg/cm²/week) and are leading to an agreeing valuation of test item I with respect to the recommendations of EN 1811 (13).

Abb. 3: Z-Scores Probenmaterial I  
Fig. 3: Z-Scores test item I
4.2 Test Item II: Nickel Release in µg/cm²/week

Vergleichsuntersuchung / Proficiency Test

<table>
<thead>
<tr>
<th>Statistic Data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of results</td>
<td>10</td>
</tr>
<tr>
<td>Number of outliers</td>
<td>0</td>
</tr>
<tr>
<td>Mean</td>
<td>24,9</td>
</tr>
<tr>
<td>Median</td>
<td>26,2</td>
</tr>
<tr>
<td>Robust Mean (X)</td>
<td>24,9</td>
</tr>
<tr>
<td>Robust standard deviation (S')</td>
<td>13,2</td>
</tr>
<tr>
<td>Target range:</td>
<td></td>
</tr>
<tr>
<td>Target standard deviation ( \hat{\sigma}' )</td>
<td>7,73</td>
</tr>
<tr>
<td>lower limit of target range</td>
<td>9,40</td>
</tr>
<tr>
<td>upper limit of target range</td>
<td>40,3</td>
</tr>
<tr>
<td>Quotient ( S'/\hat{\sigma}' )</td>
<td>1,7</td>
</tr>
<tr>
<td>Standard uncertainty ( u_s )</td>
<td>5,21</td>
</tr>
<tr>
<td>Quotient ( u_s / \hat{\sigma}' )</td>
<td>0,67</td>
</tr>
<tr>
<td>Results in the target range</td>
<td>9</td>
</tr>
<tr>
<td>Percent in the target range</td>
<td>90</td>
</tr>
</tbody>
</table>

Abb. 4: Ergebnisse Probenmaterial II
Fig. 4: Results test item II
Ergebnisse der teilnehmenden Institute: 
Results of Participants:

<table>
<thead>
<tr>
<th>Auswertenummer</th>
<th>Nickel [µg/cm²/week]</th>
<th>Abweichung [µg/cm²/Woche]</th>
<th>z'-Score</th>
<th>Hinweis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28,75</td>
<td>3,9</td>
<td>0,5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>23,634</td>
<td>-1,2</td>
<td>-0,2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>33,65</td>
<td>8,8</td>
<td>1,1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8,66</td>
<td>-16,2</td>
<td>-2,1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>35,767</td>
<td>10,9</td>
<td>1,4</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>38,89</td>
<td>14,0</td>
<td>1,8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>37,49</td>
<td>12,6</td>
<td>1,6</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>18</td>
<td>-6,9</td>
<td>-0,9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>11,75</td>
<td>-13,1</td>
<td>-1,7</td>
<td>differing calculation of surface (s. documentation)</td>
</tr>
<tr>
<td>10</td>
<td>12,08</td>
<td>-12,8</td>
<td>-1,7</td>
<td></td>
</tr>
</tbody>
</table>

Abb. 5: Z'-Scores Probenmaterial II
Fig. 5: Z'-Scores test item II
5. Documentation

5.1 Primary data

Test Item I

The single results A, B and C printed in italics were considered for the calculation of the mean by DLA. Results < 0,01 µg/cm²/week were excluded (see also assigned value, page 6).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Teilnehmer</th>
<th>Einheit</th>
<th>Abschließendes Ergebnis</th>
<th>Ergebnis A</th>
<th>Ergebnis B</th>
<th>Ergebnis C</th>
<th>Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>1</td>
<td>µg/cm²/week</td>
<td>0,055 **</td>
<td>0,0665</td>
<td>0,0995</td>
<td>&lt;LOQ</td>
<td>* Nickel release of articles in direct and prolonged contact with the skin (§ 64 LFGB B 82.02)</td>
</tr>
<tr>
<td>Nickel</td>
<td>2</td>
<td>µg/cm²/week</td>
<td>0,006</td>
<td>0,006</td>
<td>0,005</td>
<td>0,006</td>
<td>DIN EN 1811</td>
</tr>
<tr>
<td>Nickel</td>
<td>3</td>
<td>µg/cm²/week</td>
<td>0,018</td>
<td>0,006</td>
<td>0,032</td>
<td>0,015</td>
<td>ASU B82.02-6</td>
</tr>
<tr>
<td>Nickel</td>
<td>4</td>
<td>µg/cm²/week</td>
<td>0,042</td>
<td>0,04</td>
<td>0,043</td>
<td>0,043</td>
<td>according to §64 LFGB B 82.02-6</td>
</tr>
<tr>
<td>Nickel</td>
<td>5</td>
<td>µg/cm²/week</td>
<td>0,043</td>
<td>0,044</td>
<td>0,043</td>
<td>0,043</td>
<td>§64 LFGB B82.02-6 (modified)</td>
</tr>
<tr>
<td>Nickel</td>
<td>6</td>
<td>µg/cm²/week</td>
<td>0,024</td>
<td>0,004</td>
<td>0,0286</td>
<td>0,0201</td>
<td>EN1811 - DIN 17294-2</td>
</tr>
<tr>
<td>Nickel</td>
<td>7</td>
<td>µg/cm²/week</td>
<td>0,0015</td>
<td>0,0014</td>
<td>0,0019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>8</td>
<td>µg/cm²/week</td>
<td>&lt;0,05</td>
<td>&lt;0,05</td>
<td>&lt;0,05</td>
<td>&lt;0,05</td>
<td>ASU 82.02 part 6, version january 2013</td>
</tr>
<tr>
<td>Nickel</td>
<td>9</td>
<td>µg/cm²/week</td>
<td>n.n.</td>
<td>&lt;0,01</td>
<td>&lt;0,01</td>
<td>&lt;0,01</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>µg/cm²/week</td>
<td>0,006</td>
<td>0,023</td>
<td>0,007</td>
<td></td>
<td>AAS/GFA</td>
</tr>
</tbody>
</table>

* details by participant 1:
Samples were cleaned before investigation with detergent and the surface was determined. Afterwards laid in 40 ml simulant each (according to EN 1811) and incubated sealed at 30 ± 2° C for 168 h in an oven. Solution was taken for determination of nickel. Simulation of corrosion according to EN 12472 was not done. The mean of 3 single measurements was calculated for final result.

** notes by DLA to final result of participant 1
The final result given by participant 1 was in the target range and would result in a z-score of 1,3. The result C indicating „<“ was not considered by DLA for calculation of the mean, therefore a higher mean resulted in a value above the target range.
### Test Item 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Teilnehmer</th>
<th>Einheit</th>
<th>Abschließendes Ergebnis</th>
<th>Ergebnis A</th>
<th>Ergebnis B</th>
<th>Ergebnis C</th>
<th>Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>1</td>
<td>µg/cm²/week</td>
<td>28,75</td>
<td>28,917</td>
<td>29,557</td>
<td>27,785</td>
<td>* Nickel release of articles in direct and prolonged contact with the skin (§ 64 LFGB B 82.02)</td>
</tr>
<tr>
<td>Nickel</td>
<td>2</td>
<td>µg/cm²/week</td>
<td>23,634</td>
<td>18,746</td>
<td>26,123</td>
<td>26,033</td>
<td>Nickel release of articles in direct and prolonged contact with the skin (§ 64 LFGB B 82.02)</td>
</tr>
<tr>
<td>Nickel</td>
<td>3</td>
<td>µg/cm²/week</td>
<td>33,65</td>
<td>51,98</td>
<td>22,92</td>
<td>26,06</td>
<td>DIN EN 1811</td>
</tr>
<tr>
<td>Nickel</td>
<td>4</td>
<td>µg/cm²/week</td>
<td>8,66</td>
<td>8,37</td>
<td>7,21</td>
<td>10,38</td>
<td>ASU B82.02-6</td>
</tr>
<tr>
<td>Nickel</td>
<td>5</td>
<td>µg/cm²/week</td>
<td>35,767</td>
<td>34,99</td>
<td>36,72</td>
<td>35,59</td>
<td>according to §64 LFGB B 82.02-6</td>
</tr>
<tr>
<td>Nickel</td>
<td>6</td>
<td>µg/cm²/week</td>
<td>38,89</td>
<td>37,80</td>
<td>38,00</td>
<td>40,88</td>
<td>§64 LFGB B82.02-6 (modified)</td>
</tr>
<tr>
<td>Nickel</td>
<td>7</td>
<td>µg/cm²/week</td>
<td>37,49</td>
<td>39,81</td>
<td>36,31</td>
<td>36,37</td>
<td>According to DIN EN 1811-2011 Reference method for determination of nickel release. The measurement uncertainty corresponds to the norm.</td>
</tr>
<tr>
<td>Nickel</td>
<td>8</td>
<td>µg/cm²/week</td>
<td>18</td>
<td>17</td>
<td>19</td>
<td>19</td>
<td>According to DIN EN 1811-2011 Reference method for determination of nickel release. The measurement uncertainty corresponds to the norm.</td>
</tr>
<tr>
<td>Nickel</td>
<td>9</td>
<td>µg/cm²/week</td>
<td>11,75</td>
<td>11,96</td>
<td>11,61</td>
<td>11,67</td>
<td>ASU 82.02 part 6, version January 2013</td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>µg/cm²/week</td>
<td>12,08</td>
<td>12,64</td>
<td>10,13</td>
<td>13,47</td>
<td>EN 1811:2011</td>
</tr>
</tbody>
</table>

* details by participant 1:
The test item was cleaned with water and detergent and laid into the test solution, in that way all surfaces to be investigated are in contact with it and not at the bottom. The expanded measurement uncertainty is ±0,943 µg/cm²/week.
5.2 Homogeneity

5.2.1 Homogeneity test before the PT

Analysis of items by determination of nickel release according to ASU B 82.02-6 (EN 1811) by ICP-OES (13):

Test Item I

<table>
<thead>
<tr>
<th>independent samples</th>
<th>µg/cm²/week</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,085</td>
</tr>
<tr>
<td>2</td>
<td>0,089</td>
</tr>
<tr>
<td>3</td>
<td>0,061</td>
</tr>
</tbody>
</table>

Mean X 0,078
Repeatability Standard Deviation 0,015 19%

Test Item II

<table>
<thead>
<tr>
<th>independent samples</th>
<th>µg/cm²/week</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59,7</td>
</tr>
<tr>
<td>2</td>
<td>52,6</td>
</tr>
<tr>
<td>3</td>
<td>63,4</td>
</tr>
<tr>
<td>4</td>
<td>62,2</td>
</tr>
</tbody>
</table>

Mean X 59,5
Repeatability Standard Deviation 4,8 8,1%

5.2.2 Repeatability standard deviation of single tests of the participants

The repeatability standard deviations between samples were calculated with the data documented in 5.1.
For test item I exclusively results > 0,010 µg/cm²/week were considered, per participant two single results were taken.
For test item II the repeatability standard deviation was calculated from all 3 single results of participants.

Test Item I

<table>
<thead>
<tr>
<th></th>
<th>Einheit / Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wiederholstandardabweichung SD der Teilnehmer / Repeatability Standard Deviation SD of Participants</td>
<td>0,0121 µg/cm²/week</td>
</tr>
<tr>
<td>Mittelwert / Mean</td>
<td>0,043 µg/cm²/week</td>
</tr>
<tr>
<td>relative Wiederholstandardabweichung / relative SD</td>
<td>28,0 %</td>
</tr>
</tbody>
</table>

Test Item II

<table>
<thead>
<tr>
<th></th>
<th>Einheit / Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wiederholstandardabweichung SD der Teilnehmer / Repeatability Standard Deviation SD of Participants</td>
<td>1,80 µg/cm²/week</td>
</tr>
<tr>
<td>Mittelwert / Mean</td>
<td>28,9 µg/cm²/week</td>
</tr>
<tr>
<td>relative Wiederholstandardabweichung / relative SD</td>
<td>6,2 %</td>
</tr>
</tbody>
</table>
## 5.3 Analytical Methods

**Details by the participants**

### Test Item I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Teilnehmer</th>
<th>Vorbehandlung des Gegenstands</th>
<th>Berechnete Oberfläche pro Muster</th>
<th>Volumen der Prüflösung pro Muster</th>
<th>Prüflösung nach EN 1811-2012</th>
<th>Zeit und Temperatur: 168 h bei 370°C</th>
<th>Hinweise zur Analytik</th>
<th>Methode ist akkreditiert</th>
<th>Sonstige Hinweise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel 1</td>
<td>degreasing according to 1811, with common in commerce detergent</td>
<td>24,633</td>
<td>ja</td>
<td>40</td>
<td>yes</td>
<td>mean: 20,046; A: 20,006; B: 20,085; C: 21,302</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 2</td>
<td>rinsed with distilled water</td>
<td>A: 21,4; B: 24,03; C: 23,92</td>
<td>ja</td>
<td>150</td>
<td>yes</td>
<td>mean: 20,046; A: 20,006; B: 20,085; C: 21,302</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 3</td>
<td>degreasing</td>
<td>19,2</td>
<td>ja</td>
<td>40</td>
<td>yes</td>
<td>mean: 20,046; A: 20,006; B: 20,085; C: 21,302</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 4</td>
<td>no</td>
<td>A: 21,00; B: 21,00; C: 21,53</td>
<td>ja</td>
<td>a: 200</td>
<td>yes</td>
<td>measured by ICP-MS after dilution of 1:10</td>
<td>yes</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 5</td>
<td>yes</td>
<td>A: 21,5; A: 24,69; B: 23,79; C: 23,28</td>
<td>ja</td>
<td>22</td>
<td>yes</td>
<td>measured by ICP-MS after dilution of 1:10</td>
<td>yes</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 6</td>
<td>degreasing</td>
<td>23,5; A: 23,36; B: 23,00; C: 22,36</td>
<td>ja</td>
<td>23</td>
<td>yes</td>
<td>measured by ICP-MS after dilution of 1:10</td>
<td>yes</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 7</td>
<td>cleaning with detergent</td>
<td>20</td>
<td>ja</td>
<td>100</td>
<td>yes</td>
<td>mean: 20,046; A: 20,006; B: 20,085; C: 21,302</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 8</td>
<td>degreasing</td>
<td>19,91</td>
<td>ja</td>
<td>50</td>
<td>yes</td>
<td>mean: 20,046; A: 20,006; B: 20,085; C: 21,302</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel 9</td>
<td>sample degreasing</td>
<td>A: 23,2</td>
<td>-</td>
<td>50</td>
<td>yes</td>
<td>mean: 20,046; A: 20,006; B: 20,085; C: 21,302</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Test Item II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Teilnehmer</th>
<th>Vorbehandlung des Gegenstands</th>
<th>Berechnete Oberfläche pro Muster</th>
<th>Volumen der Prüflösung pro Muster</th>
<th>Prüflösung nach EN 1811-2012</th>
<th>Zeit und Temperatur: 168 h bei 370°C</th>
<th>Hinweise zur Analytik</th>
<th>Methode ist akkreditiert</th>
<th>Sonstige Hinweise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>1</td>
<td>degreasing by common in commerce detergent</td>
<td>12.19</td>
<td>ja / nein</td>
<td>15</td>
<td>yes</td>
<td>value by ICP-OES at λ=221.648 nm determined</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>2</td>
<td>rinsed with distilled water</td>
<td>12.2</td>
<td>yes</td>
<td>20</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>3</td>
<td>degreasing</td>
<td>12.14</td>
<td>yes</td>
<td>20</td>
<td>yes</td>
<td>ICP-OES</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>4</td>
<td>no</td>
<td>12.2</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>ICP-OES</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>5</td>
<td>yes</td>
<td>A: 12.170; B: 12.161; C: 12.169</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>6</td>
<td>degreasing</td>
<td>12.195</td>
<td>yes</td>
<td>12</td>
<td>yes</td>
<td>measured by ICP-MS after dilution of 1:10</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>7</td>
<td>cleaning with SDS-solution</td>
<td>13.331</td>
<td>yes</td>
<td>14</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>8</td>
<td></td>
<td>12.2</td>
<td>yes</td>
<td>10</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>9</td>
<td></td>
<td>20.23</td>
<td>yes</td>
<td>50</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>10</td>
<td>degreasing</td>
<td>12.195</td>
<td>yes</td>
<td>12</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td></td>
</tr>
</tbody>
</table>
6. Index of participant laboratories in alphabetical order

<table>
<thead>
<tr>
<th>Teilnehmer / Participant</th>
<th>Ort / Town</th>
<th>Land / Country</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Germany</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Germany</td>
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<tr>
<td></td>
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<td>Greece</td>
</tr>
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<td></td>
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<td>Germany</td>
</tr>
</tbody>
</table>

[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 17043:2010; Konformitätsbewertung – Allgemeine Anforderungen an Eignungsprüfungen / Conformity assessment – General requirements for proficiency testing
2. Verordnung / Regulation 882/2004/EU; Verordnung über amtliche Kontrollen / Regulation on official controls
3. 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
4. Richtlinie / Directive 1993/99/EU; über zusätzliche Maßnahmen im Bereich der amtlichen Lebensmittelüberwachung / on additional measures concerning the official control of foodstuffs
5. ASU §64 LFGB : Planung und statistische Auswertung von Ringversuchen zur Methodenvvalidierung
10. A Horwitz-like funktion describes precision in proficiency test; M. Thompson, P.J. Lowthian; Analyst, 120, 271-272 (1995)
12. Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing; M. Thompson; Analyst, 125, 385-386 (2000)
13. ASU §64 L 82.02-6: Referenzprüverfahren 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