**Final Report**
evaluation of proficiency test

**DLA ptAU03 (2022)**

# Iodine and Fluorine:

## in Salt

***DLA - Proficiency Tests GmbH***
*Hauptstr. 80*
*23845 Oering/Germany*

*proficiency-testing@dla-lvu.de* *www.dla-lvu.de*

*Coordinator of this PT:*
*Alexandra Scharf MSc.*

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

| | |
|---|---|
| *EP-Anbieter*<br>*PT-Provider* | **DLA - Proficiency Tests GmbH**<br>Hauptstr. 80, 23845 Oering, Germany<br><br>Geschäftsführer/CEO: Dr. Matthias Besler-Scharf<br>Stellv. Leitung/Deputy Lead: Alexandra Scharf MSc.<br><br>Tel. ++49-(0)4532-9183358<br>Mob. ++49(0)171-1954375<br>Fax. ++49(0)4102-9944976<br>eMail. proficiency-testing@dla-lvu.de |
| *EP-Nummer*<br>*PT-Number* | DLA ptAU03 (2022) |
| *EP-Koordinator*<br>*PT-Coordinator* | Alexandra Scharf MSc. |
| *Status des EP-Bericht*<br>*Status of PT-Report* | Abschlussbericht / Final report (9 January 2023)<br><br>Gültig ist die jeweils letzte Version/Korrektur des Berichts. Sie ersetzt alle vorangegangenen Versionen.<br>Only the latest version/correction of the report is valid. It replaces all preceding versions. |
| *EP-Bericht Freigabe*<br>*PT-Report Authorization* | Dr. Matthias Besler-Scharf (Technischer Leiter / Technical Manager)<br>*- gezeichnet / signed M. Besler-Scharf*<br>Alexandra Scharf MSc. (QM-Beauftragte / Quality Manager)<br>*- gezeichnet / signed A. Scharf*<br>Datum / Date: 9 January 2023 |
| *Unteraufträge*<br>*Subcontractors* | Im Rahmen dieser Eignungsprüfung wurden nachstehende Leistungen im Unterauftrag vergeben: Keine<br>As part of the present proficency test the following services were subcontracted:<br>none |
| *Vertraulichkeit*<br>*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.<br>Participant result are named anonymously with evaluation numbers in the PT report. Data of individual participants will be passed on to third parties only with prior consent of the participant. |

# Contents



The **List of Abbreviations** can be found in the
**“DLA Evaluation Guide 02.01 (2022) General Proficiency Test Schemes”**

# 1. Introduction

The participation in proficiency test (PT) 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].

The general procedure for evaluating the DLA proficiency tests can be found in the **"DLA Evaluation Guide 02.01 (2022) General Proficiency Test Schemes"**.

# 2. Realisation

## 2.1 Test material

The test material is a mixture of common in commerce table salts from European suppliers.
The raw materials were mixed, crushed, sieved (mesh 800 µm), and homogenized.

Afterwards, the samples were portioned to approximately 200 g into metallised PET film bags and chronologically numbered.

The composition (list of ingredients) of the samples is given in table 1.
The contents of analytes given in table 2 were calculated according to the manufacturers specifications.

**Table 1:** Composition of DLA-Samples

| Ingredients | PT Samples |
|---|---|
| Iodine salt with fluoride<br>Ingredients: Boiling salt, potassium fluoride, potassium iodate, separating agent: sodium ferrocyanide | 82,1 g/100 g |
| Rock salt<br>Ingredients: Rock salt, separating agent: magnesium carbonate | 17,9 g/100g |

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

**Table 2:** Calculated amounts of parameters according to the manufacturers specification and gravimetric mixture

| Parameter | Content per kg |
|---|---|
| Iodine | 16,4 mg |
| Fluorine | 255 mg |

### *2.1.1 Homogeneity testing results*

A specific description of the procedures can be found in the **"DLA Evaluation Guide 02.01 (2022) General Proficiency Test Schemes"**.

#### *Homogeneity testing by microtracer*

The microtracer analysis showed an acceptable homogeneity of the present PT samples (see Table 3). The results of microtracer analysis are given in the documentation (see 5.2.1).

**Table 3:** Results of microtracer analysis

| Evaluation method | Criterion | PT Samples |
|---|---|---|
| **Probability** (poisson distribution) | ≥ 5 % (good)<br>≥ 25% (excellent) | 98 % |
| **HorRat Value** (normal distribution) | ≤ 1,3 | 0,61 |

#### *Homogeneity of the parameters*

The calculation of the **repeatability standard deviations $S_r$ of the participants** was also used as an indicator of homogeneity. For both parameters it was ≤ 6,4% (see Table 4). Thus, they were similar to corresponding repeatability standard deviations of precision data of the standardized methods (e.g. ASU-Methods 00.00-93 and 47.03-1, s. 3.2) (see Table 7) [A-B].
The repeatability standard deviations of the participants' results are given in the documentation in the statistic data (see 4.1 to 4.2).

**Table 4:** Repeatability standard deviation $S_r$ of double determinations of the participants (coefficient of variation $CV_r$ in %)

| Parameter | $CV_r$ |
|---|---|
| Iodine | 6,38 % |
| Fluorine | 1,29 % |

Furthermore, the homogeneity was graphically characterized for information by the **trend line function of participants' results for chronological bottled single samples** (s. 5.2.2).

In case the criterion for sufficient homogeneity of the test items is not fulfilled, the impact on the target standard deviation will be verified. If necessary, the evaluation of results will be done considering the standard uncertainty of the assigned value by z'-scores (s. DLA Evaluation Guide 2.01 (2022) 3.2.7.2 and 3.2.9) [3].

### *2.1.2 Stability*

The $a_W$ values of the PT **samples in form of powder** were in the range of 0,5 (see Table 5). Therefore, a good storage stability with respect to the durability of the sample (spoilage) and the content of the PT parameters as established for comparable food matrices can be expected. The stability of the sample material was thus ensured during the investigation period under the specified storage conditions.

**Table 5:** Results of water activity ($a_W$ value).

| Evaluation method | Criterion | PT Samples |
|---|---|---|
| $a_W$ value | ≤ 0,5 | 0,53 (20,1°C) |

## 2.2 Sample shipment and information to the test

The portions of test material were sent to every participating laboratory in the 38th week of 2022. The testing method was optional. The tests should be finished at 18 November 2022 the latest.
With the cover letter along with the sample shipment, the following information was given to the participants:
*The two portions contain identical samples of iodized salt with fluorine. The analytical method for the determination of the parameters iodine and fluorine is optional.*

*Please note the attached information on the proficiency test.*
(see documentation, section 5.3 Information on the PT)

## 2.3 Submission of results

The participants submitted their results in standard forms (digital *result submission file*) which have been sent before by email in parallel to the sample shipment.
The finally calculated concentration of the parameter(s) as the average of duplicate determinations of both numbered samples was used for the statistical evaluation. For the calculation of the repeatability– and reproducibility standard deviation the single values of the double determination were used.

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

All 10 participants submitted at least one result.

# 3. Evaluation

A specific description of the concept and procedures can be found in the **"DLA Evaluation Guide 02.01 (2022) General Proficiency Test Schemes"**.

## 3.1 Quantitative Evaluation

From a total of 5 results on, a quantitative evaluation is carried out, provided that the conditions for a symmetrical distribution of the results and a joint evaluation are met. Frequently, different analytical methods may cause an anomaly in results' distribution. If this is the case, separate evaluations of the different methods with their own assigned values ($X_{pt\ METHOD\ i}$) are performed whenever possible.

Table 6 gives an overview of the evaluation characteristics, their calculation and related criteria.
The procedure is described in detail in the accompanying document: DLA Evaluation Guide 02.01 (2022).

**Table 6:** Evaluation characteristics and criterions for consensus values from participants

| Evaluation characteristics | Calculation or criterion |
|---|---|
| Assigned value ($X_{pt_{ALL}}$ *or* $X_{pt_{METHOD\ i}}$) | Robust mean (algorithm A) or median |
| Standard deviation ($S^*_{ALL}$ *or* $S^*_{METHOD\ i}$) | Standard deviation (algorithm A) |
| Target standard deviation ($\sigma_{pt}$) | *General model according to:*<br>Horwitz ($X_{pt} \geq 120$ µg/kg)<br>for **both parameters Iodine and Fluorine** |
| Target standard deviation (for information ) | *From precision experiment according to:*<br>ASU-Methods 00.00-93 and 47.03-1 (s. 3.2) [A-B]<br>for **both parameters Iodine and Fluorine** |
| Target standard deviation ($\sigma_{pt}$') | $\sigma_{pt}$ extended by standard uncertainty<br>for **none** of the parameters |
| Target range ($X_{pt} \pm 2\sigma_{pt}$ or $2\sigma_{pt}$') | $X_{pt} \pm 2\sigma_{pt}$ or $2\sigma_{pt}$' |
| Quotient $S^*/\sigma_{pt}$ or $S^*/\sigma_{pt}$' | ≤ 2,0 (PT evaluation convincing) |
| z-Score or z'-Score | -2 ≤ z-score ≤ 2 (successful)<br>-2 > z-score > 2 (warning signal)<br>-3 > z-score > 3 (action signal) |
| Kernel density estimation<br>Exclusion of outliers<br>Repeatability standard deviation ($S_r$)<br>Coefficient of Variation ($CV_r$)<br>Reproducibility standard deviation ($S_R$)<br>Coefficient of Variation ($CV_R$)<br>Standard uncertainty of assigned value ($U_{(X_{pt})}$)<br>Traceability | see DLA Evaluation Guide 02.01 (2022) |

## 3.2 Additional information for the parameters

The following information is supplied in addition to the general information of the DLA Evaluation Guide 02.01 (2022).

### Values by precision experiments

The relative repeatability standard deviations ($RSD_r$) and relative reproducibility standard deviations ($RSD_R$) given in **table 7** were determined in ring tests using the indicated methods.
The resulting **target standard deviations *σpt*,** which were identified there, were used to evaluate the results and to provide additional information for the statistical data.

**Table 7:** Relative repeatability standard deviations ($RSD_r$) and relative reproducibility standard deviations ($RSD_R$) according to selected evaluations of tests for precision and the resulting target standard deviation $\sigma_{pt}$ [A-B]

| **Parameter** | **Matrix** | **Mean** [mg/kg] | **$RSD_r$** [%] | **$RSD_R$** [%] | **σpt** [%] | **Method / Literature** |
|---|---|---|---|---|---|---|
| Iodine | Cod meat | 4,15 | 0,7 | 8,9 | 8,89 | ICP-MS/ [A] ASU 00.00-93 |
| Iodine | Iodized salt | 19,8 | 6,4 | 15 | 14,3° | ICP-MS/ [A] ASU 00.00-93 |
| Iodine | Seaweed | 40,1 | 0,9 | 6,2 | 6,17 | ICP-MS/ [A] ASU 00.00-93 |
| Fluorine | Tea | 150 | 1,76 | 4,69 | 4,52 | Potentiometric/ [B] ASU 47.03-1 |
| Fluorine | Tea | 113 | 1,65 | 9,15 | 9,08 | Potentiometric/ [B] ASU 47.03-1 |
| Fluorine | Tea | 152 | 1,98 | 6,14 | 5,98° | Potentiometric/ [B] ASU 47.03-1 |

*° used for evaluation (cf. chapter 4)*

## Values by perception

Table 8 shows selected statistic data of participants' results of the present PT compared to PT results of previous years.

**Table 8:** Characteristics of the present PT (on grey) in comparison to the previous PT since 2017 (SD = standard deviation, CV = coefficient of variation)

| Parameter | Matrix | rob. Mean [mg/kg] | rob. SD (S*) [mg/kg] | rel. SD ($VK_{S^*}$) [%] | Quotient S*/σpt | DLA Report |
|---|---|---|---|---|---|---|
| Iodine | Table salt | 18,5 | 2,60 | 14,1 | 1,0 | DLA 31/2017 |
| Iodine | Table salt | 23,2 | 2,72 | 11,7 | 0,82 | DLA 31/2019 |
| Iodine | Table salt | 18,3 | 2,62 | 14,3 | 1,4 | DLA ptAU03 (2021) |
| Iodine | Table salt | 16,4 | 2,10 | 12,8 | 1,2 | DLA ptAU03 (2022) |
| Fluorine | Table salt | 200 | 41,9 | 21,0 | 1,8° | DLA 31/2017 |
| Fluorine | Table salt | 314 | 65,9 | 21,0 | 2,0° | DLA 31/2019 |
| Fluorine | Table salt | 217 | 7,22 | 3,32 | 0,47 | DLA ptAU03 (2021) |
| Fluorine | Table salt | 214 | 12,6 | 5,88 | 0,82 | DLA ptAU03 (2022) |

*° with target standard deviation σpt'*

# 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 result chapter, all quantitative results of the participants are displayed formatted to 3 valid digits. In the documentation, all results are given as they were transmitted by the participants. The result tables are structured as below:

| Evaluation number | Parameter [Unit] | Deviation | z-Score $\sigma_{pt}$ | z-Score (Info) | Remark |
|---|---|---|---|---|---|
| | | | | | |

## 4.1 Iodine (in mg/kg)

### Proficiency Test

| **Statistic Data** | |
|---|---|
| *Number of results °* | *7* |
| *Number of outliers* | *2* |
| Mean | 16,2 |
| Median | 16,2 |
| **Robust Mean ($X_{pt}$)** | **16,4** |
| **Robust standard deviation (S*)** | **2,10** |
| *Number with 2 replicates* | *7* |
| Repeatability SD ($S_r$) | 1,03 |
| Repeatability ($CV_r$) | 6,38% |
| Reproducibility SD ($S_R$) | 2,46 |
| Reproducibility ($CV_R$) | 15,2% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **1,72** |
| Target standard deviation (for Information) | 2,34 |
| **lower limit of target range** | **13,0** |
| **upper limit of target range** | **19,8** |
| *Quotient S*/$\sigma_{pt}$* | *1,2* |
| *Standard uncertainty $U_{(Xpt)}$* | *0,993* |
| *Results in the target range* | *6* |
| *Percent in the target range* | *86%* |

° without outliers

Comments:

The target standard deviation was calculated according to the general model of Horwitz (see DLA Evaluation Guide 2.01 (2022) 3.2.6.1). In addition, the target standard deviation calculated according to the evaluation of a precision experiment (ASU §64 L 00.00-93) was given for information (see 3.2, Tab. 7).

The distribution of results showed a normal variability, with a quotient S*/$\sigma_{pt}$ below 2,0.
The robust standard deviation was in the range of previous PTs (see 3.2, Tab. 8). The repeatability standard deviation was in the range of established values for the used determination methods (s. 3.2, Tab. 7). The comparability of results is given.

86% of results were in the target range.

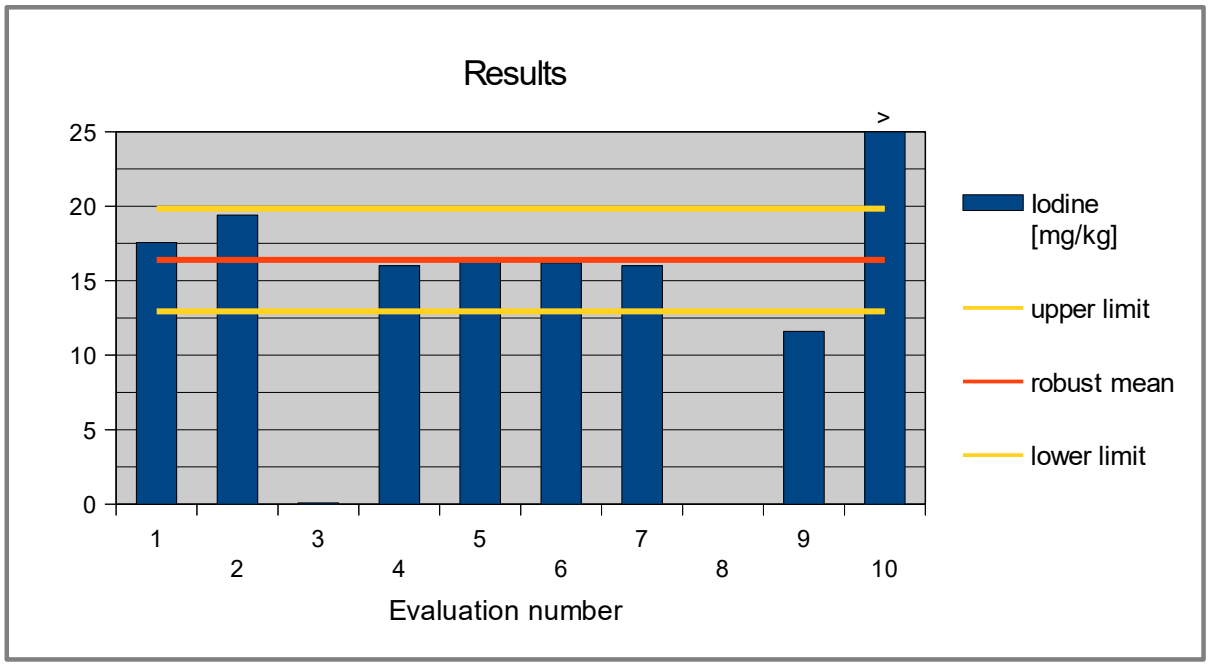



**Fig. 1:** Results Iodine

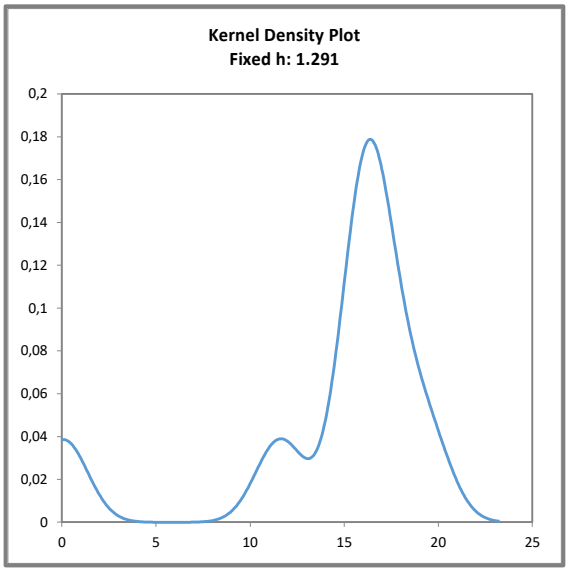



**Fig. 2: Kernel density plot of all results**
(with h = 0,75 x $\sigma pt$ of $Xpt_{ALL}$)

Comments:
The kernel density estimation shows nearly a symmetrical distribution with a side peak at 0,081 mg/kg, which can be ascribed to an outlier. One more outlier (> 150 mg/kg) was excluded from the evaluation but not shown in the kernel density estimation since it would distort the illustration of the other results. Furthermore, one smaller side peak can be seen at 11,6 mg/kg due to one result below the target range (not excluded).

**Results of Participants:**

| Evaluation number | Iodine [mg/kg] | Deviation [mg/kg] | z-Score (σpt) | z-Score (Info) | Remark |
|---|---|---|---|---|---|
| 1 | 17,6 | 1,16 | 0,68 | 0,50 | |
| 2 | 19,4 | 3,00 | 1,7 | 1,3 | |
| 3 | 0,0810 * | | | | outlier excluded |
| 4 | 16,0 | -0,40 | -0,23 | -0,17 | |
| 5 | 16,4 | -0,04 | -0,03 | -0,02 | |
| 6 | 16,2 | -0,20 | -0,11 | -0,08 | |
| 7 | 16,0 | -0,40 | -0,23 | -0,17 | |
| 8 | | | | | |
| 9 | 11,6 | -4,80 | -2,8 | -2,0 | |
| 10 | 176 | | | | outlier excluded |

* Mean calculated by DLA

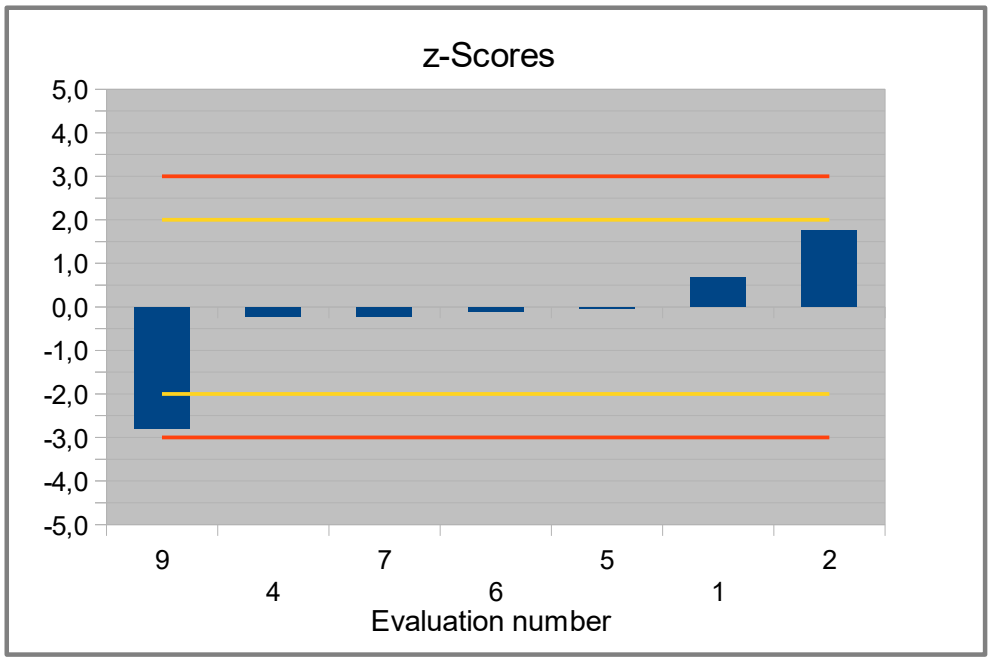



**Fig. 3:** z-Scores Iodine

## 4.2 Fluorine (in mg/kg)

### Proficiency Test

| **Statistic Data** | |
|---|---|
| *Number of results* ° | 6 |
| *Number of outliers* | 1 |
| Mean | 209 |
| Median | 217 |
| **Robust Mean ($X_{pt}$)** | **214** |
| **Robust standard deviation (S*)** | **12,6** |
| *Number with 2 replicates* | 5 |
| Repeatability SD ($S_r$) | 2,80 |
| Repeatability ($CV_r$) | 1,29% |
| Reproducibility SD ($S_R$) | 7,16 |
| Reproducibility ($CV_R$) | 3,30% |
| *Target range:* | |
| **Target standard deviation $\sigma_{pt}$** | **15,3** |
| Target standard deviation (for Information) | 12,8 |
| **lower limit of target range** | **183** |
| **upper limit of target range** | **244** |
| *Quotient S*/$\sigma_{pt}$* | *0,82* |
| *Standard uncertainty $U_{(Xpt)}$* | *6,41* |
| *Results in the target range* | *5* |
| *Percent in the target range* | *83%* |

° without outliers

Comments:

The target standard deviation was calculated according to the general model of Horwitz (see DLA Evaluation Guide 2.01 (2022) 3.2.6.1). In addition, the target standard deviation calculated according to the evaluation of a precision experiment (ASU §64 L 47.03-1) was given for information (see 3.2, Tab. 7).

The distribution of results showed a low variability, with a quotient S*/$\sigma_{pt}$ below 1,0.
The robust standard deviation was in the range of previous PTs (see 3.2, Tab. 8). The repeatability standard deviation was in the range of established values for the used determination methods (s. 3.2, Tab. 7). The comparability of results is given.

83% of results were in the target range.

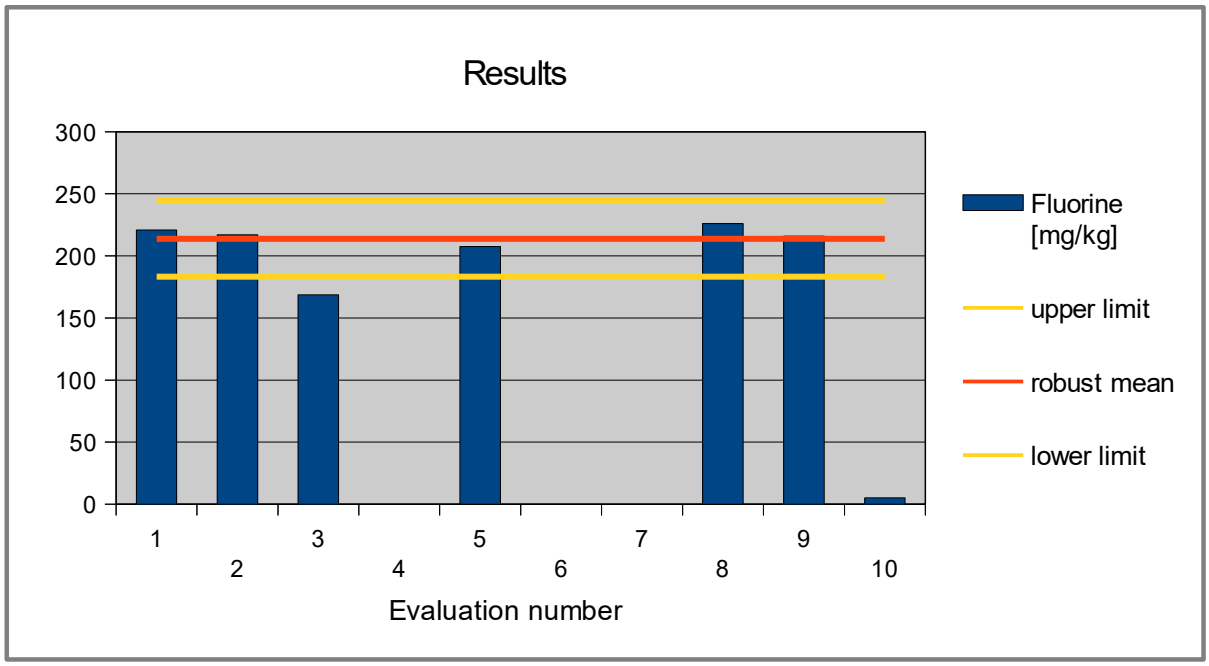



**Fig. 4:** Results Fluorine

Note:
Due to the low number of < 8 results a kernel density estimation could not be carried out.

**Results of Participants:**

| Evaluation number | Fluorine [mg/kg] | Deviation [mg/kg] | z-Score (σpt) | z-Score (Info) | Remark |
|---|---|---|---|---|---|
| 1 | 221 | 7,2 | 0,48 | 0,57 | |
| 2 | 217 | 3,3 | 0,22 | 0,26 | |
| 3 | 169 * | -45,0 | -3,0 | -3,5 | |
| 4 | | | | | |
| 5 | 207 | -6,3 | -0,41 | -0,49 | |
| 6 | | | | | |
| 7 | | | | | |
| 8 | 226 | 12,3 | 0,81 | 0,96 | |
| 9 | 216 | 2,3 | 0,15 | 0,18 | |
| 10 | 5,03 | | | | outlier excluded |

* Mean calculated by DLA

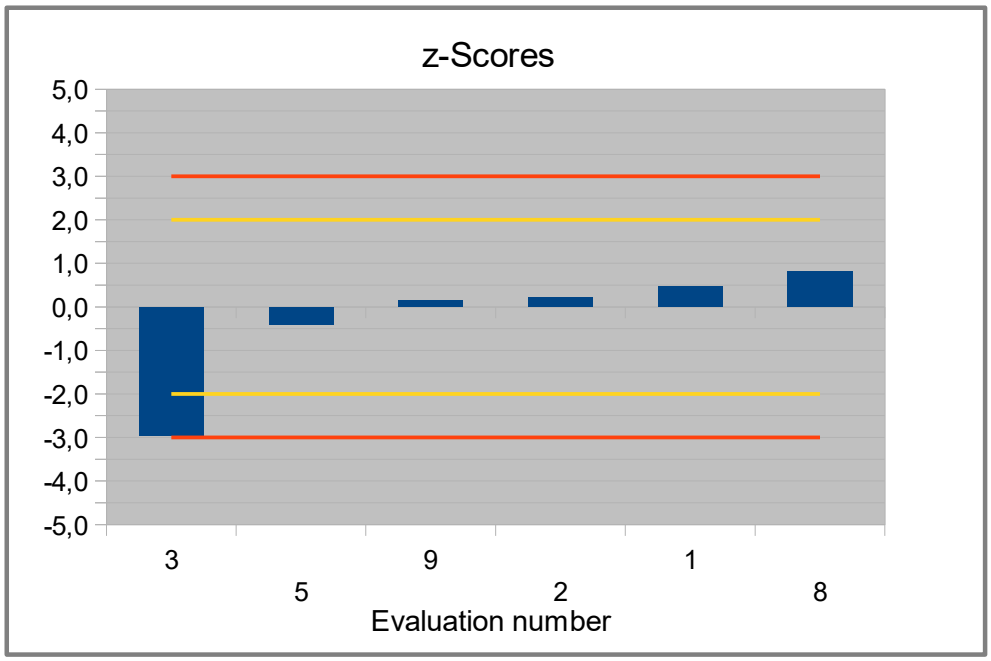



**Fig. 5:** z-Scores Fluorine

## 4.3 Participant z-Scores: overview table

### *Z-Scores for the assigned values from participants' results (consensus values)*

| Evaluation number | Iodine | Fluorine |
|---|---|---|
| | | |
| 1 | 0,68 | 0,48 |
| 2 | 1,7 | 0,22 |
| 3 | outlier | -3,0 |
| 4 | -0,23 | |
| 5 | -0,03 | -0,41 |
| 6 | -0,11 | |
| 7 | -0,23 | |
| 8 | | 0,81 |
| 9 | -2,8 | 0,15 |
| 10 | outlier | outlier |

Valuation of z-score (DIN ISO 13528:2009-01):
*-2 ≤ z-score ≤ 2 successful (in green)*
*-2 > z-score > 2 warning signal (in yellow)*
*-3 > z-score > 3 action signal (in red)*

# 5. Documentation

## 5.1 Details by the participants

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

### 5.1.1 Primary data

| Analyte | Participant | Unit | Sample I DLA No. | Sample II DLA No. | Date of analysis | Result (Mean) | Result Sample I | Result Sample II | LOQ (Limit of quantification) | Recovery included | Recovery Rate |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Day/Month | | | | | yes / no | in % |
| Iodine | 1 | mg/kg | 20 | 28 | 16. Nov | 17,56 | 17,24 | 17,88 | 1 | yes | 94,6 |
| | 2 | mg/kg | 1 | 47 | 09. Nov | 19,4 | 20,4 | 18,4 | 0,086 | no | |
| | 3 * | mg/kg | 7 | 41 | 16. Nov | 0,08 | 0,08 | 0,08 | - | no | - |
| | 3 * | mg/kg | 15 | 33 | 16. Nov | 0,082 | 0,08 | 0,083 | - | no | - |
| | 4 | mg/kg | 23 | 25 | 04/Oct | 16 | 16,4 | 15 | 0,05 | no | - |
| | 5 | mg/kg | 11 | 37 | 16. Nov | 16,351 | 16,689 | 16,013 | 1,055 | no | 98-102% |
| | 6 | mg/kg | 3 | 45 | 06/Oct | 16,2 | 17,2 | 15,2 | 0,2 | no | - |
| | 7 | mg/kg | 13 | 13 | 11/November | 16 | 15 | 17 | 3,5 mg/kg | no | |
| | 8 | mg/kg | | | | | | | | | |
| | 9 | mg/kg | 12 | 36 | 24/Oct | 11,6 | 11,7 | 11,6 | 25 mg/kg | no | - |
| | 10 | mg/kg | 18 | 30 | 04/Oct | 176 | 178 | 174 | 0,02 ppm | no | |

* Mean of both sets of results calculated by DLA for evaluation

| Analyte | Participant | Unit | Sample I DLA No. | Sample II DLA No. | Date of analysis | Result (Mean) | Result Sample I | Result Sample II | LOQ (Limit of quantification) | Recovery included | Recovery Rate |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Day/Month | | | | | yes / no | in % |
| Fluorine | 1 | mg/kg | 20 | 28 | 16. Nov | 220,96 | 221,06 | 220,86 | 25 | no | 99,8 |
| | 2 | mg/kg | 1 | 47 | 26/Oct | 217 | 220 | 214 | 13 | no | |
| | 3 * | mg/kg | 7 | 41 | 14. Nov | 176,05 | 179,2 | 172,9 | 30 | no | - |
| | 3 * | mg/kg | 15 | 33 | 14. Nov | 161,35 | 160,4 | 162,3 | 30 | no | - |
| | 4 | mg/kg | - | - | - | - | - | - | - | - | - |
| | 5 | mg/kg | 11 | 37 | 14. Nov | 207,44 | 208,03 | 206,85 | 3,05 | no | 98-102% |
| | 6 | mg/kg | | | | | | | | | |
| | 7 | mg/kg | | | | | | | | | |
| | 8 | mg/kg | 10 | 38 | 31.10.2022 and 28.11.2022 | 226 | 228 | 224 | 40 | no | 100,5 |
| | 9 | mg/kg | 12 | 36 | 24/Oct | 216 | 218 | 213 | 50 mg/kg | no | - |
| | 10 | mg/kg | 18 | 30 | 04/Oct | 5,025 | 5,52 | 4,53 | 0,02 ppm | no | |

* Mean of both results calculated by DLA

## 5.1.2 Analytical Methods

| Parameter | Partici-pant | Method description, like in an analysis report / norm / literature | Notes to sample preparation | Notes to analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| Iodine | 1 | PROCEDIMIENTO PARA DETERMINAR EL CONTENIDO DE IODO EN SAL PARA CONSUMO HUMANO POR VALORACIÓN VOLUMÉTRICA ESPECÍFICA PARA IODATO RAN-FQ-PRO-040 | Homogenize the sample once open. No further preparation is required. | Weigh 10 g of sample and dissolve in 100 mL of type I water. Add 5 mL of sulfuric acid 0,1 N and 10 mL of potassium iodide 10 % solution. Titrate sample with standardized sodium thiosulfate 0,005 N solution and add 2 mL of starch 1% when yellow colour is about to disappear, continue tirtation to colourless solution is obtained. | Potassium iodate. 0001056316. | yes | no | Sample I analysed by A-FQ-14. Sample II analysed bye A-FQ-35. |
| | 2 | § 64 L 00.00-93:2008-12 modified | Extraction witht TMAH, weight ~ 0,25 g | | | | yes | |
| | 3 | IAL 383/IV | - | Titrimetric | - | no | no | - |
| | 4 | According to DIN EN 15111 (06/2007) | - | ICP-MS | - | no | yes | - |
| | 5 | Based on EUSALT. (2005). Sodium chloride – analytical standard. Determination of total iodine, titrimetric method. EuSalt/AS 002-2005. | | | Iodide ISE standard Lot = ISEI21L1, Potassium Iodide Lot = K50514651 | no | no | |
| | 6 | VDLUFA III 11.7.1 2006 | | | | - | yes | |
| | 7 | EuSaltAS 002-2005 | | | | | yes | |
| | 8 | | | | | | | |
| | 9 | Own method code:040VA0117P02. Accredited by ISO 17025:2017. Weigh by duplicate on analytical balance approximately 10.0000 +/- 0.0009 g salt. Transfer each weighing to a 100.00 mL volumetric balloon, dissolve with deionised water, add to volume and shake. Take an aliquot of 10.00 mL and transfer it to another 100.00 mL volumetric balloon. Complete by volume with deionised water and mixing. Transfer the 100.00 mL of the solution to a 150 mL plastic cup, add 2.00 mL of ISA (NaNO3 solution 5.0 M) solution with volumetric pipette. Immerse the electrode (ionanalyzer model EA 940) in the solution and meassure iodine concentration in mg/L (A). Calibration curve from 0.250 mg/L to 5.00 mg/L is perdormed each analytical test.<br><br>mg iodide/kg= ( A *1000)/g of salt | Dilution factor was changed<br><br>mg/kg= (A*111,11/ g of salt) | - | Solution of Iodides (I-) concentration 1000 mg/L Matrix : H2O Scharlau YO0077 | no | yes | Uncertainty:+/- 2,1 mg/kg. |
| | 10 | selective electrode | dissolve 10 g in 100ml of water and take 10 ml of solution for carry on to 100 ml and analize this sample | report as iodine | | no | no | |

| Parameter | Partici-pant | Method description, like in an analysis report / norm / literature | Notes to sample preparation | Notes to analytical method | Calibration and reference material | Recovery with same matrix | Method accredited ISO/IEC 17025 | Further Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | | yes / no | yes / no | |
| Fluorine | 1 | PROCEDIMIENTO PARA DETERMINAR EL CONTENIDO DE FLÚOR EN SAL PARA CONSUMO HUMANO – MÉTODO DEL ELECTRODO DE IÓN ESPECÍFICO RAN-FQ-PRO-039 | Homogenize the sample once open. No further preparation is required. | Weigh 10 g of sample, then add 40 mL of type I water and 20 mL of HCl 1 M, take the volumen to 100 mL with type I water. Take 25 mL of this solution into a plastic flask and then add 25 mL of TISABII. Measure the amount of F- ions in the sample using the selective ion electrode. | Fluoride 1000 mg/L standard solution. Supelco HC15929514. | yes | no | Sample I analysed by A-FQ-14. Sample II analysed bye A-FQ-35. |
| | 2 | Ion-sensitive electrode, German standard procedure | | | Reference solution: Roth IC standard solution fluoride | | yes | |
| | 3 | AOAC 975.8 | - | Ion Selective Potentiometry | Fluoride Standard for IC - Sigma-Aldrich | no | yes | - |
| | 4 | - | - | - | - | - | - | - |
| | 5 | Based on EUSALT. (2005). Sodium chloride – analytical standard. Determination of Fluorides Potentiometric method. EuSalt/AS 017-2005. | | | Fluoride ISE standard Lot = ISEF522B1 , Sodium fluoride Lot = B1193650 | no | no | |
| | 6 | | | | | | | |
| | 7 | | | | | | | |
| | 8 | Fluorine with ion-selective electrode, modified QSA-O-1556-04 (derived from DIN-EN 16279: 2012-09) | homogenization (grinding) | extraction with TISAB-buffer (incl. a. o. CDTA), potentiometric detection with ion-selective electrode (metrohm) | quantification with NaF-solution (ref. mat. SAL) incl. standard-addition | yes | no | accredited so far only for feed-method (without CDTA) |
| | 9 | Own method code 040VA0117P0. Accredited by ISO 17025:2017. Weigh by duplicate on analytical balance approximately 10.0000 +/- 0.0009 g salt. Transfer each weighing to a 100.00 mL volumetric balloon, dissolve with deionised water, add to volume and shake. Take an aliquot of 10.00 mL and transfer it to another 100.00 mL volumetric balloon. Complete by volume with deionised water and mixing. Transfer 10.00 mL of the water content solution to a 50 mL plastic cup, add 10.00 mL of TISAB II solution with volumetric pipette. Immerse the electrode (ionanalyzer model EA 940) in the solution and meassure fluorine concentration in mg/L (A). Calibration curve from 0.500 mg/L to 5.00 mg/L is perdormed each analytical test. mg fluoride/kg= ( A *1000)/g of salt | - | - | Fluoride standard solution treaceable to SRM from NIST NaF in H2O 1000 mg/L Certipur® HC15929514 | no | yes | Uncertainty:+/- 6,1 mg/kg |
| | 10 | selective electrode | dissolve 10 g in 100ml of water and take 10 ml of solution for carry on to 100 ml and analize this sample | report as fluoride | | no | no | |

## 5.2 Homogeneity

### 5.2.1 Mixture homogeneity during bottling

**Microtracer Homogeneity Test**
**DLA ptAU03 (2022)**

| | | |
|---|---|---|
| Weight whole sample | 10,11 | kg |
| Microtracer | FSS-red lake | |
| Particle size | 75 – 300 | µm |
| Weight per particle | 2,0 | µg |
| Addition of tracer | 23,0 | mg/kg |

**Result of analysis**

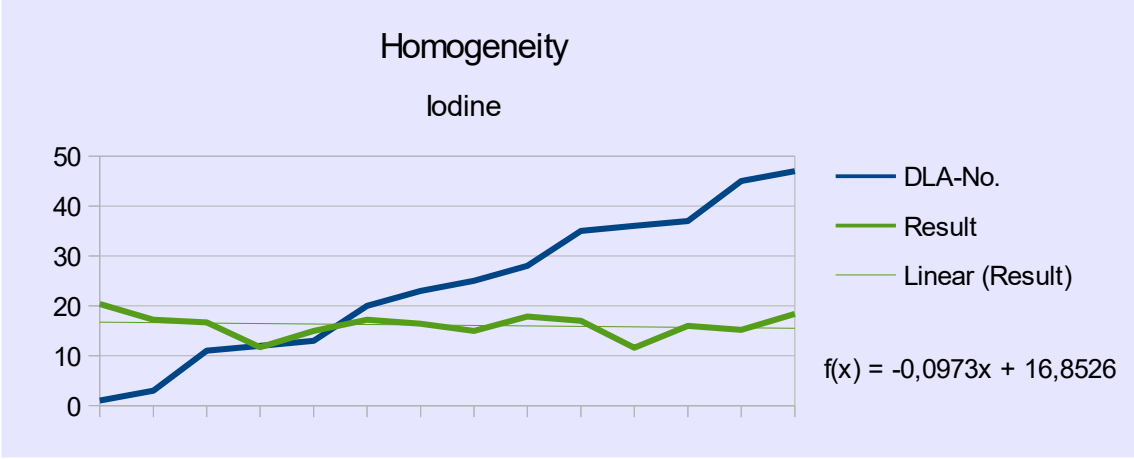
| Sample | Weight [g] | Particle number | Particles [mg/kg] |
|---|---|---|---|
| 1 | 4,94 | 70 | 28,3 |
| 2 | 5,01 | 65 | 25,9 |
| 4 | 5,03 | 71 | 28,2 |
| 6 | 5,01 | 66 | 26,3 |
| 7 | 5,00 | 70 | 28,0 |
| 8 | 5,04 | 72 | 28,6 |
| 9 | 5,02 | 60 | 23,9 |
| 10 | 4,99 | 68 | 27,3 |

| **Poisson distribution** | | |
|---|---|---|
| Number of samples | 8 | |
| Degree of freedom | 7 | |
| Mean | 67,8 | Particles |
| Standard deviation | 4,00 | Particles |
| $\chi^2$ (CHI-Square) | 1,66 | |
| **Probability** | **98** | % |
| Recovery rate | 118 | % |

| **Normal distribution** | | |
|---|---|---|
| Number of samples | 8 | |
| Mean | 27,1 | mg/kg |
| Standard deviation | 1,60 | mg/kg |
| rel. Standard deviaton | 5,91 | % |
| Horwitz standard deviation | 9,74 | % |
| **HorRat-value** | **0,61** | |
| Recovery rate | 118 | % |

### 5.2.2 Trend line function of the participants results

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



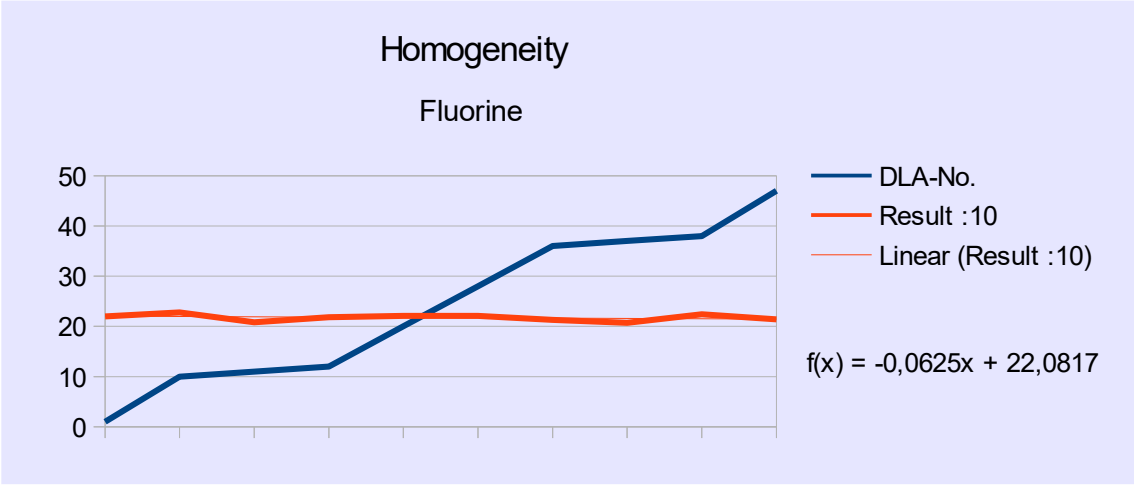




**Fig. 6:** Trend line function - sample number vs. results:
iodine and fluorine (1/1 and 1/10 shown)

## 5.3 Information on the Proficiency Test (PT)

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

| | |
|---|---|
| *PT number* | ***DLA ptAU03 (2022)*** |
| *PT name* | ***Iodine and Fluorine in Salt*** |
| *Sample matrix** | ***Samples I + II:*** *Mixure of Iodine salt with fluoride / Ingredients: boiling salt, potassium fluoride, potassium iodate, separating agent: sodium ferrocyanide, sodium carbonates and Rock salt / Ingredients: rock salt, separating agent: magnesium carbonate* |
| *Number of samples and sample amount* | *2 identical samples I + II, 200 g each.* |
| *Storage* | *Samples I + II:* ***room temperature*** |
| *Intentional use* | *Laboratory use only (quality control samples)* |
| *Parameter* | *quantitative:* ***Iodine and Fluorine*** |
| *Methods of analysis* | *Analytical methods are optional* |
| *Notes to analysis* | *The analysis of PT samples should be performed like a routine laboratory analysis.*<br>*In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights.* |
| *Result sheet* | *The results for sample I and II as well as the final results calculated as mean of the double determination (samples I and II) should be filled in the result submission file. The recovery rates, if carried out, has to be included in the calculation.* |
| *Units* | *mg/kg* |
| *Number of significant digits* | *at least 2* |
| *Further information* | *For information please specify:*<br>– *Date of analysis*<br>– *DLA-sample-numbers (for sample I and II)*<br>– *Limit of detection*<br>– *Assignment incl. Recovery*<br>– *Recovery with the same matrix*<br>– *Method is accredited* |
| *Result submission* | *The result submission file should be sent by e-mail to:*<br>***pt@dla-lvu.de*** |
| *Last Deadline* | ***the latest November 18th 2022*** |
| *Evaluation report* | *The evaluation report is expected to be completed 6 weeks after deadline of result submission and sent as PDF file by e-mail.* |
| *Coordinator and contact person of PT* | *Matthias Besler-Scharf PhD / A.Scharf MSc.* |

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

# 6. Index of participant laboratories in alphabetical order

| Participant | Town | Country |
|---|---|---|
| | | GERMANY |
| | | COLOMBIA |
| | | GERMANY |
| | | COLOMBIA |
| | | COLOMBIA |
| | | GERMANY |
| | | BRAZIL |
| | | GERMANY |
| | | COLOMBIA |
| | | LITHUANIA |

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

# 7. Index of references

The list of **references no. 1-21** can be found in the
**"DLA Evaluation Guide 02.01 (2022) General Proficiency Test Schemes"**.

***Additional specific references:***

A) ASU § 64 LFGB L 00.00-93 Bestimmung von Iod in Lebensmitteln, ICP-MS-Verfahren (Dezember 2008) [Determination of iodine in foods, ICP-MS method]
B) ASU § 64 LFGB L 47.03-1 Untersuchung von Tee, Bestimmung des Fluoridgehaltes, Potentiometrisches Verfahren (September 1997) [Analysis of tea, determination of the fluorine content, potentiometric method]