Evaluation Report
proficiency test

DLA ptSU07 (2021)

Dietetic Product I:

Vitamins A, E, D3, K1 and β-Carotene

in Drink Powder

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General Information on the proficiency test (PT)

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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 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

1. Introduction

The participation in proficiency testing schemes (PT) is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the verification and/or validation of the particular testing method [1, 5].
The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.
Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009 / ISO 13528:2015 [2, 3].

2. Realisation

2.1 Test material

The test material is a mixture of commercially available dietetic products (drink powder) as a meal replacement with the addition of beta-carotene capsules (without capsule shells) from European suppliers.

The raw materials were milled, sieved, mixed and homogenized.

The samples were then filled into portions of approx. 50g in metallized PET foil bags and numbered chronologically.

The composition (list of ingredients) and the contents of vitamins and provitamin beta-carotene calculated on the basis of the manufacturers' information are given in Tables 1 and 2.

Table 1: Composition of DLA-Samples

DLA-Sample Drink Powder

Meal replacement (Dietetic Product 1)

Ingredients: soy protein isolate 54%, skimmed milk yoghurt powder 21%, honey 20%, tricalcium phosphate, potassium citrate, aroma, trimagnesium dicitrate, release agents: silicon dioxide E551, palm oil, ferrous fumarate, L-Ascorbic acid, sweetener: sucralose E955; DL-alpha-tocopheryl acetate, nicotinamide, zinc oxide, Calcium D-Pantothenate, Manganese Sulfate, Pyridoxine Hydrochloride, Thiamine Mononitrate, riboflavin, cholecalciferol, copper gluconate, retinyl acetate, folic acid, potassium iodide, sodium selenite, D-Biotin, cyanocobalamin

Meal replacement (Dietetic Product 2)

Ingredients: soy protein 50%, honey 25%, skimmed milk yoghurt powder 22%, potassium chloride, calcium citrate, magnesium carbonate, magnesium citrate, silicic acid, vitamin C, ferrous fumarate, coloring riboflavin (vitamin B2), niacin, vitamin E, zinc oxide, manganese sulfate, calcium-D-pantothenate, vitamin B2, vitamin D, vitamin B6, vitamin B1, vitamin A, folic acid, potassium iodide, vitamin K, sodium selenite, biotin, vitamin B12

Beta-Carotene Capsules (Dietary Supplement)

Ingredients: beta carotene, carrot extract, beetroot extract (added without capsule shells)

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 vitamins and provitamin beta-carotene according to the manufacturers' specification (declared contents)

Parameter	Content per 100g
Vitamin A	640 µg
Vitamin D3	3,1 µg
Vitamin E	20 mg
Vitamin K1	83 µg
β-Carotene	6,5 mg

2.1.1 Homogeneity

The **mixture homogeneity before bottling** was examined 5-fold by determination of the parameter β-carotene by a photometric method (EuPharm 8.0/1069). The repeatability standard deviation was with 4,9% in the range of repeatability standard deviations of the standardized methods (e.g. ASU-Methods, s. 3.6.2) (see Table 4). The results of homogeneity analysis are given in the documentation (s. 5.2.1).

The calculation of the **repeatability standard deviation S_r of the participants** was also used as an indicator of homogeneity. It is 0,44% or 1,64% (without the value >500µg/100g) for vitamin K1 and in the range from 11,9% to 26,1% for all other analytes (see Table 3). The repeatability standard deviation for vitamin K1 is thus comparable with the precision data of the respective standardized methods, while it is higher for the other parameters (e.g. ASU §64 methods/ EN standards [21b, 22, 25], see 3.6.2) (cf Table 4) [21-25]. The repeatability standard deviations of the participants are also given in the statistical data (4.1 to 4.5).

Table 3: Repeatability standard deviation S_r of double determinations of the participants (coefficient of variation CV_r in %)

Parameter	**CV_r**
Vitamin A	11,9 %
Vitamin D3	26,1 %
Vitamin E	16,4 %
Vitamin K1	0,44 %
β-Carotene	16,8 %

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 Homogeneity).

In case the criterion for sufficient homogeneity of the test items is not fulfilled the impact on the target standard deviation will be verified. If necessary the evaluation of results will be done considering the standard uncertainty of the assigned value by z'-scores (s. 3.8 and 3.11) [3].

2.1.2 Stability

A water activity (aW) of < 0,5 is an important factor to ensure the stability of dry and dried products during storage. The optimal condition for storage is the aW value range of 0,15 – 0,3. In this area the lowest possible degradation rate is to be expected [16].
Experience with various DLA materials shows, with a comparable matrix and water activity (aW value < 0,5), good durability of the EP samples and storage stability against microbial spoilage and with regard to the content of the EP parameters.
The aW value of the EP samples was approx. 0,49 (19,1°C). The stability of the sample material was thus guaranteed during the investigation period under the specified storage conditions.

2.2 Sample shipment and information to the test

Two portions of test material were sent to every participating laboratory in the 41st week of 2021. The testing method was optional. The tests should be finished at 10th of December 2021 the latest.

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

The two portions contain identical samples of a dietetic food as a meal replacement with above mentioned parameters in the matrix of drink powder. The analysis methods are optional. The results of the vitamins should be given as the sum of the equivalents in the form of the vitamin compound indicated in the result submission file.

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, which have been handed out with the samples (by email).

The finally calculated concentrations of the parameter as average of duplicate determinations of both numbered samples were 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.

Of 12 participants, 11 submitted at least one result.
1 participant did not submit any 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]. If there are < 12 quantitative results and an increased difference between robust mean and median, the median may be used as the assigned value (criterion: Δ median - rob. mean > 0,3 σ_{pt}) [3].

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

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

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

The actual measurement results will be drafted. Individual results, which are outside the specified measurement range of the participating laboratory (for example with the result > 25 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*) 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 an inter-laboratory estimate of the standard deviation for the determination of each parameter on the bases of (outlier free) individual participant results. It takes into account both the repeatability standard deviation S_r and the within-laboratory standard deviation S_S. Reproducibility standard deviations of PT´s may differ from reproducibility standard deviations of ring trials, because the participating laboratories of a PT generally use different internal conditions and methods for determining the measured values.

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

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

The relative reproducibility standard deviation CV_R in percent of the mean is given as variation coefficient in the statistical data of participant for each parameter, if single results are available. The significance of CV_R is further explained in section 3.9.

3.5 Exclusion of results and outliers

Before statistical evaluation obvious blunders, such as those with incorrect units, decimal point errors, too few significant digits (valid digits) or results for another proficiency test item can be removed from the data set [2]. Even if a result e.g. with a factor >10 deviates significantly from the mean and has an influence on the robust statistics, a result of the statistical evaluation can be excluded [3].

All results should be given at least with 2 significant digits. Specifying 3 significant digits is usually sufficient.

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

Results are tested for outliers by the use of robust statistics (algorithm A): If a value deviates from the robust mean by more than 3 times the robust standard deviation, it can be classified as an outlier (see above) [3]. Due to the use of robust statistics outliers are not excluded, provided that no other reasons are present [3]. Detected outliers are only mentioned in the results section, if they have been excluded from the statistical evaluation.

3.6 Target standard deviation (for proficiency assessment)

The target standard deviation of the assigned value 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 evaluation of interlaboratory studies, where different methods are applied by the participants. On the other hand the target standard deviation from the evaluation of precision data of an precision experiment is derived from collaborative studies with specified analytical methods.
In cases in which both of the above models are unsuitable, the target standard deviation is determined using values from the findings according to 3.6.3.
For information, the z-scores of both models are given in the analysis, if available.

The target standard deviation of the general model of Horwitz (see 3.6.1) was used in the present LVU to evaluate the results of vitamin A and vitamin D3.

To evaluate the results of vitamin E and β-carotene, the target standard deviation of the evaluation of the results of a precision experiment (see 3.6.2) was used (ASU §64 methods/ EN standards [21b, 22, 25]).

In addition, the standard uncertainty was taken into account for vitamin A, vitamin E and β-carotene and the results were evaluated using z'-scores (see 3.8).

Due to the small number of < 5, the results for vitamin D3 were only evaluated for information using z-scores. The few results for vitamin K1 showed a considerable heterogeneity, so that no evaluation was carried out.

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]:

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

The relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviation (RSD_R) given in Table 4 were determined in ring tests using the indicated methods.
The resulting target standard deviations σ_{pt}, which were identified there, were used to evaluate the results and to provide additional information for the statistical data.

Table 4: Relative repeatability standard deviations (RSD_r) and relative reproducibility standard deviations (RSD_R) according to selected evaluations of precision experiments and the resulting target standard deviation σ_{pt} [18-25]

Parameter	**Matrix**	**Mean**	**RSD_r**	**RSD_R**	**σ_{pt}**	**Method / Literature**
Vitamin A	milk powder	653 µg/100 g	2,1%	3,4%	3,06%[1]	HPLC [23]
Vitamin D3	milk powder	14,30 µg/100 g	5,2%	5,5%	4,09%	HPLC [21]
Vitamin D3	milk powder	9,95 µg/100 g	8,2%	13,6%	12,3%[1]	HPLC [21b]
Vitamin D3	infant food, liquid	1,38 µg/100 g	5,9%	12,1%	11,4%	HPLC [21]
Vitamin D3	infant food, powder	10,1 µg/100 g	2,4%	7,1%	6,89%	HPLC [21]
Vitamin E	oat powder	0,279 mg/100g	9,0%	16,8%	15,5%	HPLC [22]
Vitamin E	milk powder	9,89 mg/100 g	4,0%	7,0%	6,40%	HPLC [22]
Vitamin E	milk powder	10,2 mg/100 g	3,0%	12,8%	12,6%[1]	HPLC [22]
Vitamin K1	6 infant food (mean)	77,37 µg/100 g	4,47%	5,91%	4,99%[1]	HPLC [25]
β-Carotene	mixed vegetables	18,05 mg/100g	3,9%	15%	14,7%[1]	HPLC [24]
β-Carotene	pudding powder	1,531 mg/100g	5,6%	9,3%	8,42%	HPLC [24]
β-Carotene	vitamin drink	2,248 mg/100g	2,9%	6,5%	6,17%	HPLC [24]
Coenzyme Q10	Raw Materials and Food Supplements	42-1000 mg/g	2,2 - 5,0 %	-	-	HPLC-UV [20]

[1] *used in evaluation or given for information (s. chapter 4)*

3.6.3 Value by perception

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

For the present evaluation the target standard deviation according to 3.6.1 or 3.6.2 was regarded suitable.

Table 5 shows selected statistic data of participants' results of present PT compared to PT results of previous years.

Table 5: Characteristics of the present PT (on dark grey) in comparison to previous PTs since 2016 (SD = standard deviation, CV = coefficient of variation, MV = multi-vitamin)

Parameter	**Matrix** (Powder)	**robust Mean**	**rob. SD (S*)**	**rel. SD (VK_{S*})**	**Quotient S^*/σ_{pt}**	**DLA-Report**
Vitamin A	MV-Capsule Powder	21900 µg/100g	2870 µg/100g	13,1%	1,8	DLA 47/2016
Vitamin A	MV-Capsule Powder	7131 µg/100g	1058 µg/100g	14,8%	1,8	DLA 45/2018
Vitamin A	MV-Capsule Powder	50071 µg/100g	6345 µg/100g	12,7%	2,0	DLA ptSU02 2020
Vitamin A	Drink Powder	729 µg/100g	247 µg/100g	33,9%	1,5*	DLA ptSU07 2021
Vitamin D3	MV-Capsule Powder	146 µg/100g	10,3 µg/100g	7,05%	0,46	DLA 47/2016
Vitamin D3	MV-Capsule Powder	455 µg/100g	74,4 µg/100g	16,4%	1,3	DLA 45/2018
Vitamin D3	MV-Capsule Powder	515 µg/100g	117 µg/100g	22,8%	1,8	DLA ptSU02 2020
Vitamin D3	Drink Powder	5,20 µg/100g**	1,37 µg/100g	26,4%	1,1	DLA ptSU07 2021
Vitamin E	MV-Capsule Powder	988 mg/100g	211 mg/100g	21,4%	1,7	DLA 47/2016
Vitamin E	MV-Capsule Powder	760 mg/100g	148 mg/100g	19,5%	1,5	DLA 45/2018
Vitamin E	MV-Capsule Powder	234 mg/100g	64,0 mg/100g	27,4%	1,8*	DLA ptSU02 2020
Vitamin E	Drink Powder	16,5 mg/100g	4,27 mg/100g	25,9%	1,5*	DLA ptSU07 2021
Vitamin K1	MV-Capsule Powder	933 µg/100g	121 µg/100g	13,0%	1,1	DLA 47/2016
Vitamin K1	MV-Capsule Powder	954 µg/100g	632 µg/100g	66,2%	-	DLA 45/2018
Vitamin K1	MV-Capsule Powder	1039 µg/100g°	604 µg/100g	49,8%	2,1*	DLA ptSU02 2020
Vitamin K1	Drink Powder	***	-	-	-	DLA ptSU07 2021

Parameter	Matrix (Powder)	robust Mean	rob. SD (S*)	rel. SD (VK_{S*})	Quotient S^*/σ_{pt}	DLA-Report
β-Carotene	MV-Capsule Powder	32,2 mg/100g	9,70 mg/100g	30,1%	2,0	DLA 47/2016
β-Carotene	MV-Capsule Powder	27,7 mg/100g	8,45 mg/100g	30,5%	1,6*	DLA 45/2018
β-Carotene	MV-Capsule Powder	4,26 mg/100g	2,11 mg/100g	49,4%	2,0*	DLA ptSU02 2020
β-Carotene	Drink Powder	1,40 mg/100g	0,352 mg/100g	25,0%	1,2*	DLA ptSU07 2021

° assigned value (Xpt): median
** with target standard deviation σpt'*
*** values given for information*
**** no statistical evaluation possible*

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 valid z-Score for each parameter is indicated as z-Score (σ_{pt}) while the value referred to as the z-Score (Info) is purely informative. The two z-scores are calculated with 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.
An error or cause analysis can be carried out by checking the analysis process including understanding and implementation of the measurement by the staff, details of the measurement procedure, calibration of equipment and composition of reagents, transmission error or an error in the calculation, in the trueness and precision and use of reference material. If necessary, the problems must be addressed through appropriate corrective action [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. 3.11). The z'-score represents the relation of the deviation of the result (x_i) of the participant from the respective consensus value (X) to the square root of quadrat sum of the target standard deviation (σ_{pt}) and the standard uncertainty ($U_{(Xpt)}$) [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 cofficient of variation (CV_R)

The variation coefficient (CV_R) of the reproducibility (= relative reproducibility standard deviation) is calculated from the reproducibility standard deviation S_R 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_R 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 levels or the performance evaluation of the participating laboratories 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 of the assigned value

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

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

If $U_{(Xpt)} \leq 0{,}3\ \sigma_{pt}$ the standard uncertainty of the assigned value needs not to be included in the interpretation of the results of the PT [3]. Values exceeding 0,3 imply, that the target standard deviation could be too low with respect to the standard uncertainty of the assigned value.

The traceability of the assigned value is ensured on the basis of the consensus value as a robust mean of the participant results.

4. Results

Comments to the distribution of the results:

The kernel density estimation for vitamin E shows an approximately symmetrical distribution of the results with a secondary peak at approx. 26 mg/100g, which is due to one participant result outside the target range (see 4.3 vitamin E).

Due to the number of < 8 results, a kernel density estimation was not carried out for the parameters vitamin A, D3 and beta-carotene.

Comments to the statistic data:

For vitamin K1 there were only 4 results with a high degree of variation, so that no statistical evaluation could be carried out. Due to the small number of results, the evaluation for vitamin D3 was carried out for information only.

The target standard deviations were calculated for all parameters according to the model of Horwitz or according to the data of a precision experiment (ASU §64 Methods/ EN standards [21b, 22, 25]). The evaluation after Horwitz was preferably used as long as the quotients S^*/σ_{pt} were in the range of ≤ 2,0. In all other cases, the target standard deviation calculated from ASU §64 precision data was used (see p.10).

For vitamin A, vitamin E and β-carotene, the distribution of results showed an increased variability. The quotients S^*/σ_{pt} were partly far above 2,0. The parameters were therefore evaluated using the z'-score, taking into account the standard uncertainty. The quotients S^*/σ_{pt}' were then 1,2 and 1,5 (see Table 5).

For vitamin D3, the distribution of results showed a normal variability. The quotient S^*/σ_{pt} was 1,1 (see Table 5).

The robust standard deviations are in the range of former PTs (cf. 3.6.3), while the repeatability and reproducibility standard deviations are mostly above established values for the determination methods used (cf. 3.6.2). Due to the partly small number of results the comparability of the results can be limited.

80% to 100% of the results are within the respective target range.

The robust means of the participants' results were for vitamin A and vitamin E at 114% and 83% of the vitamin contents calculated according to the manufacturers' information (see Table 2), while the robust means of vitamin D and β-carotene were clearly above (167%) or below (22%), respectively.

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 ($X_{pt} - 2\sigma_{pt}$) or ($X_{pt} - 2\sigma_{pt}$') *
upper limit of target range ($X_{pt} + 2\sigma_{pt}$) or ($X_{pt} + 2\sigma_{pt}$´) *
Quotient S/σ_{pt} or S*/σ_{pt}'*
Standard uncertainty U(X_{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 table below, the results of the participating laboratories are formatted in 3 valid digits**:

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

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

4.1 Vitamin A (as Retinol without Provitamins in µg/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5
Number of outliers	0
Mean	729
Median	723
Robust Mean (x_{pt})	**729**
Robust standard deviation (S*)	**247**
Number with 2 replicates	5
Repeatability SD (S_r)	86,5
Repeatability (CV_r)	11,9%
Reproducibility SD (S_R)	226
Reproducibility (CV_R)	31,1%
Target range:	
Target standard deviation σ_{pt}'	**163**
Target standard deviation (for Information)	22,3
lower limit of target range	**403**
upper limit of target range	**1054**
Quotient S/σ_{pt}'*	*1,5*
Standard uncertainty $U_{(Xpt)}$	*138*
Results in the target range	*4*
Percent in the target range	*80%*

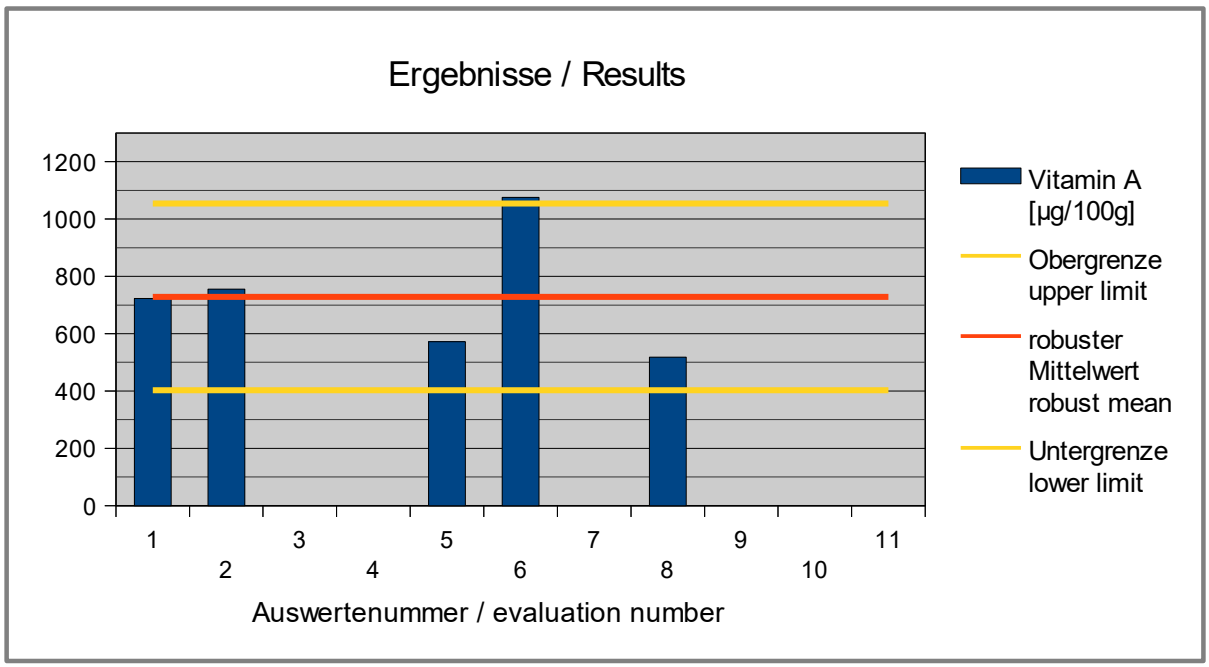

Abb. / Fig. 1: Ergebnisse / Results Vitamin A

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Vitamin A [µg/100g]	Abweichung [µg/100g] Deviation [µg/100g]	z'-Score ($\sigma_{pt'}$)	z-Score (Info)	Hinweis Remark
1	723	-5,6	-0,03	-0,25	
2	755	26,4	0,16	1,2	
3					
4					
5	572	-157	-0,96	-7,0	
6	1075	346	2,1	16	
7					
8	518	-211	-1,3	-9,5	
9					
10					
11					

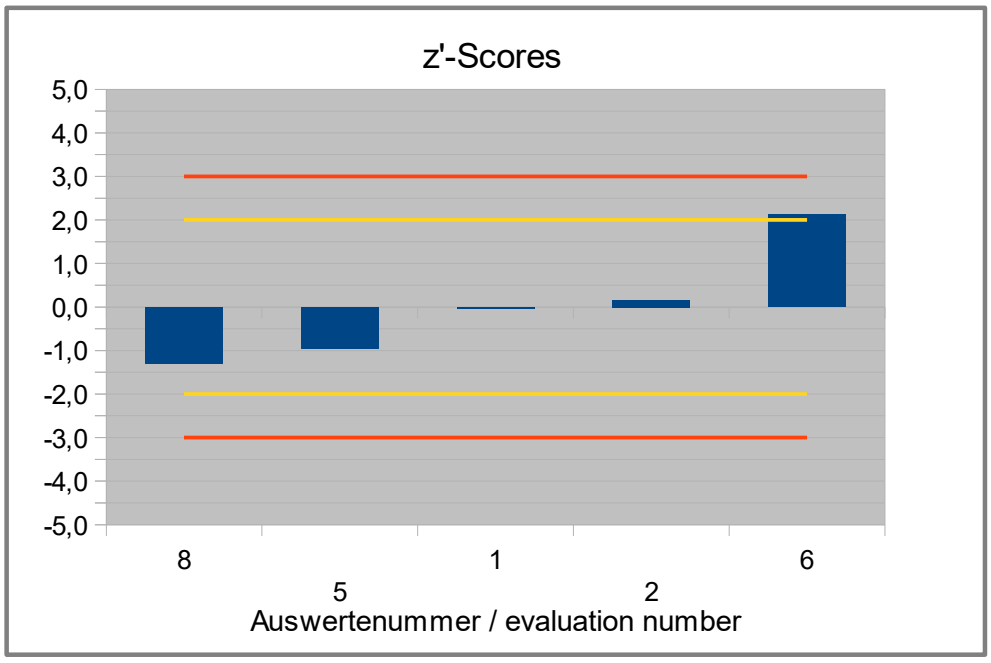

Abb. / Fig. 2: z'-Scores Vitamin A

4.2 Vitamin D3 (as Cholecalciferol in µg/100g)

The following evaluation was carried out for information only.

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	4
Number of outliers	0
Mean	5,20
Median	5,22
Robust Mean (X_{pt})	**5,20**
Robust standard deviation (S*)	**1,37**
Number with 2 replicates	4
Repeatability SD (S_r)	1,36
Repeatability (CV_r)	26,1%
Reproducibility SD (S_R)	1,54
Reproducibility (CV_R)	29,7%
Target range:	
Target standard deviation σ_{pt}	**1,30**
Target standard deviation (for Information)	0,640
lower limit of target range	**2,60**
upper limit of target range	**7,80**
Quotient S/σ_{pt}*	*1,1*
Standard uncertainty $U_{(Xpt)}$	*0,859*
Results in the target range	*4*
Percent in the target range	*100%*

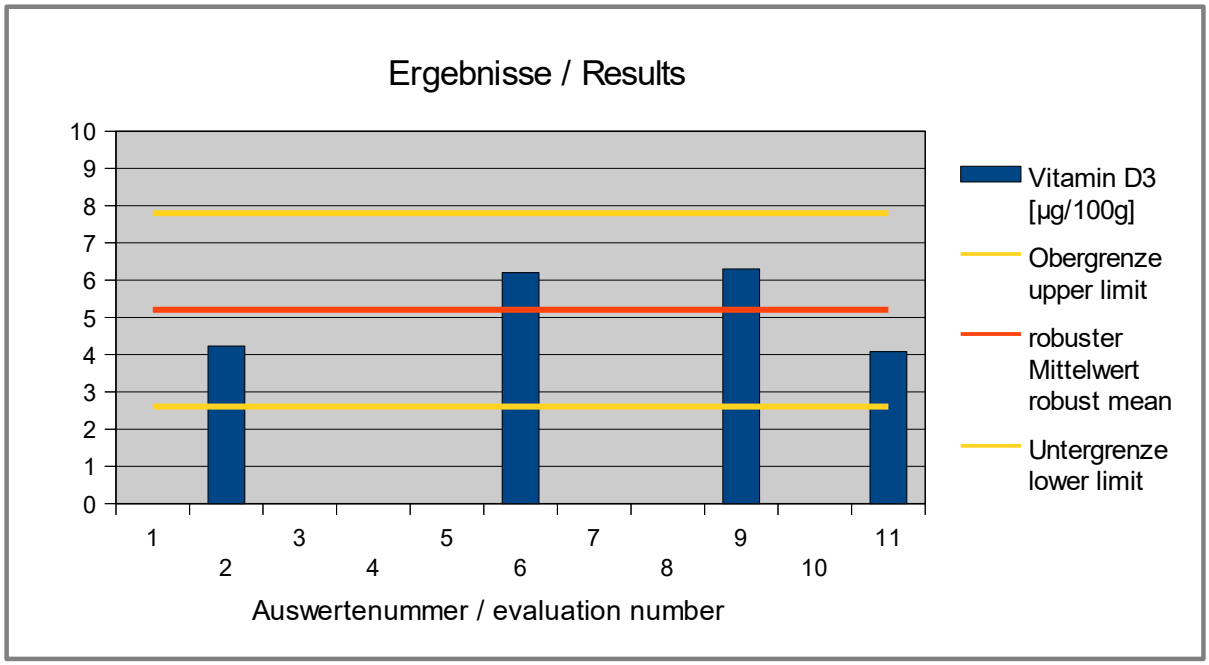

Abb. / Fig. 3: Ergebnisse / Results Vitamin D3

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Vitamin D3 [µg/100g]	Abweichung [µg/100g] Deviation [µg/100g]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1					
2	4,23	-0,97	-0,75	-1,5	
3					
4					
5					
6	6,20	1,00	0,77	1,6	
7					
8					
9	6,30	1,10	0,84	1,7	
10					
11	4,08	-1,12	-0,86	-1,8	

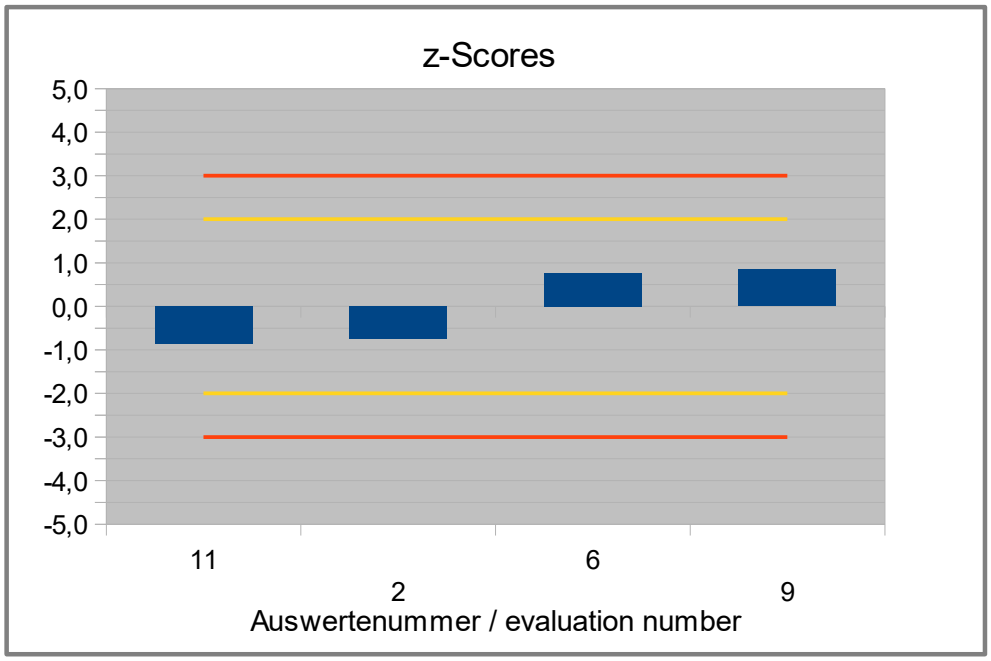

Abb. / Fig. 4: z-Scores Vitamin D3

4.3 Vitamin E (as D-α-Tocopherol in mg/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	8
Number of outliers	0
Mean	16,9
Median	15,8
Robust Mean (x_{pt})	**16,5**
Robust standard deviation (S*)	**4,27**
Number with 2 replicates	7
Repeatability SD (S_r)	2,77
Repeatability (CV_r)	16,4%
Reproducibility SD (S_R)	5,40
Reproducibility (CV_R)	31,9%
Target range:	
Target standard deviation $\sigma_{pt'}$	**2,81**
Target standard deviation (for Information)	1,22
lower limit of target range	**10,9**
upper limit of target range	**22,1**
Quotient S/$\sigma_{pt'}$*	*1,5*
Standard uncertainty $U_{(Xpt)}$	*1,89*
Results in the target range	*7*
Percent in the target range	*88%*

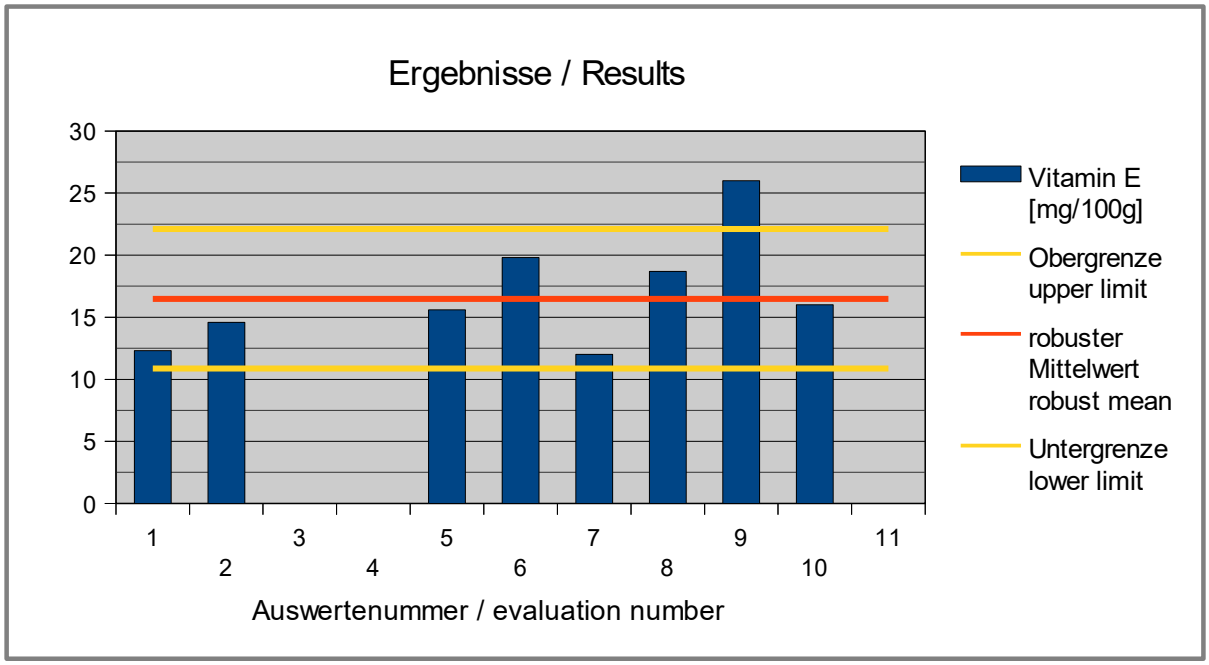

Abb. / Fig. 5: Ergebnisse / Results Vitamin E

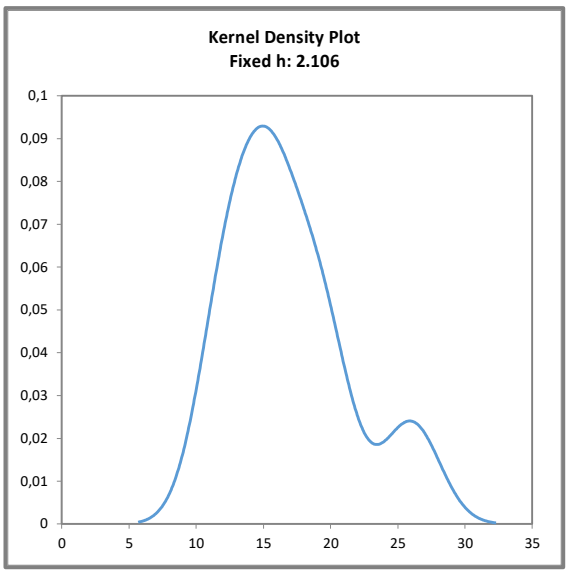

Abb. / Fig. 6:
Kerndichte-Schätzung der Ergebnisse (mit h = 0,75 x σ_{pt} von Xpt)

Kernel density plot of results (with h = 0,75 x σ_{pt} von Xpt)

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Vitamin E [mg/100g]	Abweichung [mg/100g] Deviation [mg/100g]	z'-Score ($\sigma_{pt'}$)	z-Score (Info)	Hinweis Remark
1	12,3	-4,18	-1,5	-3,4	
2	14,6	-1,89	-0,67	-1,5	
3					
4					
5	15,6	-0,88	-0,31	-0,72	
6	19,8	3,32	1,2	2,7	
7	12,0	-4,48	-1,6	-3,7	
8	18,7	2,22	0,79	1,8	
9	26,0	9,52	3,4	7,8	
10	16,0	-0,48	-0,17	-0,40	
11					

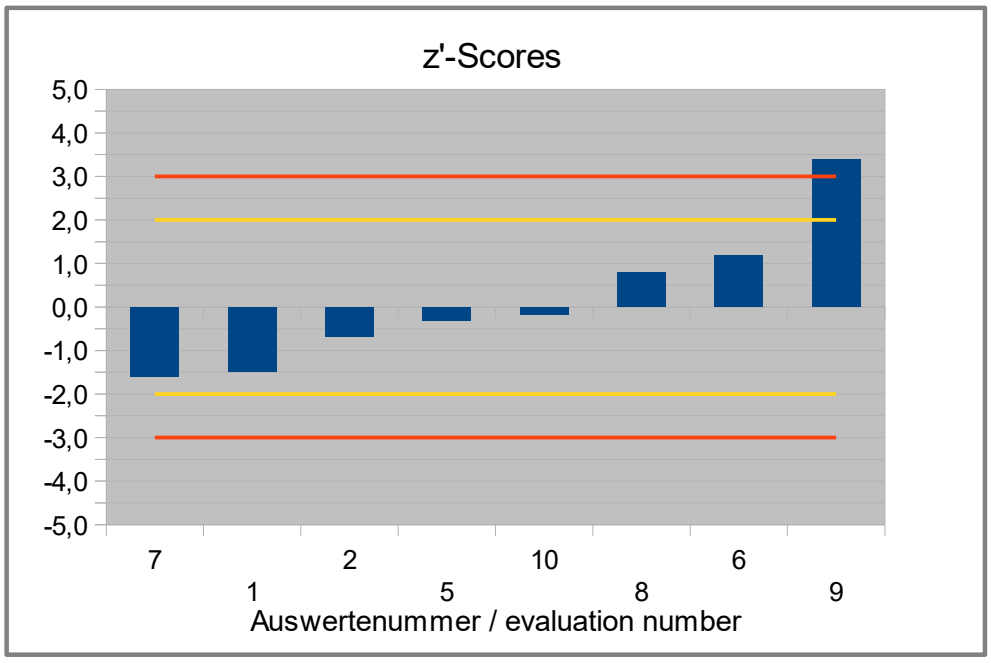

Abb. / Fig. 7: z'-Scores Vitamin E

4.4 Vitamin K1 (as Phylloquinone in µg/100g)

Due to the small number and the heterogeneous distribution of the results, no statistical analysis was carried out.
The characteristics below are for informational purposes only.

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	4
Number of outliers	0
Mean	169
Median	75,5
Robust Mean	169
Robust standard deviation (S*)	268
Number with 2 replicates	4
Repeatability SD (S_r)	0,744
Repeatability (CV_r)	0,440%
Reproducibility SD (S_R)	237
Reproducibility (CV_R)	140%

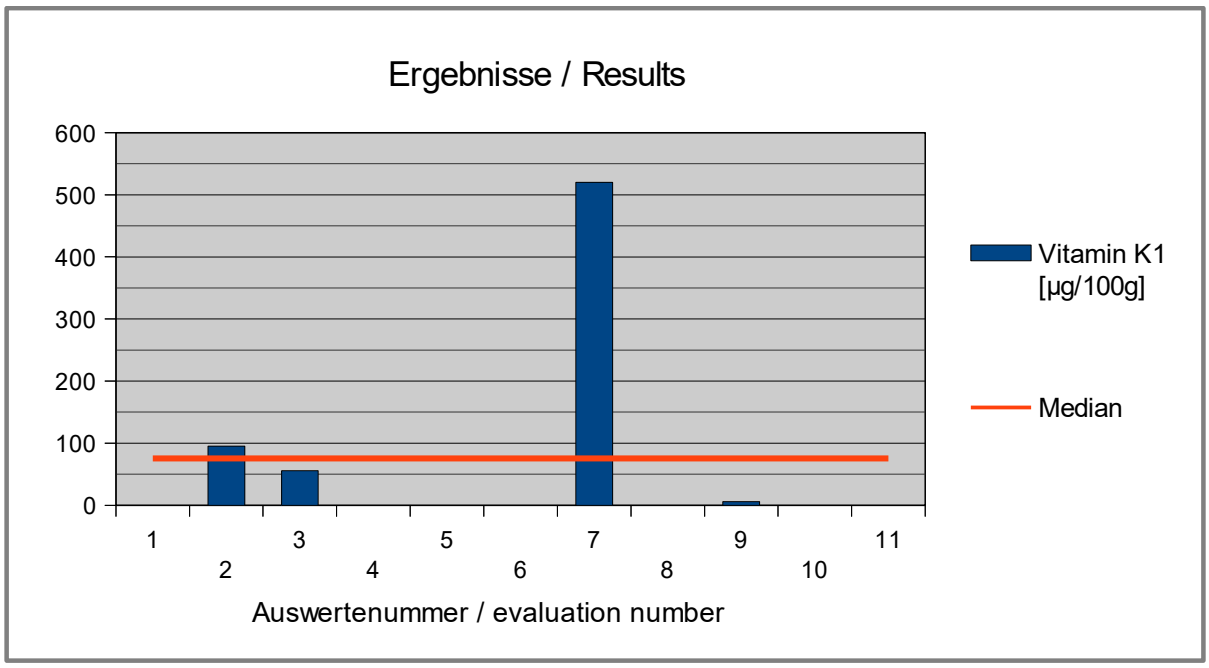

Abb. / Fig. 8: Ergebnisse / Results Vitamin K1

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	Vitamin K1 [µg/100g]	Abweichung [µg/100g] Deviation [µg/100g]	z-Score (σ_{pt})	z-Score (Info)	Hinweis Remark
1					
2	95,3				
3	55,8				
4					
5					
6					
7	520				
8					
9	6,00				
10					
11					

4.5 Beta-Carotene (without other Provitamins in mg/100g)

Vergleichsuntersuchung / Proficiency Test

Statistic Data	
Number of results	5°
Number of outliers	1
Mean	1,40
Median	1,34
Robust Mean (x_{pt})	**1,40**
Robust standard deviation (S*)	**0,352**
Number with 2 replicates	5
Repeatability SD (S_r)	0,236
Repeatability (CV_r)	16,8%
Reproducibility SD (S_R)	0,352
Reproducibility (CV_R)	25,1%
Target range:	
Target standard deviation σ_{pt}'	**0,285**
Target standard deviation (for Information)	0,151
lower limit of target range	**0,833**
upper limit of target range	**1,98**
Quotient S/σ_{pt}'*	*1,2*
Standard uncertainty $U_{(xpt)}$	*0,197*
Results in the target range	*5*
Percent in the target range	*100%*

° *results without outlier (result no. 7)*

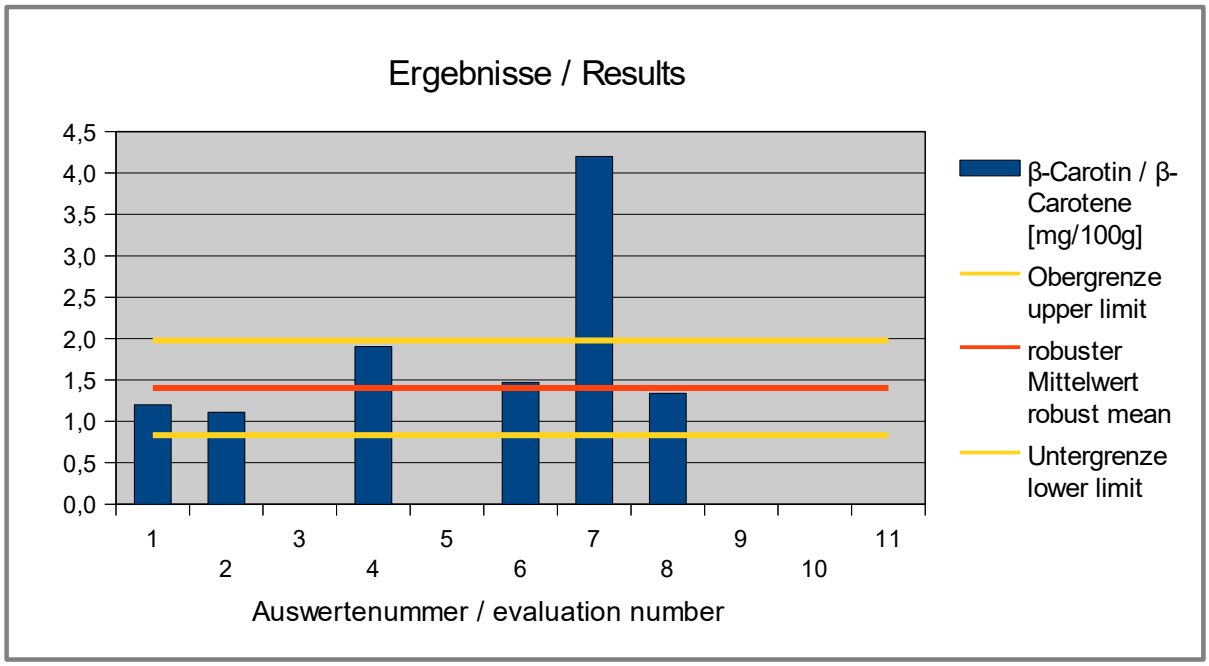

Abb. / Fig. 9: Ergebnisse β-Carotin / Results β-Carotene

Ergebnisse der Teilnehmer:
Results of Participants:

Auswerte-nummer Evaluation number	β-Carotin / β-Carotene [mg/100g]	Abweichung [mg/100g] Deviation [mg/100g]	z'-Score ($\sigma_{pt'}$)	z-Score (Info)	Hinweis Remark
1	1,20	-0,20	-0,72	-1,4	
2	1,11	-0,29	-1,0	-2,0	
3					
4	1,90	0,50	1,7	3,3	
5					
6	1,47	0,07	0,23	0,43	
7	4,20				Ausreisser/Outlier
8	1,34	-0,06	-0,23	-0,43	
9					
10					
11					

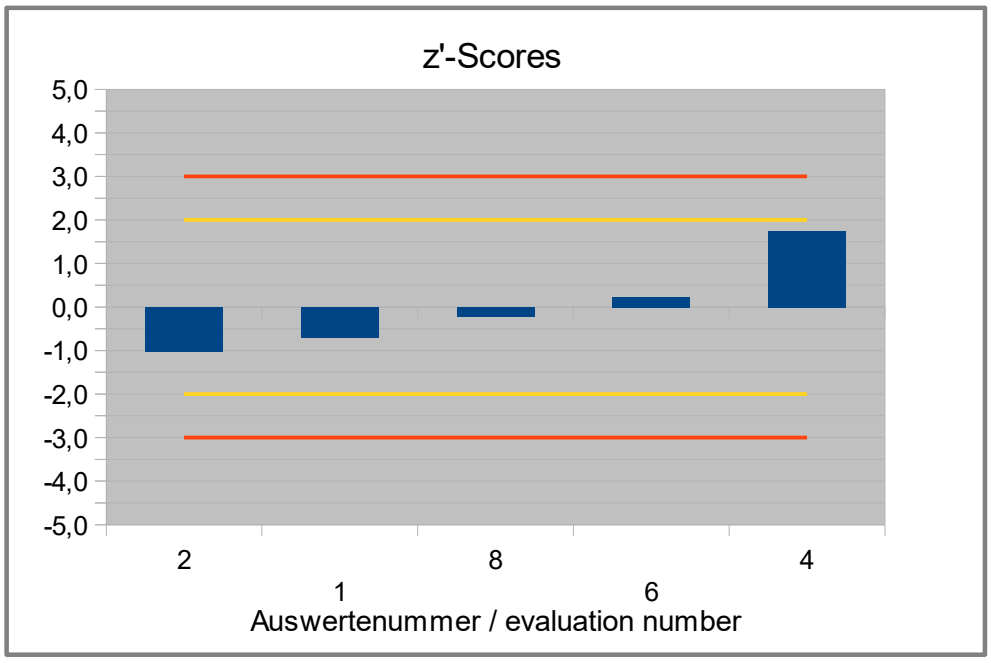

Abb. / Fig. 10: z'-Scores β-Carotin / β-Carotene

4.6 Participants' z-Scores: Overview table

Evaluation number	Vitamin A	Vitamin D3	Vitamin E	Vitamin K1	Beta-Carotene
	z'-Score	z-Score	z'-Score	z'-Score	z'-Score
1	-0,03		-1,5		-0,72
2	0,16	-0,75	-0,67		-1,0
3					
4					1,7
5	-0,96		-0,31		
6	2,1	0,77	1,2		0,23
7			-1,6		
8	-1,3		0,79		-0,23
9		0,84	3,4		
10			-0,17		
11		-0,86			

Bewertung des z-Scores / valuation of z-score (DIN ISO 13528:2009-01):
-2 ≤ z-score ≤ 2 erfolgreich / successful (in green)
-2 > z-score > 2 „Warnsignal“ / warning signal (in yellow)
-3 > z-score > 3 „Eingriffssignal“ / action signal (in red)

5. Documentation

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

5.1 Details by the participants

5.1.1 Primary data

Analyte	Participant	Unit	Sample No. 1	Sample No. 2	Date of analysis	Result (Mean)	Result 1	Result 2	Limit of quantification	Incl. RR	Recovery rate [%]
Vitamin A (as retinol without pro-vitamins)	1	µg/100g	22	66	12. Nov	723	696	750			
	2	µg/100g	21	67	30. Nov	755	830	680	50	no	/
	3	µg/100g									
	4	µg/100g									
	5	µg/100g	15	73	21.10.2021	572	601	542	290	no	
	6	µg/100g	5	83	23.11.	1075	1132	1017	150	no	
	7	µg/100g									
	8	µg/100g	24	64	12. Nov	518	427	608			
	9	µg/100g									
	10	µg/100g									
	11	µg/100g									

Analyte	Participant	Unit	Sample No. 1	Sample No. 2	Date of analysis	Result (Mean)	Result 1	Result 2	Limit of quantification	Incl. RR	Recovery rate [%]
Vitamin D3 (as Cholecalciferol)	1	µg/100g									
	2	µg/100g	21	67	27/Oct	4,23	4,66	3,8	0,5	no	/
	3	µg/100g									
	4	µg/100g									
	5	µg/100g									
	6	µg/100g	5	83	18.11.	6,2	5,4	7	2	no	
	7	µg/100g	8	80	09/Dec	<20	<20	<20	20	no	-
	8	µg/100g									
	9	µg/100g	14	74	06/Dec	6,3	7,9	4,7	1	yes	30
	10	µg/100g									
	11	µg/100g	13	71	21.01.2022	4,08	4,63	3,54	0,04	no	105

Analyte	Participant	Unit	Sample No. 1	Sample No. 2	Date of analysis	Result (Mean)	Result 1	Result 2	Limit of quantification	Incl. RR	Recovery rate [%]
Vitamin E (as D-α-Tocopherol)	1	mg/100g	22	66	12. Nov	12,3	12,7	11,9			
	2	mg/100g	21	67	30. Nov	14,59	15,25	13,93	0,15	no	/
	3	mg/100g									
	4	mg/100g									
	5	mg/100g	15	73	20.10.2021	15,6	16,2	14,9	0,5	no	
	6	mg/100g	5	83	28.10.2021	19,8	19,4	20,23	3,38	no	
	7	mg/100g	8	80	25. Nov	12	11	12	1,1	no	-
	8	mg/100g	24	64	16. Nov	18,7	18,1	19,3			
	9	mg/100g	14	74	06/Dec	26	21	31	0	yes	24
	10	mg/100g	62		08. Nov	16	16				
	11	mg/100g									

Analyte	Participant	Unit	Sample No. 1	Sample No. 2	Date of analysis	Result (Mean)	Result 1	Result 2	Limit of quantification	Incl. RR	Recovery rate [%]
Vitamin K1 (as Phyllo-quinone)	1	µg/100g									
	2	µg/100g	21	67	26. Nov	95,25	94,8	95,7	1	no	/
	3	µg/100g	19	69	07.12.2021	55,8	54,8	56,7		no	
	4	µg/100g									
	5	µg/100g									
	6	µg/100g									
	7	µg/100g	8	80	17. Nov	520	520	520	15	no	-
	8	µg/100g									
	9	µg/100g	14	74	06/Dec	6	5,9	6	0,1	yes	34
	10	µg/100g									
	11	µg/100g									

Analyte	Participant	Unit	Sample No. 1	Sample No. 2	Date of analysis	Result (Mean)	Result 1	Result 2	Limit of quantification	Incl. RR	Recovery rate [%]
β -Carotene (without other provit-amins)	1	mg/100g	22	66	22. Nov	1,2	1,27	1,13			
	2	mg/100g	21	67	15. Nov	1,11	0,75	1,47	0,05	no	/
	3	mg/100g									
	4	mg/100g	4	84	08/Dec	1,9	1,86	1,94	n/a	yes	90-110%
	5	mg/100g									
	6	mg/100g	5	83	02.11.	1,47	1,44	1,49	0,32	no	
	7	mg/100g	8	80	09. Nov	4,2	4,1	4,3	3	no	-
	8	mg/100g	24	64	26/Oct	1,34	1,38	1,29			
	9	mg/100g									
	10	mg/100g									
	11	mg/100g									

5.1.2 Analytical Methods

Analyte	Participant	Method description	Sample preparation	Measuring method	Calibration and reference material	Recovery with same matrix	Method accredited	Further remarks
Vitamin A (as retinol without provitamins)	1						Yes	
	2	Internal method - PNTA0145 HPLC/UV						
	3							
	4							
	5	ASU 00.00 – 63/1, 2015-06	saponified			no	Yes	
	6	03-32-MAA-M-VITAE	(Weight 5 g, residue taken up with 10.0 ml FM) Weight 10 g, residue taken up with 5.0 ml FM				Yes	
	7							
	8	In-house method		HPLC-VWD			no	
	9							
	10							
	11							

Analyte	Participant	Method description	Sample preparation	Measuring method	Calibration and reference materiel	Recovery with same matrix	Method accredited	Further remarks
Vitamin D3 (as Cholecalciferol)	1							
	2	Internal method - PNTA0202 LC/MS-MS)						
	3							
	4							
	5							
	6	03-410-MAA-M-VITAMIN_D					yes	
	7	MI_559_2020_Rev4	-	-	Cholecalciferol	no	yes	
	8							
	9	in-house method	alkaline saponification, liquid-liquid extraction	LC-MSMS	external calibration function	yes	no	
	10							
	11	QSA-O-2124-02; 2021-07	Saponification with ethanol. KOH, extraction with isooctane and derivative. w.PTAD	LC-MS/MS	cal. with internal standard; several reference materials (DLA 39-2015; FAPAS T21120QC)	yes	yes	

Analyte	Participant	Method description	Sample preparation	Measuring method	Calibration and reference material	Recovery with same matrix	Method accredited	Further remarks
Vitamin E (as D-α-Tocopherol)	1						Yes	
	2	Internal method - PNTA0145-HPLC/FD						
	3							
	4							
	5	ASU 00.00 – 62, 2015-06	saponified			no	Yes	
	6	03-32-MAA-M-VITAE					Yes	
	7	MI_126_2013_Rev4	-	-	DL-alpha-Tocopherol	no	yes	
	8	ASU §64 LFGB L49.00-5:1998-09		HPLC-FLD			Yes	
	9	in-house method	alkaline saponification, liquid-liquid extraction	LC-MSMS	external calibration function	yes	no	
	10	Vitamins E COFRAC NF EN 12822 (HPLC-Fluo)				yes	yes	
	11							

Analyte	Participant	Method description	Sample preparation	Measuring method	Calibration and reference material	Recovery with same matrix	Method accredited	Further remarks
Vitamin K1 (as Phylloquinone)	1							
	2	Internal method - PNTA0178 HPLC/FD						
	3	§ 64 LFGB L00.00-86, (2004-07), modified	8 g were homogenized and thereof approx. 0.5 g weighed in	HPLC with fluorescence detector	4-point calibration; Reference material: FAPAS Infant Formula		yes	PT material was inhomogeneous
	4							
	5							
	6							
	7	MI_569_2020_Rev2	-	-	Phylloquinone	no	yes	
	8							
	9	in-house method	solid-liquid extraction	LC-MSMS	external calibration function	yes	no	
	10							
	11							

Analyte	Participant	Method description	Sample preparation	Measuring method	Calibration and reference material	Recovery with same matrix	Method accredited	Further remarks
β -Carotene (without other provitamins)	1						Yes	
	2	Internal method - PNTQ1121 HPLC/DAD						
	3							
	4	Liquid extraction and test on HPLC	Sample is extracted by THF and water	HPLC-PDA	USP	no	yes	NA
	5							
	6	total carotene 03-32-MAA-M-CAROA					Yes	
	7	MI_036_2011_Rev4	-	-	Beta-Carotene	no	no	
	8	In-house method		HPLC-VWD			no	
	9							
	10							
	11							

5.2 Homogeneity

5.2.1 Homogeneity analysis of the bottled PT samples

Homogeneity test based on the photometric determination of β-carotene (EuPharm 8.0/1069 mod.):

beta-Carotin

Independent samples	mg/100g
1	0,782
2	0,742
3	0,794
4	0,716
5	0,806

General Mean	0,768	
Repeatability standard deviation	0,0377	4,91%

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:

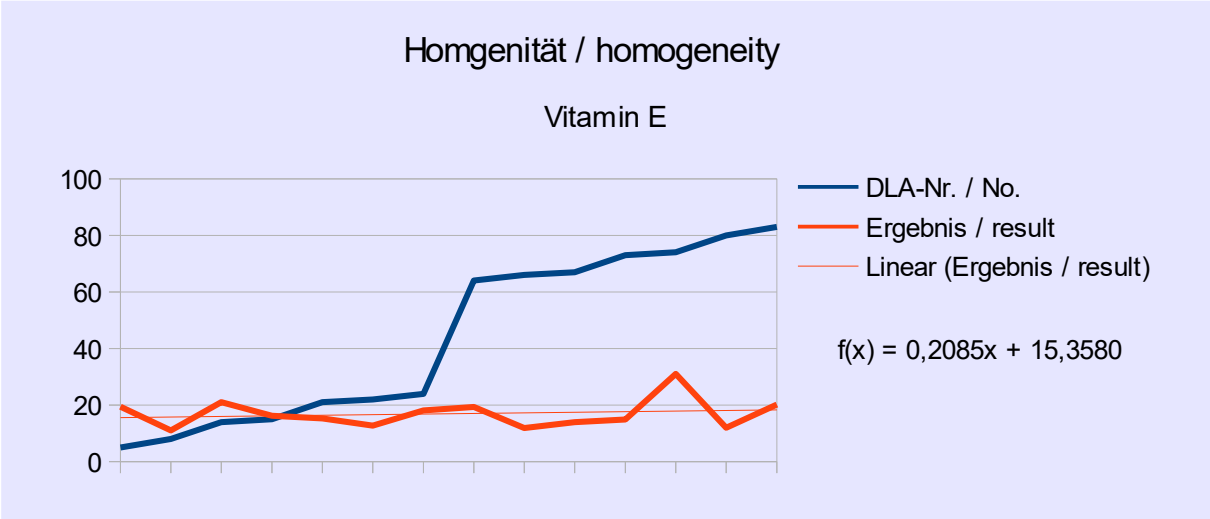

Abb./Fig. 11:
Trendfunktion Probennummern vs. Ergebnisse: Vitamin E
trend line function sample number vs. results: Vitamin E

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 ptSU07-2021***
PT name	***Dietetic Food I: Vitamines A, E, D3, K1 and β-Carotene in Meal Replacement***
*Sample matrix**	***Samples I + II:*** *Dietetic food as a meal replacement (drink powder) / ingredients: soy protein isolate, skimmed milk powder, yoghurt powder, honey, vitamins, minerals and other food additives*
Number of samples and sample amount	*2 identical samples I + II, 50 g each.*
Storage	*Samples I + II:* *room temperature (PT period), cooled 2 - 10°C (long term)*
Intentional use	*Laboratory use only (quality control samples)*
Parameter	*quantitative: Vitamines A, E, D3, K1 and β-Carotene* *Contents: The contents are of the order of the nutrient reference values per recommended daily dose (approx. 25 g)*
Methods of analysis	*Analytical methods are optional*
Notes to analysis	*The analysis of PT samples should be performed like a routine laboratory analysis.* *In general we recommend to homogenize a representative sample amount before analysis according to good laboratory practice, especially in case of low sample weights.*
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/100 g and µg/100 g, respectively (see results file)*
Number of significant digits	*at least 2*
Further information	*For information please specify:* – *Date of analysis* – *DLA-sample-numbers (for sample I and II)* – *Limit of detection* – *Assignment incl. Recovery* – *Recovery with the same matrix* – *Method is accredited*
Result submission	*The result submission file should be sent by e-mail to:* ***pt@dla-lvu.de***
Last Deadline	***the latest December 10th 2021***
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*

** 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

Teilnehmer / Participant	Ort / Town	Land / Country
		FRANCE
		GREAT BRITAIN
		Germany
		ITALY
		Germany
		Germany
		USA
		Germany
		Germany
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[Die Adressdaten der Teilnehmer wurden für die allgemeine Veröffentlichung des Auswerte-Berichts nicht angegeben.]

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