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Report on the 14th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in food supplements

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Abstract

This report presents the results of the fourteenth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAH) on the determination of the four EU marker PAHs, benz[a]anthracene (BAA), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF) and chrysene (CHR), in food supplements, particularly in fish oil and spirulina powder. It was conducted under ISO Standard 17043 accreditation.
The test materials used in this exercise were commercial products naturally contaminated (spirulina) or spiked with the 4 markers PAHs (fish oil). Participants also received a solution of PAHs in solvent of their choice (either toluene or acetonitrile) with disclosed content for the verification of their instrument calibration.
Reference values were used to benchmark the results reported by participants. Both National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States were admitted as participants.
The participants were free to choose the method of analysis. The performance of the participating laboratories in the determination of the target PAHs in test materials was expressed by z-scores. Satisfactory performance expressed by z-scores was assigned to about 83.6 % of the reported results.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

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1 Executive summary

This report presents the results of a proficiency test (PT) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAH) on the determination of the four EU marker PAHs, benz[*a*]anthracene (BAA), benzo[*a*]pyrene (BAP), benzo[*b*]fluoranthene (BBF) and chrysene (CHR) in food supplements.

This group of food items might contain high levels of PAHs. However, their levels depend a lot on the specific type of food supplement. Upon availability of further data DG SANCO will evaluate the need for setting maximum levels. Therefore, the network of NRLs should demonstrate its preparedness for this type of analysis.

The test materials used in this exercise were naturally contaminated spirulina powder and commercial fish oil spiked with the 4 EU markers PAHs. Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with known PAH content for verification of their instrument calibration.

The PT was conducted under ISO Standard 17043 accreditation. Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States participated. Twenty-six NRLs and 15 OCLs subscribed for participation.

The test materials were characterised at the EURL PAH. The assigned values and their uncertainties were determined by using a validated method based on isotope dilution mass spectrometry..

Participants were free to choose the method of analysis. The performance of the participating laboratories in the determination of the target PAHs in the test materials was expressed by z-scores and zeta-scores, which are indicators for the degree of agreement with a reference value. Additionally, the compliance of reported method performance characteristics was checked against provisions given in legislation.

This proficiency test demonstrated the competence of the participating laboratories in the analysis of regulated PAHs in spirulina and fish oil. More than 83% of the reported test results were graded with z-scores that were below an absolute value of two, indicating acceptable agreement with the assigned reference values of the test material.

2 Introduction

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Joint Research Centre operates the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons in Food (EURL-PAH). One of its core tasks is to organise inter-laboratory comparisons (ILCs) for the National Reference Laboratories (NRLs) [1, 2].

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic compounds and can be found in the environment. In food, PAHs may be formed during industrial food processing and domestic food preparation, such as smoking, drying, roasting, baking, frying, or grilling.

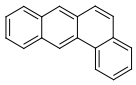
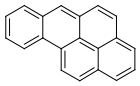
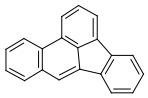
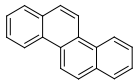
In 2002 the European Commission's Scientific Committee on Food identified 15 individual PAHs as being of major concern for human health. These 15 EU priority PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene (BAP) as a marker for a "total-PAH content" [3]. The toxicological importance of these compounds was confirmed in October 2005 by the International Agency for Research on Cancer (IARC), which classified BAP as carcinogen to human beings (IARC group 1), cyclopenta[*cd*]pyrene - CPP, dibenzo[*a,h*]anthracene - DHA, and dibenzo[*a,l*]pyrene - DLP as probably carcinogenic to human beings (group 2a), and nine other EU priority PAHs as possibly carcinogenic to human beings (group 2b) [4].

As a consequence, the European Commission (EC) issued Commission Regulation (EC) No 1881/2006 setting maximum levels of benzo[*a*]pyrene in food, Commission Regulation (EC) No 333/2007 laying down sampling methods and performance criteria for methods of analysis for the official control of benzo[*a*]pyrene levels in foodstuffs, and Commission Recommendation 2005/108/EC on the further investigation into the levels of PAHs in certain foods [5, 6, 7].

To evaluate the suitability of BAP as a marker for occurrence and toxicity of PAHs in food, the European Commission asked the European Food Safety Authority (EFSA) for a review of the previous risk assessment on PAHs carried by the Scientific Committee on Food (SCF).

The scientific opinion on PAHs in food was published by EFSA in June 2008 [8]. EFSA concluded that benzo[*a*]pyrene was not a suitable indicator for the occurrence of PAHs in food and that four (PAH4) or eight PAHs (PAH8) were more suitable indicators for the occurrence of PAHs in food. However, PAH8 do not provide much added value compared to PAH4. Following these conclusions the Standing Committee on the Food Chain and Animal Health agreed to base risk management measures on four PAHs (PAH4) - BAA, BAP, BBF, and CHR. However, maximum levels for BAP would be maintained to ensure comparability with historical data. In the following the PAH4 will be also indicated as "the four EU marker PAHs" and are listed in Table 1. A maximum level for the sum of the four PAHs was included in the amendment of Commission Regulation (EC) No 1881/2006 [6]. Coherently, also Commission Regulation (EC) No 333/2007 [7] which lays down minimum method performance criteria was revised by Commission Regulation (EC) No 836/2011.

Table 1: Names and structures of the four EU marker PAHs.

1	**Benz[*a*]anthracene (BAA)**		**2**	**Benzo[*a*]pyrene (BAP)**	
3	**Benzo[*b*]fluoranthene (BBF)**		**4**	**Chrysene (CHR)**	

3 Scope

As specified in Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules [2], one of the core duties of EURLs is to organise inter-laboratory comparison tests (ILCs).

This inter-laboratory comparison aimed to evaluate the comparability of results reported by NRLs and EU official food control laboratories (OCLs) for the four EU marker PAHs in food supplements. The appropriateness of the reported measurement uncertainty was also tested as this parameter is important in the compliance assessment of food with EU maximum levels.

The PTwas designed and evaluated under the umbrella of IRMM's accreditation according to ISO Standard 17043:2010 [9].

4 Participating Laboratories

Officially nominated NRLs and OCLs of the EU Member States were admitted as participants. The participants are listed in Table 2 and Table 3 respectively.

Table 2: List of participating National Reference Laboratories

Institute	***Country***
AGES - Österreichische Agentur für Gesundheit und Ernährungssicherheit, Kompetenzzentrum Cluster Chemie	AUSTRIA
Scientific Institute of Public Health	BELGIUM
SGL - State General Laboratory, Environmental and other Food Contamination Laboratory	CYPRUS
Nàrodní referenční laboratoř pro polycyklické aromatické uhlovodíky - Státní veterinární ústav Praha	CZECH REPUBLIC
Division of Food Chemistry, National Food Institute, Technical University of Denmark	DENMARK
Veterinary and Food Administration, Chemical Laboratory	DENMARK
Tartu Laboratory of Health Board	ESTONIA
EVIRA - Finnish Food Safety Authority	FINLAND
LABERCA - Laboratoire d'Etude des Résidus et des Contaminants dans les Aliments	FRANCE
BVL - Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	GERMANY
GCSL - General Chemical State Laboratory - Food Division - Laboratory	GREECE
Central Agricultural Office, Food & Feed Safety Directorate, Food Residues Toxicological Dept.	HUNGARY

Central Agricultural Office, Food and Feed Safety Directorate, Feed	HUNGARY
The Public Analyst's Laboratory Dublin	IRELAND
Istituto Superiore di Sanità	ITALY
BIOR - Institute of Food Safety, Animal Health and Environment	LATVIA
National Veterinary Laboratory (National Food and Veterinary Risk Assessment Institute)	LITHUANIA
National Health Laboratory of Luxembourg	LUXEMBOURG
RIKILT- Institute of Food Safety	THE NETHERLANDS
NIFES - National Institute of Nutrition and Seafood Research	NORWAY
National Institute of Public Health - National Institute of Hygiene	POLAND
SVUPUDK - State Veterinary and Food Institute Dolný Kubín	SLOVAKIA
Zavod za zdravstveno varstvo Maribor	SLOVENIA
AESAN - Centro Nacional de Alimentaciòn (Spanish Food Safety and Nutrition Agency)	SPAIN
SLV - Livsmedelsverket	SWEDEN
FERA - The Food and Environment Research Agency	UNITED KINGDOM

From the 26 NRLs registered for participation only 1 NRL did not report results due to technical problems. One NRL did not register for participation in the PT.

Table 3: List of participating Official Food Control Laboratories

Institute	***Country***
MA 38 - Lebensmitteluntersuchungsanstalt der Stadt Wien	AUSTRIA
LARECO	BELGIUM
CVUA-Münsterland-Emscher-Lippe	GERMANY
Chemisches Untersuchungsamt der Stadt Hagen	GERMANY
Thüringer Landesamt für Lebensmittelsicherheit und Verbraucherschutz	GERMANY
CVUA Rheinland	GERMANY
Berlin-Brandenburg State Laboratory	GERMANY
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit	GERMANY
Institut für Hygiene und Umwelt, Hamburg	GERMANY
Landesamt für Verbraucherschutz Sachsen-Anhalt	GERMANY
CVUA Karlsruhe	GERMANY
Landesuntersuchungsamt - Institut für Lebensmittelchemie, Speyer	GERMANY
CVUA Rhein Ruhr Wupper	GERMANY
GV.CONSELLERIA SANIDAD.Centro Salud Pública	SPAIN
Nofalab	THE NETHERLANDS

Fifteen OCLs registered for participation in the PT, two OCLs did not report any results. One OCL reported results only for BAP in the fish oil sample.

5 Time frame

The PT was announced on the IRMM web page and invitation letters were sent to the laboratories on 2 April 2014 with deadline for registration 24 April 2014 (see ANNEX 1 and ANNEX 2). Test samples were dispatched (see ANNEX 3) on 7 May 2014 and the deadline for reporting of results was set to 10 June 2014. Instructions for analysis and reporting of results were supplied to the participants together with the test samples. The respective documents are presented in ANNEX 4.

6 Confidentiality

The Lab codes of participants are disclosed only to the participants, unless they were enrolled in the study by a third party, covering the participation fee. In this case the Lab codes of the respective laboratories will be also disclosed to the enrolling third party. In all other cases Lab codes will only be disclosed on a request and upon the written consent of the participant.

7 Test materials

7.1 Preparation

The test items of this PT were spirulina powder and fish oil. Participants also received a solution of the 4 EU markers PAHs either in acetonitrile or in toluene (according to their choice, see ANNEX 3) with disclosed concentrations, which allowed them to check their instrument calibration against an independent reference. Participants received the technical specifications (see ANNEX 5) of the chosen solution together with the test material.

Spirulina powder and fish oil food supplements were purchased from a local pharmacy. Spirulina powder was homogenised and aliquots of about 20 g were packed in amber glass screw cap vials, and stored in the freezer. Both aliquots of spirulina and fish oil test samples were analysed for native PAH contents. Spirulina powder contained PAHs at content levels suitable for the purpose of this ILC, whereas the native analyte contents of the fish oil sample were for each compound below 0.3 µg/kg. Therefore, the rest of about 2 l fish oil was spiked with a PAH standard solution containing the four EU marker PAHs to the levels given in Table 4. After spiking, the test sample was homogenized over night by intensive stirring. Aliquots of about 20 ml were packed into amber glass screw cap vials and stored in the freezer.

The standard solutions were prepared from neat certified reference materials (BCR®), (purchased at the Institute for Reference Materials and Measurements, Geel, Belgium,). Single standard stock solutions of each analyte were produced by substitution weighing of neat substances on a microbalance and dissolution in toluene. Mixed standards were prepared gravimetrically from the single standard stock solutions in the respective solvents and further diluted to the concentrations specified in ANNEX 5. The standard solutions were ampouled and flame sealed under inert atmosphere in 2 ml amber glass ampoules.

7.2 Homogeneity and stability

The spirulina powder and fish oil were tested for significant inhomogeneity, according to the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [10], and for sufficient homogeneity according to ISO 13528 [11]. Homogeneity was tested by method consisted of sample extraction by pressurized liquid extraction, size-exclusion chromatography followed by solid phase extraction clean-up and gas-chromatography with mass-spectrometric detection. The method precision complied with the requirements laid down in ISO 13528 [11].

Homogeneity experiments included duplicate analysis of 10 samples randomly selected among the amber glass vials prepared for dispatch along the packing sequence. The duplicate analyses

were performed in random order. The test materials were rated sufficiently homogenous and no trend was observed. Details of the homogeneity tests are given in ANNEX 6.1 and 6.2. For BAA in spirulina the F-test failed because the between sample (ampoules) variability was significantly higher than the within sample variability. This was detected due to the high precision of the duplicate analyses of each sample (within sample variability). However, both tests requirements of IUPAC protocol and the ISO standard proved sufficient homogeneity, meaning that the residual analyte content difference between vials (inhomogeneity) does not significantly influence the performance statement (z-score) of a particular laboratory.

The stability of both test materials was evaluated by applying an isochronous experimental design.

Nine randomly selected samples from each of both matrices were stored at three different conditions over a three month's period from the production of the material to the end of the submission of the results.

The first sets of 3 samples each were stored at the recommended condition - refrigerator (~ 5 C°) for fish oil and room temperature (22 C°) for spirulina. The second sets of 3 samples each were stored at -80 C°) and 5 C° for the whole period of the study. The third sets of 3 samples each were stored at 22 C° (only spirulina), 5 C° and -80 C° for half of the period. At the end of the test period, all 9 samples were analysed in duplicate under repeatability conditions.

No significant difference of the analyte contents among the test samples was found. Hence stability of the samples can be assumed under the recommended conditions over the whole period of the ILC (ANNEX 7.1 and 7.2)

7.3 Assigned value and standard deviation for proficiency assessment

The assigned values were determined for both materials at the EURL PAH applying method based on isotope dilution mass spectrometry[12] (WI-D-0607). This implied the preparation of standard solutions from two totally independent sources - NIST SRM 2260a and neat certified reference materials BCR® from IRMM. The analytical method was fully validated by collaborative trial and is accredited according to ISO 17025. This method will become a European standard in short time. The respective associated uncertainties of the assigned values were calculated based on GUM approach [13].

The assigned value for the sum of PAH4 was calculated from the individual assigned values and its corresponding uncertainty was calculated from the uncertainties of the individual assigned values applying the law of error propagation. The effect of correlation between the measurements of the individual analytes was evaluated by estimating the uncertainty of the sum of PAH4, either considering covariance or ignoring them. However, the difference between the two uncertainty values was marginal for both test material. For the test material spirulina powder the expanded uncertainty value considering covariance would increase from 1.13 µg/kg to 1.18 µg/kg, whereas it would decrease for fish oil from 0.58 µg/kg to 0.52 µg/kg. Due to the small differences and for reasons of enhanced transparency of the calculations, it was decided to apply for the evaluation of the results reported for the sum of PAH4 uncertainty values ignoring covariance. The assigned values and the associated expanded uncertainties (k=2) are given in Table 4 and Table 5.

The standard deviation for proficiency assessment, σ_P, was set for the individual analytes equal to the maximum tolerable uncertainty (Uf), which is calculated according to Equation 2 [7]. A LOD value of 0.30 µg/kg, and α equal to 0.2 were applied for this purpose. The standard deviation for proficiency testing was calculated for the SUM4PAH parameter from the σ_P - values of the individual analytes applying the law of error propagation.

Equation 2 $$U_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2}$$ [7]

where U_f relates to the maximum tolerated standard measurement uncertainty, LOD to the limit of detection, α to a numeric factor depending on the concentration C as given in Commission Regulation (EC) No 333/2007, amended by Regulation (EC) 836/2011.

The assigned values and respective uncertainties together with the target standard deviations of the target PAHs are listed in Table 4 and Table 5.

Table 4: Assigned values and their associated expanded uncertainties (k=2) for the fish oil test item, expressed on product basis.

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	**3.33**	**0.28**	0.68	20.5
Chrysene	CHR	**3.57**	**0.39**	0.73	20.4
Benzo[*b*]fluoranthene	BBF	**4.34**	**0.26**	0.88	20.3
Benzo[*a*]pyrene	BAP	**3.29**	**0.19**	0.68	20.5
Sum of the four marker PAHs	SUM4PAH	**14.54**	**0.58**	1.49	10.3

Table 5: Assigned values and their associated expanded uncertainties (k=2) for the spirulina test item, expressed on product basis.

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	**4.64**	**0.31**	0.94	20.3
Chrysene	CHR	**11.77**	**0.88**	2.36	20.0
Benzo[*b*]fluoranthene	BBF	**9.90**	**0.60**	1.98	20.1
Benzo[*a*]pyrene	BAP	**3.56**	**0.24**	0.73	20.4
Sum of the four marker PAHs	SUM4PAH	**29.87**	**1.13**	3.30	11.1

σ_p standard deviation for proficiency assessment.
U expanded uncertainty of the assigned value (k=2).

8 Design of the proficiency test

The design of the PT foresaw triplicate analysis of the test items and reporting on product basis of the individual results of replicate analyses for the single analytes. Additionally a "value for proficiency assessment", in the following denoted as "final value", was requested, expressed on product basis, for both the single analytes and the sum of the four PAHs. All results had to be reported corrected for recovery (and recovery had to be stated in a questionnaire together with other parameters of the method applied); final results had also to be accompanied by the respective expanded measurement uncertainty and the coverage factor. Only "final values" were used for performance assessment.

Participants were asked to report besides analysis results also details of the performance for the applied method of analysis. (See ANNEX 8).

Each participant received at least one ampoule of a solution of the target PAHs in the chosen solvent (2 ml), with disclosed content, and two crimp cap amber glass vials containing the spirulina powder test sample as well as the fish oil test material.

9 Evaluation of Laboratories

9.1 General

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the test materials, which was expressed by z-scores [11]. Zeta-scores were calculated in addition considering the uncertainty of the test results as estimated by each participant.

The compliance with legislation of the performance characteristics of the method used to determine the 4 marker PAHs was evaluated as well.

The results as reported by participants are listed in ANNEX 9. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed.

9.2 Evaluation criteria

z-Scores

z-Scores were calculated based on the final values. Equation 3 presents the formula for calculation of z-scores.

Equation 3 $$z = \frac{\left(x_{lab} - X_{assigned}\right)}{\sigma_P}$$ [11]

where z refers to the z-score, x_{lab} to the reported "final value", $X_{assigned}$ to the assigned value, and σ_P to the standard deviation for proficiency testing.

zeta-Scores

In addition to z-scores, zeta-scores were calculated. Zeta-scores describe the agreement of the reported result with the assigned value within the respective uncertainties. Zeta-scores were calculated according to Equation 4.

Equation 4 $$zeta = \frac{x_{lab} - X_{assigned}}{\sqrt{u_{lab}^2 + u_{assigned}^2}}$$ [11]

where *zeta* refers to the zeta-score, x_{lab} to the reported "final value", $X_{assigned}$ to the assigned value, u_{lab} to the standard measurement uncertainty of the reported result, and $u_{assigned}$ to the standard uncertainty of the assigned value.

Whenever uncertainty was not reported by the laboratory, the corresponding zeta-score was not calculated.

Unsatisfactorily large zeta-scores might be caused by underestimated measurement uncertainties, large bias, or a combination of both. On the contrary, satisfactory zeta scores might be obtained even with high bias if the uncertainty is sufficiently high. However, legislation specifies maximum tolerable standard uncertainties. Uncertainties exceeding them are not considered fit-for-purpose. Therefore, the uncertainties reported by the participants for the 4 marker PAHs were checked whether they comply with the thresholds provided by the "fitness-for-purpose" function (Equation 2). The results reported by the participants and the maximum tolerated LOD of 0.30 µg/kg were used for the calculation of the respective threshold values. Non-compliant reported uncertainties are highlighted in Table 7 and Table 8.

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [9]. The following scheme is applied for the interpretation of z-scores:

$|score| \leq 2.0$ = satisfactory performance
$2.0 < |score| < 3.0$ = questionable performance
$|score| \geq 3.0$ = unsatisfactory performance

9.3 Evaluation of results

z-Scores were attributed only to the final values. The individual results of replicate analyses were not rated.

Each laboratory had to report a total of 34 results; therefore the expected number of results of the 41 reporting participants was 1394. One NRL and two OCLs didn't report results due to technical problems; one OCL reported results only for BAP in fish oil. In total 1233 results were submitted, which equals to 88.5 %. The results, reported by participants are presented in ANNEX 9.

Statistical evaluation of the results was performed using PROLab software [14]. Robust mean values and robust standard deviations of the final values reported by the participants were calculated according to Algorithm A+S of ISO13528:2005 [11].

It should be noted that the robust means calculated from the participants' results (ANNEX 9) fall inside the confidence interval of the assigned values for all the parameters and matrices. Robust standard deviations for the 4 marker PAHs in fish oil were, except for CHR, lower than the target standard deviations, while for PAHs in spirulina powder they were, except for BAP, slightly higher. The difference in the robust standard deviations for both test items could be explained by the fact that fish oil is a homogeneous liquid and does not need an extraction step. Consequently lower variability of result could be expected for fish oil.

Satisfactory z-scores obtained 83.6 % of the results reported by the participants. Only 8.5% of the results fall in the unsatisfactory performance range, indicated by z-scores equal or above an absolute value of three (Figure 1). Taking into account the complex test materials and the fact that participants did not have much experience with such not yet regulated matrices (see ANNEX 8), the overall performance may be considered satisfactory.

17 participants have 100% (10) of satisfactory z-scores, while 10 participants (24%) have less than 80% satisfactory z-scores.

Figure 2 and Figure 3 provide overviews of the individual z-scores assigned to the results for spirulina powder and fish oil test material for NRLs and OCLs respectively. The larger the triangles, the larger were the differences to the assigned values. Red triangles indicate z-scores above an absolute value of three, whereas yellow triangles represent z-scores in the questionable performance range. For unsatisfactory scores, the corresponding score values are presented next to the triangles. Remarkably large deviations from the assigned values were accumulated in the results of a few laboratories only. Both the direction of deviation and the magnitude of deviation indicate for the particular laboratory constant bias affecting the determination of all analytes. Such bias might be caused by e.g. aliquotation mistakes, mistakes in the preparation of calibration standards, or calculation errors. Concerned laboratories shall perform root cause analysis and remediate the source of error.

The numerical values of the calculated z-scores are compiled in Table 6 for both food supplement test items. z-Scores with an absolute value of ≥ 3 (unsatisfactory) are given in bold, red font on a red background, while the questionable z-scores are highlighted in yellow on a yellow background.

Figure 1: Histogram of z-scores corresponding to the "final values for proficiency assessment" reported by the NRLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH in both samples

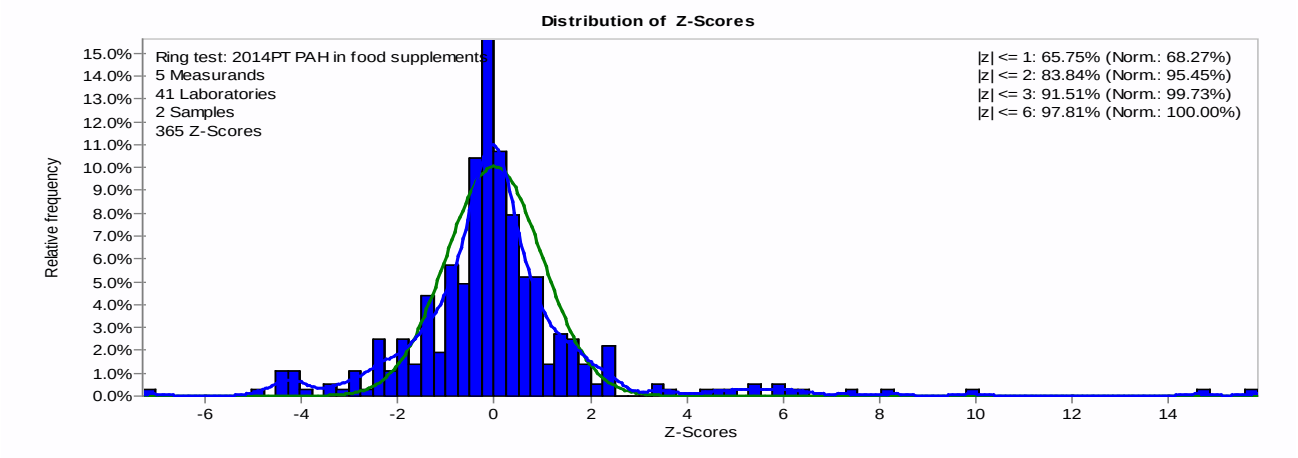


Figure 2: Graphical presentation of z-scores corresponding to the "final values for proficiency assessment" reported by the NRLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the two test materials.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented next to the triangles for the last two performance categories.

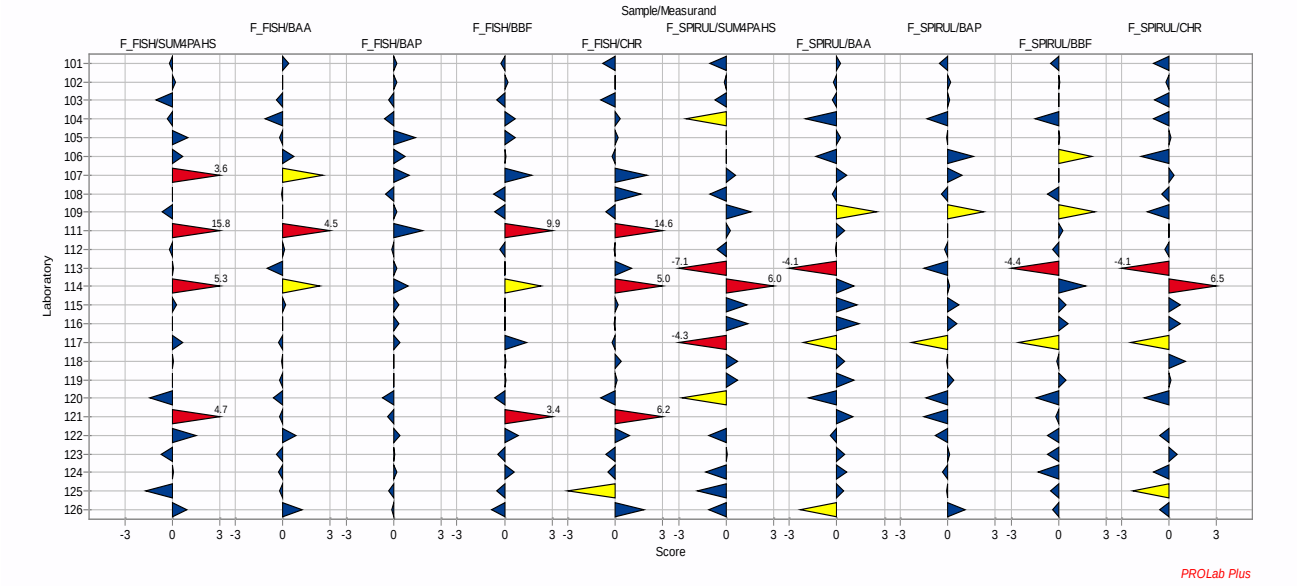
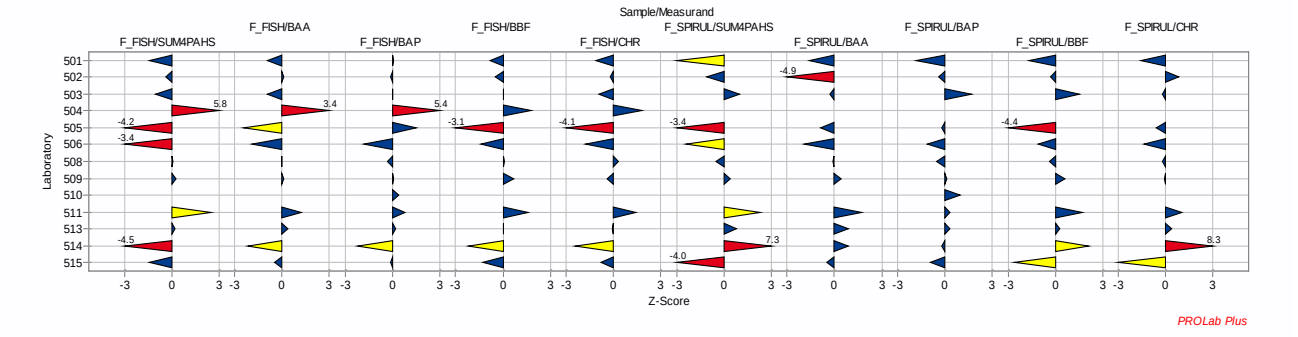


Figure 3: Graphical presentation of **z-scores** corresponding to the "final values for proficiency assessment" reported by the OCLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the two test materials.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented next to the triangles for the last two performance categories.



Comparing overall performance, the percentage of successful and questionable z-scores is similar for both samples, while regarding analytes, performance was best for BAP indicated by the highest number of satisfactory z-scores - 95%, while the lowest number (84%) was recorded for CHR.

Table 7 and 8 present the respective zeta-scores. Data outside the satisfactory performance range are highlighted in red. The assessment of the performance of the participants based on the reported measurement uncertainty gave a slightly less favourable picture. 80.2 % of the zeta-scores assigned for the four individual analytes and for the SUM4PAH were within the satisfactory performance range, while 8.7% were non-satisfactory. It has to be noted that the absolute values of the zeta-scores were for many participants much higher than the z-scores attributed to the same results.

Estimating realistic measurement uncertainty values still causes problems for a number of participants. The compliance of the reported uncertainty values with the threshold values given by the "fitness-for-purpose" function U_f was assessed and non-complying uncertainties are highlighted in yellow. However, attention should be paid to unrealistically low uncertainties, reported by some participants. Comparing the precision estimated from the results of the three replicate analyses with the uncertainty reported with the final values, it becomes obvious that some laboratories based their uncertainty estimates purely on the standard deviation of the three replicate analyses. The relative expanded uncertainty reported by the participants for all parameters and samples varied widely - between 1% and 60% with 23 values below 5% and 20 values above 50% (Figure 4).

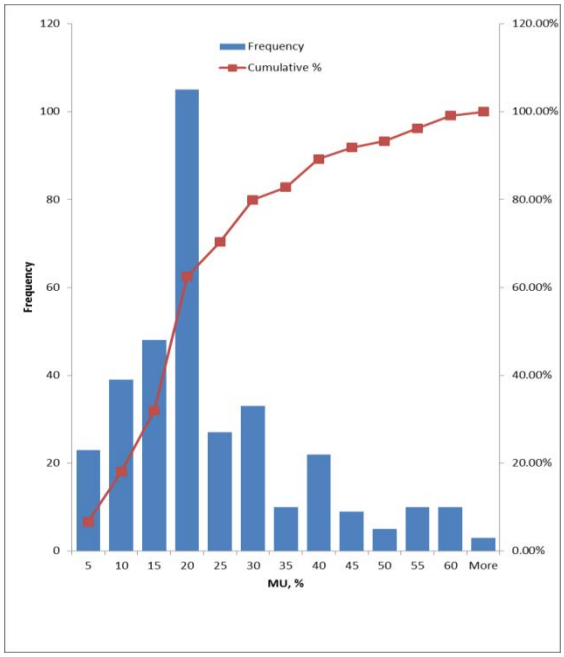


Figure 4 Histogram of the relative expanded uncertainties allocated to the reported results for the four PAHs in spirulina powder and fish oil.

Hence the EURL PAH will continue to pay special attention to this parameter, in the PTs to come, as measurement uncertainty has major implications on the assessment of compliance of food with European legislation.

Another point to pay attention to is the way of reporting results in terms of number of decimal digits. Inconsistencies were noted in the number of significant figures of reported measurement results and associated uncertainties, which were sometimes also inconsistent with the number of digits of maximum limits, set in legislation. The EURL PAH will address this issue at the coming workshop as a harmonised way of reporting results makes part of the proper implementation of EU legislation.

The graphical representations of the distribution of results for the individual analytes are given in ANNEX 9 together with respective Kernel density plot.

For each analyte the figures show the individual analysis results of the three replicate determinations.

Table 6: Compilation of z-scores calculated from the "final values" reported by the participants for the two test materials:

z-scores outside the satisfactory range (|z| > 2) are indicated by red (unsatisfactory) and yellow (questionable) background; empty cells - z-score not calculated

	Sample/Measurand									
Lab Code	F_FISH/ SUM4PAHS	F_FISH/ BAA	F_FISH/ BAP	F_FISH/ BBF	F_FISH/ CHR	F_SPIRUL/ SUM4PAHS	F_SPIRUL/ BAA	F_SPIRUL/ BAP	F_SPIRUL/ BBF	F_SPIRUL/ CHR
	NATIONAL CONTROL LABORATORIES (NRLs)									
101	-0.2	0.4	0.2	-0.2	-0.8	-1.0	0.2	-0.5	-0.5	-1.0
102	0.2	0.0	0.2	0.2	0.0	-0.1	-0.2	0.2	0.1	-0.2
103	-1.0	-0.4	-0.3	-0.5	-0.9	-0.7	-0.3	0.1	0.0	-0.9
104	-0.3	-1.1	-0.6	0.7	0.3	-2.5	-2.0	-1.3	-1.5	-1.0
105	1.0	-0.2	1.4	0.7	0.2	0.0	0.2	-0.1	0.1	0.1
106	0.7	0.7	0.7	0.1	-0.2	0.0	-1.3	1.6	2.1	-1.8
107	3.6	2.5	1.0	1.7	2.0	0.6	0.6	0.9	0.0	0.3
108	0.0	-0.1	-0.5	-0.7	1.6	-1.0	-0.3	-0.4	-0.7	-0.5
109	-0.6	0.0	0.2	-0.6	-0.6	1.6	2.5	2.3	2.3	-1.4
110										
111	15.8	4.5	1.8	9.9	14.6	0.3	0.5	0.0	0.3	0.0
112	-0.2	0.1	-0.1	-0.3	-0.1	-0.6	-0.1	-0.2	-0.4	-0.3
113	0.1	-1.0	0.2	0.0	1.0	-7.1	-4.1	-1.5	-4.4	-4.1
114	5.3	2.3	0.9	2.3	5.0	6.0	1.1	0.1	1.7	6.5
115	0.3	0.2	0.3	0.0	0.2	1.3	1.3	0.7	0.5	0.7
116	0.0	0.0	0.3	0.0	-0.1	1.4	1.4	0.6	0.6	0.7
117	0.7	-0.3	0.4	1.4	-0.2	-4.3	-2.1	-2.3	-2.5	-2.4
118	0.1	-0.1	0.0	0.1	0.4	0.7	0.5	-0.1	-0.1	1.0
119	0.0	-0.2	0.0	0.1	0.1	0.7	1.1	0.4	0.5	0.1
120	-1.4	-0.6	-0.7	-0.6	-0.9	-2.8	-1.8	-1.4	-1.4	-1.6
121	4.7	-0.2	-0.4	3.4	6.2		1.0	-1.5	-0.2	
122	1.5	0.8	0.4	0.9	0.9	-1.1	-0.4	-0.8	-0.7	-0.6
123	-0.7	-0.4	0.1	-0.4	-0.6	0.1	0.5	0.1	-0.7	0.5
124	0.1	-0.3	0.2	0.6	-0.5	-1.3	0.6	-0.3	-1.3	-1.0
125	-1.7	-0.2	-0.3	-0.5	-3.0	-1.8	0.4	-0.1	-0.5	-2.3
126	0.9	1.2	-0.1	-0.8	1.8	-1.1	-2.3	1.1	-0.4	-0.6
	OFFICIAL CONTROL LABORATORIES (OCLs)									
501	-1.4	-0.9	0.1	-0.8	-1.1	-3.0	-1.6	-1.8	-1.7	-1.6
502	-0.4	0.1	-0.1	-0.5	-0.2	-1.1	-4.9	-0.4	-0.3	0.8
503	-1.0	-0.9	0.0	0.0	-0.9	1.0	-0.3	1.7	1.5	-0.2
504	5.8	3.4	5.4	1.8	1.8					
505	-4.2	-2.4	1.5	-3.1	-4.1	-3.4	-0.9	-0.2	-4.4	-0.6
506	-3.4	-1.9	-1.8	-1.4	-1.8	-2.4	-1.9	-1.1	-1.1	-1.4
507										
508	0.1	0.0	-0.3	0.1	0.3	-0.5	-0.1	-0.5	-0.4	-0.2
509	0.3	0.1	0.1	0.7	-0.4	0.4	0.4	0.1	0.6	-0.1
510			0.4					1.0		
511	2.5	1.2	0.8	1.6	1.4	2.3	1.7	0.3	1.7	1.0
512										
513	0.2	0.4	0.2	0.0	-0.1	0.8	0.9	0.3	0.3	0.4
514	-4.5	-2.2	-2.2	-2.2	-2.4	7.3	0.9	-0.2	2.1	8.3
515	-1.4	-0.5	-0.1	-1.3	-0.8	-4.0	-0.5	-0.9	-2.6	-3.0

Table 7: Compilation of zeta-scores calculated from the "final values" reported by the NRLs and OCLs for test material fish oil, the reported corresponding expanded relative measurement uncertainties, as well as assigned values and expanded uncertainties of the analyte contents:

zeta-scores outside the satisfactory range (|zeta| > 2) are highlighted in red. Yellow highlighted cells indicate measurement uncertainty values that either did not comply with the thresholds given by the "fitness-for-purpose" function U_f (BAA, BAP, BBF, and CHR), or were not in agreement with the uncertainty value derived from the uncertainties of the individual analytes (SUM parameter; empty cells - z-score not calculated.

	BAA			BAP			BBF			CHR			SUM		
Assigned value +/- U, µg/kg	3.33	±	0.28	3.29	±	0.19	4.34	±	0.26	3.57	±	0.39	14.54	±	0.58
	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score
Lab code	µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%	
	National Reference Laboratories (NRLs)														
101	3.6	42	0.4	3.4	41	0.2	4.2	40	-0.2	3	40	-0.9	14.2	41	-0.1
102	3.32	26	0.0	3.43	34	0.2	4.54	30	0.3	3.6	22	0.1	14.89	15	0.3
103	3.08	6	-1.5	3.1	13	-0.9	3.86	16	-1.4	2.93	12	-2.4	13		
104	2.55	64	-0.9	2.88	58	-0.5	4.98	54	0.5	3.76	58	0.2	14.16	29	-0.2
105	3.2	20	-0.4	4.2	20	2.1	5	20	1.3	3.7	20	0.3	16	10	1.7
106	3.84	20	1.2	3.78	20	1.3	4.46	20	0.3	3.46	21	-0.3	15.54	10	1.2
107	5.01	27	2.4	3.98	13	2.6	5.87	27	1.9	5.07	13	4.0	19.93	46	1.2
108	3.26	40	-0.1	2.93	40	-0.6	3.68	40	-0.9	4.71	40	1.2	14.6	40	0.0
109	3.3	17	-0.1	3.4	36	0.2	3.8	24	-1.1	3.1	20	-1.3	13.6	13	-1.0
110															
111	6.4	16	5.7	4.5	19	2.8	13.07	17	7.8	14.27	16	9.3	38.24	9	13.5
112	3.4	22	0.2	3.2	17	-0.3	4.1	5	-1.4	3.5	17	-0.2	14.2	33	-0.1
113	2.677	55	-0.9	3.394	55	0.1	4.297	55	0.0	4.316	55	0.6	14.685	55	0.0
114	4.93	20	3.1	3.88	20	1.5	6.4	20	3.2	7.25	20	4.9	22.45	20	3.5
115	3.438	8	0.5	3.488	7	1.3	4.329	7	-0.1	3.705	2	0.7	14.96	6	0.8
116	3.3	23	-0.1	3.5	20	0.6	4.3	30	-0.1	3.5	20	-0.2	14.5	13	0.0
117	3.12	20	-0.6	3.56	20	0.7	5.55	20	2.1	3.39	20	-0.5	15.6	20	0.7
118	3.25	22	-0.2	3.28	19	0.0	4.39	17	0.1	3.83	27	0.5	14.76	20	0.1
119	3.17	15	-0.6	3.31	10	0.1	4.41	15	0.2	3.63	13	0.2	14.52	7	0.0
120	2.89	7	-2.6	2.82	10	-2.8	3.82	7	-2.8	2.91	12	-2.5	12.44	5	-5.2
121	3.2	13	-0.5	3	14	-1.3	7.3	14	5.6	8.1	19	5.7	21.6		
122	3.89	11	2.2	3.55	15	0.9	5.15	6	4.0	4.24	12	2.1	16.83	15	1.8
123	3.07	16	-0.9	3.33	12	0.2	3.96	14	-1.2	3.1	18	-1.4	13.46	28	-0.6
124	3.136	34	-0.4	3.417	28	0.3	4.872	26	0.8	3.225	28	-0.7	14.651	29	0.1
125	3.2	30	-0.3	3.1	30	-0.4	3.9	30	-0.7	1.4	30	-7.6	12	15	-2.7
126	4.16	15	2.4	3.22	13	-0.3	3.61	16	-2.3	4.91	14	3.4	15.91	29	0.6
	Official Control Laboratories (OCLs)														
501	2.74	20	-1.9	3.33	20	0.1	3.66	20	-1.8	2.79	20	-2.3	12.51	20	-1.6
502	3.4	15	0.2	3.2	10	-0.5	3.9	10	-1.9	3.4	20	-0.4	13.9	22	-0.4
503	2.7	3	-4.4	3.3	2	0.1	4.3	5	-0.2	2.9	8	-3.0	13.1	5	-3.4
504	5.65	4	12.9	6.9	3	25.7	5.9	5	7.9	4.88	3	6.3	23.3		
505	1.7	25	-6.4	4.3	25	1.9	1.6	25	-11.5	0.6	25	-14.2	8.2	50	-3.1
506	2.05	12	-6.9	2.1	15	-6.4	3.1	13	-5.1	2.26	18	-4.6	9.51		
507															
508	3.35	20	0.1	3.12	20	-0.5	4.42	20	0.2	3.79	20	0.5	14.7	20	0.1
509	3.38	0.6	0.4	3.37	2	0.8	4.94	5	3.5	3.31	6	-1.2	15	3	1.3
510				3.543											
511	4.14	5	4.8	3.84	11	2.5	5.75	12	3.9	4.57	8	3.8	18.31		
512															
513	3.57	20	0.6	3.4	20	0.3	4.35	20	0.0	3.52	20	-0.1	14.8	20	0.2
514	1.8	33	-4.7	1.8	40	-4.0	2.4	28	-5.4	1.8	34	-4.9	7.8	36	-4.7
515	3	39	-0.5	3.2	27	-0.2	3.2	28	-2.4	3	40	-0.9	12.4	27	-1.3

Table 8: Compilation of zeta-scores calculated from the "final values" reported by the NRLs and OCLs for test material spirulina, the corresponding expanded relative measurement uncertainties, as well as assigned values and expanded uncertainties of the analyte contents**:**

*zeta-scores outside the satisfactory range (|zeta| > 2) are highlighted in red. Yellow highlighted cells indicate measurement uncertainty values that either did not comply with the thresholds given by the "fitness-for-purpose" function U_f (BAA, BAP, BBF, and CHR), or were not in agreement with the uncertainty value derived from the uncertainties of the individual analytes (SUM parameter)**;** empty cells - z-score not calculated*

	BAA			BAP			BBF			CHR			SUM		
Assigned value +/- U, µg/kg	4.64	±	0.31	3.56	±	0.24	9.9	±	0.6	11.77	±	0.88	29.87	±	1.13
	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score
Lab code	µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%	
	National Reference Laboratories (NRLs)														
101	4.8	40	0.2	3.2	41	-0.5	9	40	-0.5	9.4	40	-1.1	26.4	40.2	-0.7
102	4.47	26	-0.3	3.68	34	0.2	10.05	30	0.1	11.24	22	-0.3	29.44	15	-0.2
103	4.38	22	-0.5	3.6	8	0.2	9.86	9	-0.1	9.73	9	-2.1	27.6		-4.0
104	2.79	64	-2.0	2.59	58	-1.3	6.82	54	-1.7	9.52	58	-0.8	21.72	32	-2.3
105	4.8	22	0.3	3.5	30	-0.1	10	30	0.1	12	30	0.1	30	17	0.0
106	3.38	20	-3.4	4.69	20	2.3	14.11	20	2.9	7.56	20	-3.6	29.75	12	-0.1
107	5.22	22	1.0	4.18	20	1.43	9.84	22	-0.1	12.56	22	0.5	31.79	42	0.3
108	4.4	40	-0.3	3.25	40	-0.5	8.46	40	-0.8	10.6	40	-0.5	26.7	40	-0.6
109	7	18	3.7	5.2	18	3.3	14.4	17	3.5	8.5	17	-2.9	35.1	9	3.0
110															
111	5.15	16	1.2	3.57	19	0.0	10.56	17	0.7	11.72	16	0.0	31	9	0.7
112	4.5	11	-0.5	3.4	14	-0.6	9.1	15	-1.1	11	13	-0.7	28	27	-0.5
113	0.748	60	-14.3	2.488	60	-1.4	1.078	60	-20.0	2.054	60	-9.0	6.369	60	-11.8
114	5.63	20	1.7	3.63	20	0.2	13.38	20	2.5	27.18	20	5.4	49.82	20	4.0
115	5.9	15	2.7	4.08	9	2	10.81	2	2.8	13.37	8	1.6	34.15	6	3.6
116	6	23	1.9	4	20	1.1	11.1	30	0.7	13.5	20	1.1	34.5	12	2.1
117	2.66	20	-6.4	1.9	20	-7.4	5	20	-8.4	6.12	20	-5.3	15.7	20	-8.5
118	5.11	22	0.8	3.46	19	-0.3	9.61	17	-0.3	14.09	27	1.1	32.26	20	0.7
119	5.65	15	2	3.83	10	1	10.81	15	1	11.95	13	0.2	32.23	7	2
120	2.92	21	-5.0	2.51	23	-3.4	7.2	15	-4.4	8	18	-3.3	20.63	10	-8.1
121	5.6	15	2.1	2.5	16	-4.5	9.5	14	-0.5						
122	4.23	9	-1.7	2.96	10	-3.1	8.42	8	-3.3	10.47	1	-1.5	26.08	10	-2.7
123	5.12	16	1.1	3.6	12	0.2	8.53	14	-2.1	12.83	18	0.7	30.08	28	0.0
124	5.19	72	0.3	3.376	52	-0.2	7.387	39	-1.7	9.453	50	-0.9	25.407	53	-0.7
125	5	30	0.5	3.5	30	-0.1	8.9	30	-0.7	6.3	30	-4.2	24	15	-3.1
126	2.43	17	-8.6	4.38	18	2.0	9.02	20	-0.9	10.37	20	-1.0	26.19	38	-0.7
	Official Control Laboratories (OCLs)														
501	3.17	20	-4.2	2.22	20	-5.3	6.6	20	-4.6	8.02	20	-4.1	20.02	20	-4.7
502	0	20	-29.9	3.3	20	-0.7	9.3	20	-0.6	13.7	20	1.3	26.3	22	-1.2
503	4.4	1	-1.5	4.8	7	6.3	12.8	2	9.0	11.2	7	-1.0	33.2	3	4.4
504															
505	3.8	25	-1.7	3.4	25	-0.4	1.2	25	-25.9	10.3	25	-1.1	18.7	50	-2.37
506	2.83	25	-4.7	2.77	12	-3.9	7.8	14	-3.4	8.37	26	-2.9	21.77		-14.3
507															
508	4.58	20	-0.1	3.19	20	-1.1	9.02	20	-0.9	11.4	20	-0.3	28.2	20	-0.6
509	5.04	3	2.3	3.64	5	0.5	11.09	3	3.6	11.48	3	-0.6	31.24	0.9	2
510				4.317											
511	6.21	12	3.9	3.75	18	0.5	13.34	16	3.1	14.21	12	2.6	37.51		
512															
513	5.53	20	1.5	3.76	20	0.5	10.5	20	0.5	12.6	20	0.6	32.4	20	0.8
514	5.5	39	0.8	3.4	44	-0.2	14	34	1.7	31.3	41	3.0	54.2		
515	4.2	53	-0.4	2.9	40	-1.1	4.7	47	-4.5	4.8	57	-4.9	16.6	47	-3.37

As could be seen from the Kernel density plots (see ANNEX 9) for the fish oil test sample the distributions of results are close to the Gaussian distribution. For the spirulina test sample the distributions were slightly different. They contained a major mode which was close to the Gaussian distribution, but also shoulders corresponding to results significantly lower respectively higher than the results reported by the majority of participants. Separating the results by analysis technique revealed that results obtained by GC-MS and GC-MS/MS agreed well with the major modes and the assigned values. However, significant differences were found for HPLC-FLD measurements. The results produced with this technique showed with the exception of CHR bimodal kernel density plots, with major modes below the assigned values. Participants applying HPLC-FLD for the determination of PAHs in food supplements are requested to report to the EURL PAH possible reasons for this divergence.

The test on equivalence for results obtained by HPLC and GC techniques failed for both test samples for CHR and BbF.

The figures in ANNEX 10 are an aid to allow laboratories to compare the performance of their method with that of other participants with respect to bias (closeness to the assigned value, plotted on the x-axis) and precision (the standard deviation for repeatability, plotted on the y-axis). A vertical solid bold line depicts the assigned value; laboratories are represented by blue dots (mean value of the replicates and the associated standard deviation of the replicates). The light blue area indicates the satisfactory performance area, which is defined by the assigned value $\pm 2\sigma_P$ along the x-axis and by the average repeatability standard deviation of the results reported by the participants along the y-axis. The latter was obtained by analysis-of-variance of the data set received for each analyte. Participants whose data are outside the satisfactory performance area should perform root cause analysis and report to the EURL PAH reasons for the deviation.

9.4 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire filled in by the participants (ANNEX 8). Data are presented as reported.

For most of the participants, food supplements and especially spirulina was not within the scope of their accreditation. While many participants have previous experience with the analysis of fish oil, spirulina is new to almost all of them.

More than half of the participants (19) used GC with different types of mass spectrometers and 16 labs used HPLC-FLD for determination of PAHs. Equivalence tests revealed that the performance in the determination of CHR and BbF was linked for both matrices to the analytical technique used. Most probably interferences caused this difference, which were especially reported for the spirulina test sample.

The survey on instrument calibration revealed that 10 participant did not use internal standards. However those are mainly laboratories applying HPLC-FLD for the measurements. One laboratory used GC-MS/MS in combination with matrix matched calibration, and two participants reported the application of standard addition technique.

Almost all participant (except 2) reported results corrected for recovery (on purpose, or implicitly corrected by internal standards).

Most participants report measurement uncertainties together with the test results. Three participants provide uncertainty values only upon exceedence of maximum levels specified in legislation, another three participants provide them upon request by the customer, and another three participants do not provide it at all.

Compliance with legislation was evaluated on basis of requirements set in Regulation (EC) No 333/2007 as amended by Regulation (EU) No 836/2011 [7]. Only one NRL reported non-compliant LOD/LOQ values and two others did not report any LOD/LOQ value.

Commission Regulation (EC) No 333/2007 requires reporting of analysis results with the same number of significant figures as the maximum levels laid down in legislation are expressed. The compliance with this provision was evaluated for the fish oil test material, which would fall under category 6.1.1 of Commission Regulation (EU) No 835/2011. Red cells in the tables in ANNEX 9 indicate data that would not comply with this provision (either too few or too many significant figures).

The values for recovery complied with the limits specified in Commission Regulation (EU) No 836/2011. However, it cannot be evaluated whether recovery was understood as yield, as requested, and not as apparent (relative) recovery, which might be indicated by recovery values close to 100 %.

The evaluation of the compliance of reported measurement uncertainties with provisions given in legislation was discussed in 9.3.

Comments of the participants regarding this inter-laboratory comparison are summarised in ANNEX 8.

10 Follow-up actions for underperforming laboratories

All laboratories that got "questionable" or "non-satisfactory" performance ratings (z-scores) are urged to perform root cause analysis, and to implement corrective actions. Follow up actions will be organised by the EURL PAH for underperforming NRLs. In a first step, they will have to report in writing to the EURL PAH the results of their root-cause analysis and corrective actions taken.

11 Conclusions

Thirty eight participants provided analysis results. The performance of most participants was satisfactory. In total 83.6 % of the results reported by NRLs and OCLs respectively obtained a satisfactory z-score, which is an overall acceptable performance taking into account the level of difficulty of the matrices and the fact that participant did not have much experience with them as they are not regulated.

Participants are requested to pay attention to the estimation of realistic measurement uncertainty values and its way of reporting.

The great majority of participants in this inter-laboratory comparison applied analytical methods which, with regard to performance characteristics, were compliant with EU legislation. However, some participants are requested to improve in this respect.

12 Acknowledgements

The organisers would like to thank Beatriz de la Calle and Franz Ulberth (all from IRMM, Geel, Belgium) for their accurate revision of this report, the Standards for Innovation and sustainable Development (SID) Unit at IRMM for ampouling of test materials, and all NRLs and OCLs for their cooperation.

13 References

1 EU, *COMMISSION REGULATION (EC) No 776/2006 of 23 May 2006 amending Annex VII to Regulation (EC) No 882/2004 of the European Parliament and of the Council as regards Community reference laboratories.* Official Journal of the European Union, 2006. **L 136**: p. 3-8. Available from: http://eur-ex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:136:0003:008:EN: PDF

2 EU, *Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules.* Official Journal of the European Communities, 2004. **L191**: p. 1-52. Available from:

http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2004:191:0001:0052:EN:PDF

3 *EU, Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food*. (2002). Available from: http://europa.eu.int/comm/food/fs/sc/scf/out153_en.pdf

4 *IARC. Overall Evaluations of Carcinogenicity to Humans.* IARC Monographs on the Evaluation of Carcinogenic Risks to humans (2006). Available from: http://monographs.iarc.fr/ENG/Classification/crthgr01.php

5 *EU, Commission Recommendation (2005/108/EC) of 4 February 2005 on the further investigation into the levels of polycyclic aromatic hydrocarbons in certain foods.* Official Journal of the European Union, 2005. L 34: p. 43-45. Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:034:0043:0045:EN:PDF

6 *EU, Commission Regulation (EC) No 835/2011 of 19 August 2011, amending Regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in foodstuffs setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Union, 2006.* ***L 215: p. 4-8****. Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011 :215:0004:0008:EN:PDF*

7 *EU, COMMISSION REGULATION (EU) No 836/2011 of 19 August 2011 amending Regulation (EC) No 333/2007, laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs*: Official Journal of the European Union, 2011. **L 215**: p. 9-16 Available from http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:215:0009:0016:EN:PDF

8 *EFSA, Scientific Opinion of the Panel on Contaminants in the Food Chain on a request from the European Commission on Polycyclic Aromatic Hydrocarbons in Food*. The EFSA Journal, 2008. 724: p. 1-114. Available from: http://www.efsa.europa.eu/EFSA/efsa_locale-1178620753812_1211902034842. htm

9 *ISO/IEC 17043:2010*. "Conformity assessment -- General requirements for proficiency testing providers". Geneva, Switzerland

10. *IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories*. http://www.iupac.org/publications/pac/2006/pdf/7801x0145.pdf

11. ISO 13528:2005 "Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons", issued by International Organisation for Standardisation, Geneva, Switzerland

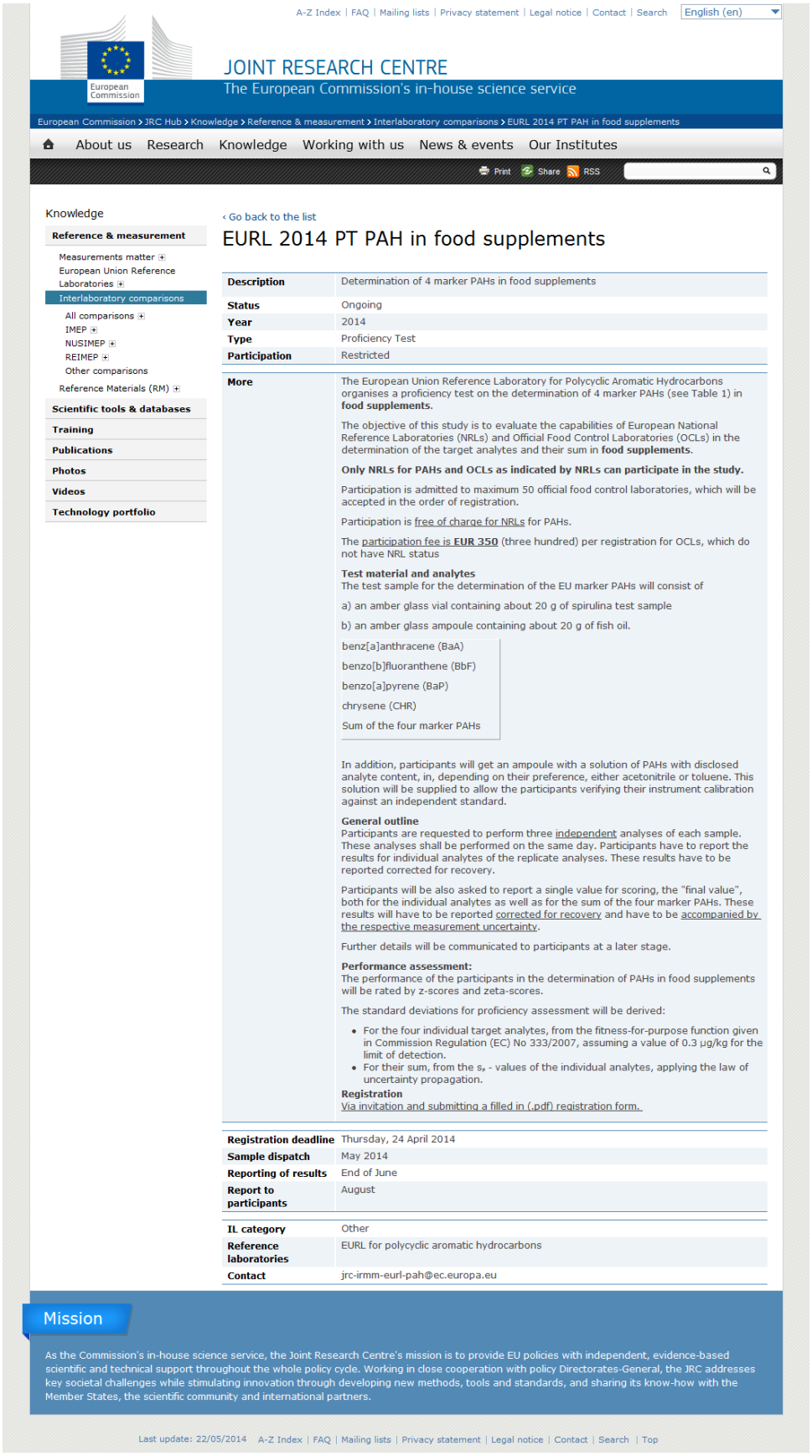
12 WI-D-0607 Determination of 4 EU target PAHs in fatty food matrices by pressurized liquid extraction, size-exclusion chromatography followed by solid phase extraction clean-up and gas-chromatography with mass-spectrometric detection, EURL PAH

13 *Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections*)

14 *Software for PT programs and collaborative studies, PROLab*; http://quodata.de/en/software/for-interlaboratory-tests.html

ANNEXES

ANNEX 1: Announcement of the PT - A) on the IRMM webpage



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European Commission

JOINT RESEARCH CENTRE
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European Commission > JRC Hub > Knowledge > Reference & measurement > Interlaboratory comparisons > EURL 2014 PT PAH in food supplements

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Knowledge

- **Reference & measurement**
  - Measurements matter
  - European Union Reference Laboratories
  - Interlaboratory comparisons
    - All comparisons
    - IMEP
    - NUSIMEP
    - REIMEP
    - Other comparisons
  - Reference Materials (RM)
- **Scientific tools & databases**
- **Training**
- **Publications**
- **Photos**
- **Videos**
- **Technology portfolio**

‹ Go back to the list

EURL 2014 PT PAH in food supplements

Description	Determination of 4 marker PAHs in food supplements
Status	Ongoing
Year	2014
Type	Proficiency Test
Participation	Restricted

More

The European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons organises a proficiency test on the determination of 4 marker PAHs (see Table 1) in **food supplements**.

The objective of this study is to evaluate the capabilities of European National Reference Laboratories (NRLs) and Official Food Control Laboratories (OCLs) in the determination of the target analytes and their sum in **food supplements**.

Only NRLs for PAHs and OCLs as indicated by NRLs can participate in the study.

Participation is admitted to maximum 50 official food control laboratories, which will be accepted in the order of registration.

Participation is free of charge for NRLs for PAHs.

The participation fee is **EUR 350** (three hundred) per registration for OCLs, which do not have NRL status

Test material and analytes
The test sample for the determination of the EU marker PAHs will consist of

a) an amber glass vial containing about 20 g of spirulina test sample

b) an amber glass ampoule containing about 20 g of fish oil.

- benz[a]anthracene (BaA)
- benzo[b]fluoranthene (BbF)
- benzo[a]pyrene (BaP)
- chrysene (CHR)
- Sum of the four marker PAHs

In addition, participants will get an ampoule with a solution of PAHs with disclosed analyte content, in, depending on their preference, either acetonitrile or toluene. This solution will be supplied to allow the participants verifying their instrument calibration against an independent standard.

General outline
Participants are requested to perform three independent analyses of each sample. These analyses shall be performed on the same day. Participants have to report the results for individual analytes of the replicate analyses. These results have to be reported corrected for recovery.

Participants will be also asked to report a single value for scoring, the "final value", both for the individual analytes as well as for the sum of the four marker PAHs. These results will have to be reported corrected for recovery and have to be accompanied by the respective measurement uncertainty.

Further details will be communicated to participants at a later stage.

Performance assessment:
The performance of the participants in the determination of PAHs in food supplements will be rated by z-scores and zeta-scores.

The standard deviations for proficiency assessment will be derived:

- For the four individual target analytes, from the fitness-for-purpose function given in Commission Regulation (EC) No 333/2007, assuming a value of 0.3 µg/kg for the limit of detection.
- For their sum, from the s_p - values of the individual analytes, applying the law of uncertainty propagation.

Registration
Via invitation and submitting a filled in (.pdf) registration form.

Registration deadline	Thursday, 24 April 2014
Sample dispatch	May 2014
Reporting of results	End of June
Report to participants	August
IL category	Other
Reference laboratories	EURL for polycyclic aromatic hydrocarbons
Contact	jrc-irmm-eurl-pah@ec.europa.eu

Mission

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle. Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new methods, tools and standards, and sharing its know-how with the Member States, the scientific community and international partners.

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Announcement of the PT - B) via email

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 01/04/2014

Interlaboratory comparison of the EURL for Polycyclic Aromatic Hydrocarbons (PAHs) on the DETERMINATION of EU MARKER PAHs in food supplements

Dear Sir/Madam,

Registration for participation in the inter-laboratory comparison study organised by the EURL PAH on the determination of the 4 marker PAHs in food supplements is **open from now until 25th April 2014**.

Participation is mandatory and free of charge for National Reference Laboratories (NRLs) for PAHs. Confidentiality of participants and respective results is granted.

In support to the NRLs, to facilitate fulfilling their tasks as included in Regulation (EC) No 882/2004, EU Official Food Control Laboratories (OCLs) falling under the responsibility of the NRLs may participate in the study. **The participation fee for official food control laboratories is 350 Euro per participation.**

The target analytes are listed in the following Table.

benz[*a*]anthracene (BaA)
benzo[*b*]fluoranthene (BbF)
benzo[*a*]pyrene (BaP)
chrysene (CHR)
SUM of the 4 marker PAHs

Results have to be reported corrected for recovery and accompanied by the respective measurement uncertainty for both the individual PAHs and the sum of the four marker PAHs.

Each participant will be provided with
a) an amber glass vial containing about 20 g of spirulina test sample
b) an amber glass ampoule containing about 20 g of fish oil.

Participants will also receive a standard solution in either acetonitrile or toluene with disclosed content; which might be used for verification of instrument calibration.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-crl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

This inter-laboratory comparison is organised under accreditation to ISO 17043.

Detailed information will be soon available the EU-RL website:
http://irmm.jrc.ec.europa.eu/EURLs/EURL_PAHs/interlaboratory_comparisons/Pages/index.aspx

Timing:

- **Deadline for registration: 25th April 2014**
- Dispatch of samples: **beginning of May.** A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser
- Deadline for reporting of results: **4 weeks after the dispatch of the samples.**

Registration procedure:

This year EURL PAHs is planning to use ProLab software not only for statistical elaboration of data but as a communication platform with the participant for exchange of information and data. Therefore the registration to the PT will be done by submission of the PDF Registration Form which you will receive via mail.

PT coordinator	**Second contact**
Stefanka Bratinova	Zuzana Zelinkova
Fax: 0032-14-571783 e-mail: jrc-irmm-crl-pah@ec.europa.eu	

Participants are requested to indicate the preferred solvent type of the standard solutions (either toluene or acetonitrile) prior to dispatch of samples via a separate email.

Distribution of information:
The NRLs are kindly requested to distribute as soon as possible this information and the blank Registration form to the OCLs under their responsibility, and to assist the EURL in identifying laboratories that are eligible to participate in the study.

Access of NRLs to performance data of official food control laboratories:
Two options:

1) *NRL enrols OCLs and covers participation fee*.
   NRL submits to EURL list of participants including name and address of laboratory, and details of the contact person (name, address - no post box! - email and telephone number). The coverage of the participation fees has to be confirmed and details for invoicing (e.g. order number) have to be provided. It shall be made clear, that the full participation fee is payable upon dispatch of the test samples. In return, the performance data of the respective official food control laboratories will be disclosed to the NRL.

2) The *OCL (identified as such by the respective NRL) enrols itself* in the inter-laboratory comparison *and covers the participation fee*.
The NRL will get access to performance data of the OCL only upon providing to the EURL for PAHs a letter of consent.

In case you may wish clarification of open questions, please do not hesitate to contact the EURL team via:

JRC-IRMM-EURL-PAH@ec.europa.eu

With kind regards,

Stefanka Bratinova

Cc: Thomas Wenzl, Beatriz de la Calle, Franz Ulberth

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-eurl-pah@ec.europa.eu

Web site: http://irmm.jrc.ec.europa.eu

ANNEX 2: Registration form

EUROPEAN COMMISSION
DIRECTORATE-GENERAL - JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
European Union Reference Laboratory for PAH

REGISTRATION FORM

2014 PT- PAHs in FOOD SUPPLEMENTS

This inter-laboratory comparison targets the analysis of the 4 EU marker PAHs (benzo[*a*]pyrene, benz[*a*]anthracene, benzo [*b*]fluoranthene, and chrysene) in a food supplements. The set of test samples will be distributed in the beginning of May and will consisting of:

a)an amber glass vial containing about 20 g of spirulina sample, and
b)an amber glass ampule containing about 20 g of fish oil

Results have to be reported for the individual PAHs as well as for the sum of the four PAHs within 4 weeks from sample dispatch.

In addition, a solution of PAHs in solvent will be supplied to participants with disclosed concentration of the analytes, in order to allow participants to verify their instrument calibration. Therefore, results have not to be reported for this material. Participants are requested to choose either toluene or acetonitrile as solvent for the solution of PAHs in solvent.

This inter-laboratory comparison is organised under accreditation to ISO 17043.

Participation is MANDATORY and free of charge for National Reference Laboratories.

The PARTICIPATION FEE is 350 Euro for Official Food Control Laboratories per participation

Orgaisation					
Department					
Address					
City		Zip		Country	
Contact person				e-mail	
Enrolment OCL					
Preferred Solvent					
Date Field					

Submit by Email

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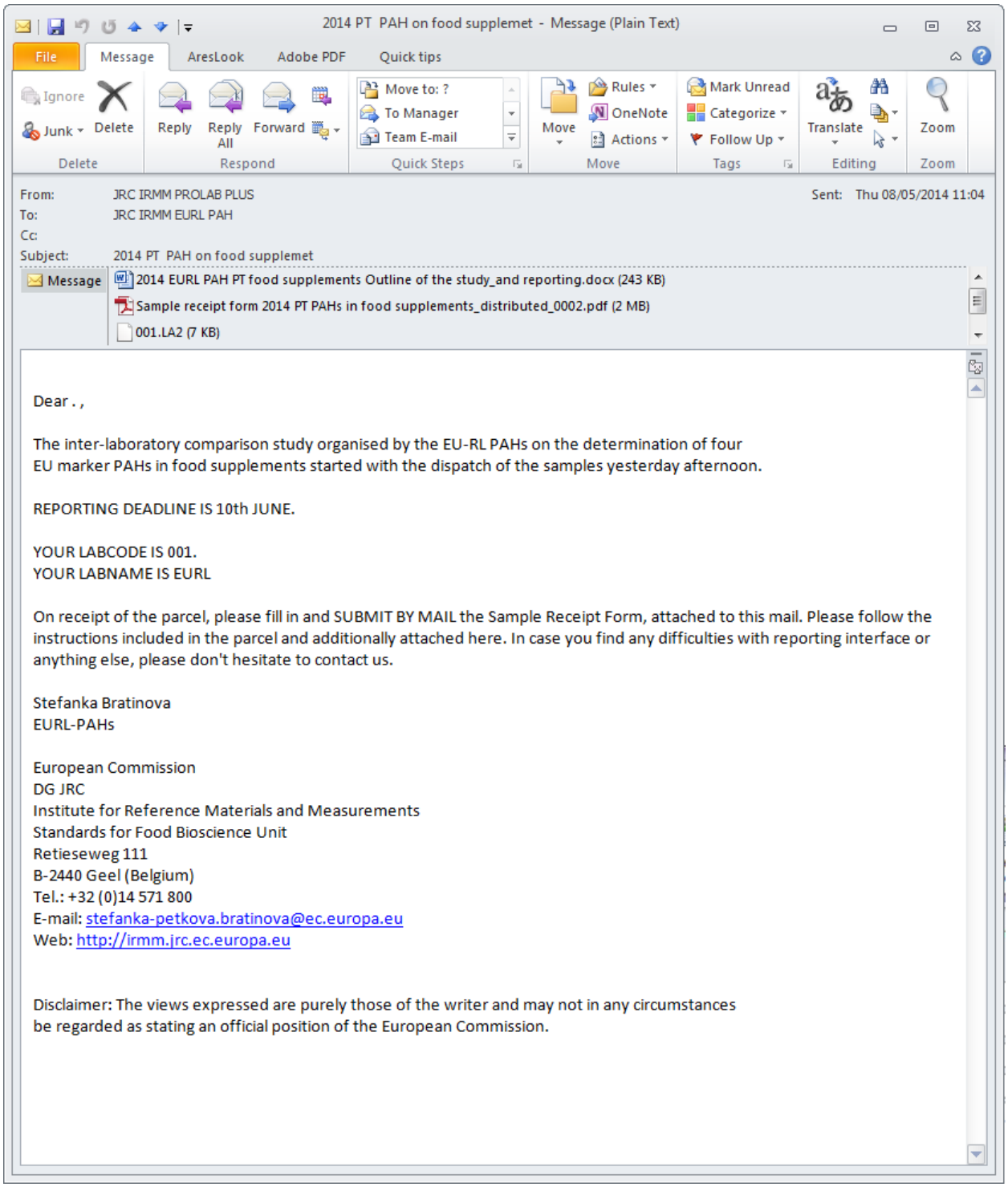
Telephone: direct line (32-14) 571 229. Fax: (32-14) 571 783. E-

mail: jrc-irmm-eurl-PAH@ec.europa.eu

ANNEX 3: Announcement of material dispatch



2014 PT PAH on food supplemet - Message (Plain Text)

File | Message | AresLook | Adobe PDF | Quick tips

Ignore | Junk | Delete | Reply | Reply All | Forward | Move to: ? | To Manager | Team E-mail | Move | Rules | OneNote | Actions | Mark Unread | Categorize | Follow Up | Translate | Zoom

Delete | Respond | Quick Steps | Move | Tags | Editing | Zoom

From: JRC IRMM PROLAB PLUS
Sent: Thu 08/05/2014 11:04
To: JRC IRMM EURL PAH
Cc:
Subject: 2014 PT PAH on food supplemet

Message
2014 EURL PAH PT food supplements Outline of the study_and reporting.docx (243 KB)
Sample receipt form 2014 PT PAHs in food supplements_distributed_0002.pdf (2 MB)
001.LA2 (7 KB)

Dear . ,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of four EU marker PAHs in food supplements started with the dispatch of the samples yesterday afternoon.

REPORTING DEADLINE IS 10th JUNE.

YOUR LABCODE IS 001.
YOUR LABNAME IS EURL

On receipt of the parcel, please fill in and SUBMIT BY MAIL the Sample Receipt Form, attached to this mail. Please follow the instructions included in the parcel and additionally attached here. In case you find any difficulties with reporting interface or anything else, please don't hesitate to contact us.

Stefanka Bratinova
EURL-PAHs

European Commission
DG JRC
Institute for Reference Materials and Measurements
Standards for Food Bioscience Unit
Retieseweg 111
B-2440 Geel (Belgium)
Tel.: +32 (0)14 571 800
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Web: http://irmm.jrc.ec.europa.eu

Disclaimer: The views expressed are purely those of the writer and may not in any circumstances be regarded as stating an official position of the European Commission.

ANNEX 4: Documents sent to participants - OUTLINE and REPORTING INSTRUCTIONS

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 5 May 2014

2014 PT - PAHs in food supplements

Dear Madame/Sir,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of four EU marker PAHs in food supplements starts with the dispatch of the samples.

The target analytes are the four EU marker PAHs (benzo[*a*]pyrene, benzo[*b*]fluoranthene, benz[*a*]anthracene, and chrysene) and their sum. The participants are requested to report results on all of them.

Each participant will be provided with a crimp cap amber vials containing a portion of spirulina powder, naturally contaminated with PAHs, a sealed amber glass ampule filled with spiked fish oil and a known standard solution in either toluene or acetonitrile for checking of the instrument calibration against an external reference.

Outline of the study

The participating laboratories shall apply for the analyses a method of their choice.

The laboratories shall report the results by **10 June 2014 at the latest** following the instructions provided further on in this document.

The participants are requested to report for both samples the results obtained from three replicate analyses. They also have to report for each sample a final value for proficiency assessment. Results have to be reported corrected for recovery, and the results for proficiency assessment ("final values") have to be accompanied by the respective measurement uncertainty (also for the sum parameter).

Participants are also requested to report together with the results details of the applied analysis method and some method performance characteristics of the applied analysis method.

Test materials and analytes

1. One crimp cap amber vial, labelled as "EU-RL PAHs PT 2014 Interlaboratory comparison 423, 4 EU PAHs in food supplements – SPIRULINA", containing about 20 g of a *naturally contaminated homogenised spirulina powder*. The concentration of the individual analytes is in the range of about 0.5 µg/kg to 10 µg/kg. The analyte content shall be determined in triplicate. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value". The homogeneity is proven at the level of 2.5 g test portion

Store the spirulina powder sample at room temperature, protected of light.

Retieseweg 111, B-2440 Geel – Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.
E-mail: jrc-irmm-crl-pah@ec.europa.eu

2. One sealed amber glass ampoule, labelled as as "EU-RL PAHs PT 2014 Interlaboratory comparison 423, 4 EU PAHs in food supplements – fish oil", containing about 20 g of spiked fish oil sealed in inert atmosphere. The concentration of the individual analytes is in the range of 0.5 µg/kg to 10 µg/kg. The analyte content shall be determined in triplicate. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value". The homogeneity is proven at the level of 2 g test portion.

If not analysed immediately, store the fish oil sample refrigerated below 8°C

3. Depending of your preference, one ampoule, labelled as "PAH4 in acetonitrile", or "PAH4 in toluene", with about 1 ml of a solution of *4 EU priority PAHs in acetonitrile, respectively toluene*. The analyte concentration of your preferred solution is given in the attached document. The solutions may be used by the participants to check their instrument calibration against an independent reference. Participants do not have to report results for this solution.

Please bear in mind that the solutions *do not contain any internal standard*. The standard solution in acetonitrile contains small amounts of toluene, which stem from the preparation of stock solution from neat materials.

Reporting the results

Data generated by the participants will be collected by using a software RingDat, supplementary to ProLab software, used until now for professional data handling and statistical analyses of interlaboratory tests results.

You will receive by mail some files for reporting results. You should follow the following instructions:

1. Download a simple data entry program RingDat free from the QuoData web page using following link:

http://quodata.de/ringdat_en.php

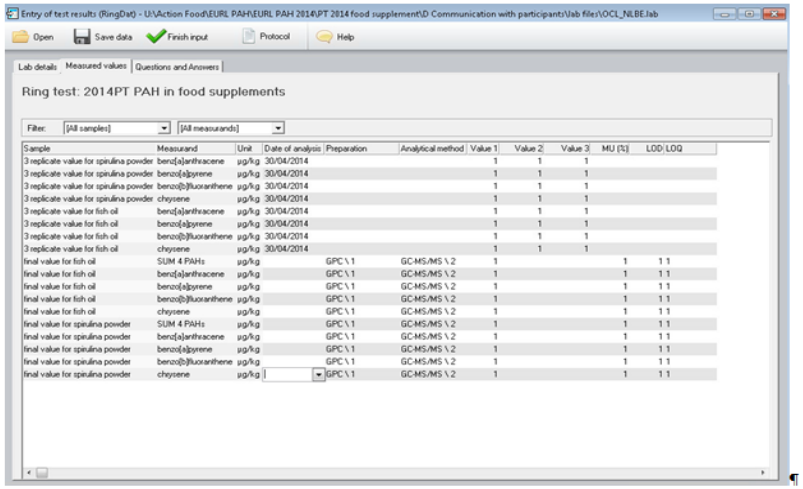
User: *ringdat*
Password: *prolabdata*

2. Save to the same folder the two lab specific files with the extension **"*.LAB"** and **"*.LA2"**, generated by the ProLab software and provided to each laboratory individually (personal files) by this mail.

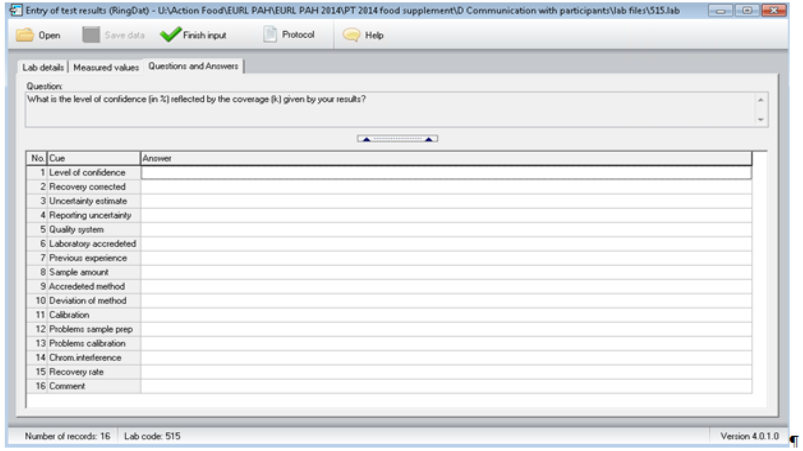
3. Start the RingDat.exe program and open **"*.LAB"** file for reporting the results. A table will appear with cells for every measurand/sample combination

- the name of each laboratory and the samples are codified by the software, so that each participant will receive samples with unique codified numbers (i.e., 058);
- The **"*.LA2"** file contains information about the participant – laboratory name and laboratory code;
- The **"*.LAB"** file is unique to each laboratory (personal) and contains information about the samples and measurands that have to be analysed and reported.
- First tab contains the detailed information for the laboratory

- Second tab contains table for entering the results. You could filter the entries by sample or by measurand.



- Third tab contains a general questionnaire.



4. Fill in the result table with your data. On the pictures above, minimum required field to be filled are shown. Please report only **ONE** final value per sample/measurand, together with method uncertainty, information for the method used and respective LOD, LOQ. For the three replicate analysis this additional information is not necessary to be filled.

5. Afterwards, please fill in the questionnaire on the next tab.

6. After finishing the input, save the file using the button on the top menu of the window. You could change the inputs after saving the file as long as you haven't pushed "Finish input" button. At the end finalise the data entry by pushing the "Finish input" button.

7. Send only the **"*.LAB"** file back to us by e-mail on our functional mail box -- jrc-irmm-eurl-pah@ec.europa.eu

8. In case you want **to correct some of yours entries after finishing the input, you should use the original *.LAB file** downloaded from the mail.

In case of questions please do not hesitate to contact us.

With kind regards,

Stefanka Bratinova
EURL-PAHs

SAMPLE RECEIPT

EUROPEAN COMMISSION
DIRECTORATE-GENERAL - JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
European Union Reference Laboratory for PAH

Confirmation of the receipt of the samples: RECEIPT FORM

2014 PT- PAHs in food supplements

Orgaisation					
Department					
City		**Zip**		**Country**	
Contact person					

Content of the parcel

a) One amber glass vial containing about 20 g of fish oil
b) One amber glass vial containing about 20 g of spirulina powder
c) One brown glass ampoule with 1 ml standard solution of PAHs in solvent (known concentrations)
d) A specification sheet for the item b) content (standard solution), e-mailed as well
e) Material safety data sheets for acetonitrile / toluene
f) One inter-laboratory comparison sample receipt form (= this form), which is e-mailed as well to be filed and send electronically

Fish oil is ampulled under inert atmosphere. After being opened it is very sensitive to oxidation. **Please analyse the test sample as soon as possible after opening.**

IF NOT ANALYSED IMMEDIATLY AFTER RECEIVING THE PARCEL, PLEASE PUT THE TEST SAMPLES IN THE REFRIGERATOR.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 229. Fax: (32-14) 571 783. E-mail: jrc-irmm-eurl-PAH@ec.europa.eu

Please ensure that the items listed below have been received undamaged, and then describe the relevant statement:

Date of the receipt of the test sample		
All items have been received undamaged	○ Yes	○ No
If NO, please list damaged items		
All items have been received undamaged	○ Yes	○ No
If YES, please list missing items		
Serial number of the fish oil sample you received		
Serial number of the spirulina sample you received		

Date Field

Submit by Email

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 229. Fax: (32-14) 571 783. E-mail: jrc-irmm-eurl-PAH@ec.europa.eu

ANNEX 5: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 30/04/2014

Standard solution specification sheet	PAH4 in ACETONITRILE
Date of production: 04/04/2014	Total volume: 1 mL
Expiry date: *October 2014*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/mL)	U** ±%
1	Benz[*a*]anthracene	56-55-3	63.9	50.2	0.4
2	Benzo[*a*]pyrene	50-32-8	63.8	50.1	0.5
3	Benzo[*b*]fluoranthene	205-99-2	63.5	49.9	0.6
4	Chrysene	218-01-9	63.5	50.00	0.4
5	SUM PAH4		254.6	200.3	0.9

** The concentrations were calculated taking into account the purity statements of the single products. The concentration values are based on the gravimetrical preparation data.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Acetonitrile:Toluene (m/m 99.4:0.6)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.
E-mail: jrc-irmm-eurl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

TOLUENE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 30/04/2014

Standard solution specification sheet	PAH4 in TOLUENE
Date of production: 04/04/2014	Total volume: 1 mL
Expiry date: *October 2014*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/mL)	U** ±%
1	Benz[*a*]anthracene	56-55-3	57.8	50.1	0.4
2	Benzo[*a*]pyrene	50-32-8	57.7	50.0	0.5
3	Benzo[*b*]fluoranthene	205-99-2	57.5	49.8	0.6
4	Chrysene	218-01-9	57.5	49.9	0.4
5	SUM PAH4		230.6	199.9	0.9

** The concentrations were calculated taking into account the purity statements of the single products. The concentration values are based on the gravimetrical preparation data.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Toluene

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.
E-mail: jrc-irmm-eurl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

ANNEX 6.1.: Homogeneity of the fish oil test material

Analyte: **BAA**

	n =	10		
	mean =	3.2226	22%	= **σ-trg(%)**
0.000596162	**s_x =**	0.0244	0.7090	= **σ-trg**
√MSW =	**s_w =**	0.0374		
	s_s =	0.0102	0.2127	= **0,3*s**

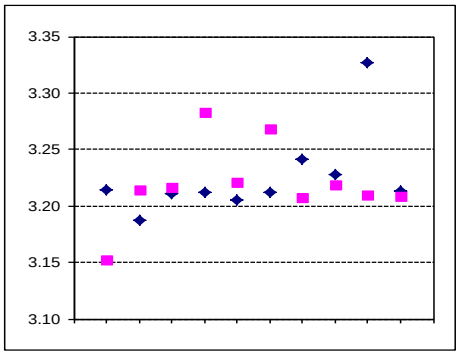
ISO-13528	passed		
F =	0.85234248	3.02038295	= Fcrit
	passed		

IUPAC

(MSB-MSW)/2	-0.0001	0.0865 = F1*(0,3*s)^2+F2*MSW
	passed	

Bottle	Result a	Result b	diff	sum	avg
Ampoule 07	3.21	3.15	0.06	6.37	3.18
Ampoule 17	3.19	3.21	-0.03	6.40	3.20
Ampoule 23	3.21	3.22	-0.01	6.43	3.21
Ampoule 39	3.21	3.28	-0.07	6.50	3.25
Ampoule 43	3.21	3.22	-0.02	6.43	3.21
Ampoule 58	3.21	3.27	-0.06	6.48	3.24
Ampoule 65	3.24	3.21	0.03	6.45	3.22
Ampoule 70	3.23	3.22	0.01	6.45	3.22
Ampoule 77	3.33	3.21	0.12	6.54	3.27
Ampoule 81	3.21	3.21	0.00	6.42	3.21

	∑(diff)^2 =	0.02797756
	var(sum)/2 =	0.00119 =MSB



Analyte: **CHR**

	n =	10		
	mean =	3.3175	22%	= **σ-trg(%)**
0.001178401	**s_x =**	0.0343	0.7298	= **σ-trg**
√MSW =	**s_w =**	0.0580		
	s_s =	0.0225	0.2190	= **0,3*s**

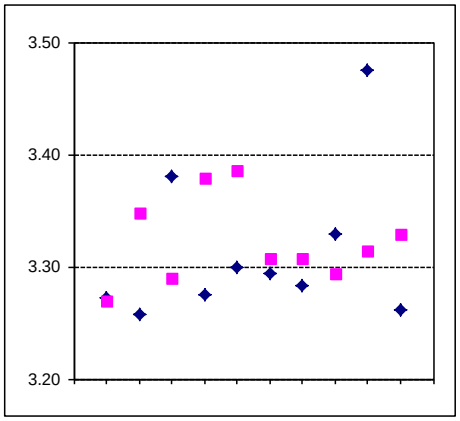
ISO-13528	passed		
F =	0.69950682	3.02038295	= Fcrit
	passed		

IUPAC

(MSB-MSW)/2	-0.0005	0.0935 = F1*(0,3*s)^2+F2*MSW
	passed	

Bottle	Result a	Result b	diff	sum	avg
Ampoule 07	3.27	3.27	0.00	6.54	3.27
Ampoule 17	3.26	3.35	-0.09	6.61	3.30
Ampoule 23	3.38	3.29	0.09	6.67	3.33
Ampoule 39	3.28	3.38	-0.10	6.65	3.33
Ampoule 43	3.30	3.39	-0.09	6.69	3.34
Ampoule 58	3.29	3.31	-0.01	6.60	3.30
Ampoule 65	3.28	3.31	-0.02	6.59	3.29
Ampoule 70	3.33	3.29	0.04	6.62	3.31
Ampoule 77	3.47	3.31	0.16	6.79	3.39
Ampoule 81	3.26	3.33	-0.07	6.59	3.30

	∑(diff)^2 =	0.0673847
	var(sum)/2 =	0.00236 =MSB



Analyte: **BBF**

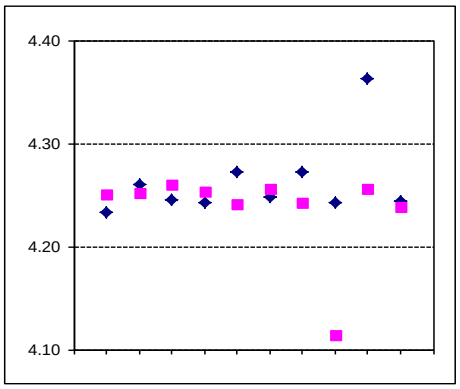
	n =	10		
	mean =	4.2495	22%	= **σ-trg(%)**
0.000988195	s_x =	0.0314	0.9349	= **σ-trg**
√MSW =	s_w =	0.0390		
	s_s =	0.0151	0.2805	= **0,3*s**

ISO-13528	passed		
F =	1.30235433	3.02038295	= Fcrit
	passed		

IUPAC

(MSB-MSW)/2	0.0002	0.1494	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 07	4.23	4.25	-0.02	8.48	4.24
Ampoule 17	4.26	4.25	0.01	8.51	4.26
Ampoule 23	4.24	4.26	-0.02	8.50	4.25
Ampoule 39	4.24	4.25	-0.01	8.50	4.25
Ampoule 43	4.27	4.24	0.03	8.51	4.26
Ampoule 58	4.25	4.26	-0.01	8.50	4.25
Ampoule 65	4.27	4.24	0.03	8.51	4.26
Ampoule 70	4.24	4.11	0.13	8.36	4.18
Ampoule 77	4.36	4.26	0.11	8.62	4.31
Ampoule 81	4.24	4.24	0.01	8.48	4.24
		∑(diff)^2 =	0.03035104		
		var(sum)/2 =		0.00198 =MSB	



Analyte: **BAP**

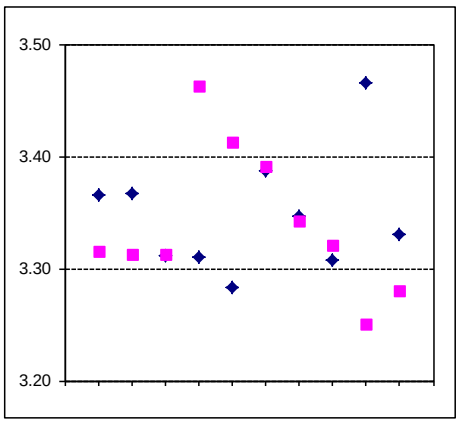
	n =	10		
	mean =	3.3439	22%	= **σ-trg(%)**
0.000827561	s_x =	0.0288	0.7356	= **σ-trg**
√MSW =	s_w =	0.0688		
	s_s =	0.0392	0.2207	= **0,3*s**

ISO-13528	passed		
F =	0.35013199	3.02038295	= Fcrit
	passed		

IUPAC

(MSB-MSW)/2	-0.0015	0.0963	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 07	3.36	3.32	0.05	6.68	3.34
Ampoule 17	3.37	3.31	0.05	6.68	3.34
Ampoule 23	3.31	3.31	0.00	6.62	3.31
Ampoule 39	3.31	3.46	-0.15	6.77	3.39
Ampoule 43	3.28	3.41	-0.13	6.70	3.35
Ampoule 58	3.39	3.39	0.00	6.78	3.39
Ampoule 65	3.35	3.34	0.00	6.69	3.34
Ampoule 70	3.31	3.32	-0.01	6.63	3.31
Ampoule 77	3.47	3.25	0.21	6.72	3.36
Ampoule 81	3.33	3.28	0.05	6.61	3.31
		∑(diff)^2 =	0.0945427		
		var(sum)/2 =		0.00166 =MSB	



ANNEX 6.2.: Homogeneity of the spirulina test material

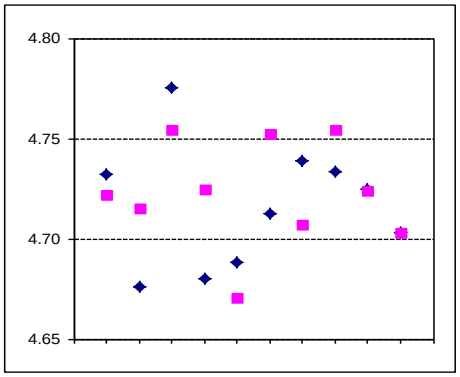
Analyte: **BAA**

	n =	10		
	mean =	4.7195	22%	= **σ-trg(%)**
0.00062423	**s_x =**	0.0250	1.0383	= **σ-trg**
√MSW =	**s_w =**	0.0192		
	s_s =	0.0210	0.3115	= **0,3*s**

ISO-13528	passed		
F =	3.37639989	3.02038295	= Fcrit
	failed		

IUPAC			
(MSB-MSW)/2	0.0004	0.1828	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 05	4.73	4.72	0.01	9.45	4.73
Ampoule 16	4.68	4.72	-0.04	9.39	4.70
Ampoule 27	4.78	4.75	0.02	9.53	4.76
Ampoule 39	4.68	4.72	-0.04	9.40	4.70
Ampoule 57	4.69	4.67	0.02	9.36	4.68
Ampoule 63	4.71	4.75	-0.04	9.46	4.73
Ampoule 71	4.74	4.71	0.03	9.45	4.72
Ampoule 85	4.73	4.75	-0.02	9.49	4.74
Ampoule 98	4.72	4.72	0.00	9.45	4.72
Ampoule 113	4.70	4.70	0.00	9.41	4.70



	∑(diff)^2 =	0.00739521
	var(sum)/2 =	0.00125 =MSB

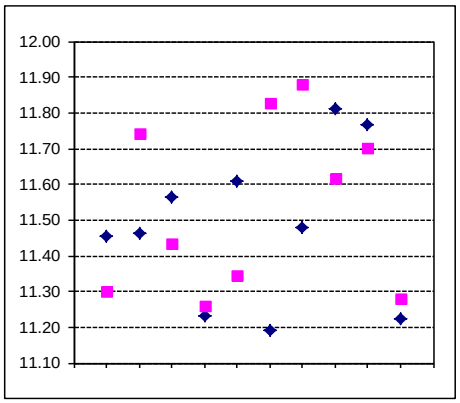
Analyte: **CHR**

	n =	10		
	mean =	11.5094	22%	= **σ-trg(%)**
0.031665425	**s_x =**	0.1779	2.5321	= **σ-trg**
√MSW =	**s_w =**	0.1999		
	s_s =	0.1081	0.7596	= **0,3*s**

ISO-13528	passed		
F =	1.5854284	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	0.0117	1.1251	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 05	11.45	11.30	0.15	22.75	11.38
Ampoule 16	11.46	11.74	-0.28	23.21	11.60
Ampoule 27	11.56	11.44	0.13	23.00	11.50
Ampoule 39	11.23	11.26	-0.03	22.49	11.25
Ampoule 57	11.61	11.34	0.26	22.95	11.48
Ampoule 63	11.19	11.83	-0.64	23.02	11.51
Ampoule 71	11.48	11.88	-0.40	23.36	11.68
Ampoule 85	11.81	11.62	0.20	23.43	11.72
Ampoule 98	11.77	11.70	0.06	23.47	11.73
Ampoule 113	11.22	11.28	-0.06	22.51	11.25



	∑(diff)^2 =	0.79891151
	var(sum)/2 =	0.06333 =MSB

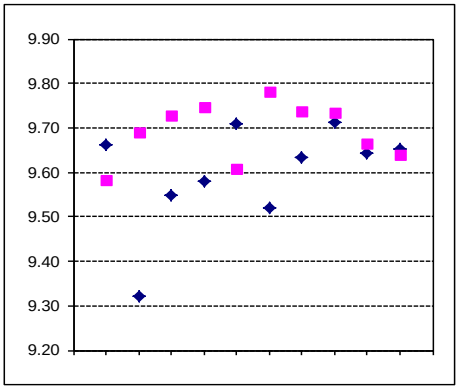
Analyte: **BBF**

	n =	10		
	mean =	9.6451	22%	**= σ-trg(%)**
0.003192585	s_x =	0.0565	2.1219	**= σ-trg**
√MSW =	s_w =	0.1207		
	s_s =	0.0640	0.6366	**= 0,3*s**

ISO-13528	passed		
F =	0.43812468	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0041	0.7766	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 05	9.66	9.58	0.08	19.25	9.62
Ampoule 16	9.32	9.69	-0.37	19.01	9.50
Ampoule 27	9.55	9.73	-0.18	19.28	9.64
Ampoule 39	9.58	9.75	-0.17	19.33	9.66
Ampoule 57	9.71	9.61	0.10	19.32	9.66
Ampoule 63	9.52	9.78	-0.26	19.30	9.65
Ampoule 71	9.63	9.74	-0.10	19.37	9.69
Ampoule 85	9.71	9.73	-0.02	19.45	9.72
Ampoule 98	9.64	9.67	-0.02	19.31	9.66
Ampoule 113	9.65	9.64	0.01	19.29	9.65



$\sum$**(diff)^2** = 0.29147729

var(sum)/2 = 0.00639 =MSB

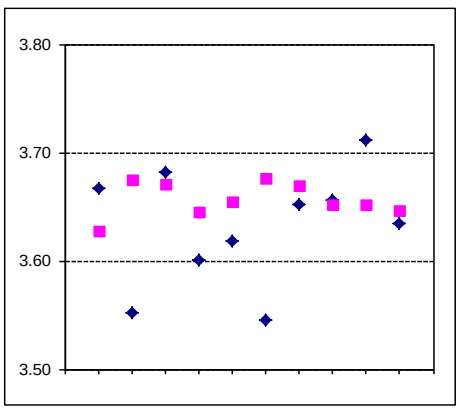
Analyte: **BAP**

	n =	10		
	mean =	3.6444	22%	**= σ-trg(%)**
0.000600542	s_x =	0.0245	0.8018	**= σ-trg**
√MSW =	s_w =	0.0451		
	s_s =	0.0204	0.2405	**= 0,3*s**

ISO-13528	passed		
F =	0.59017008	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0004	0.1108	= F1*(0,3*s)^2+F2*MSW
	passed		

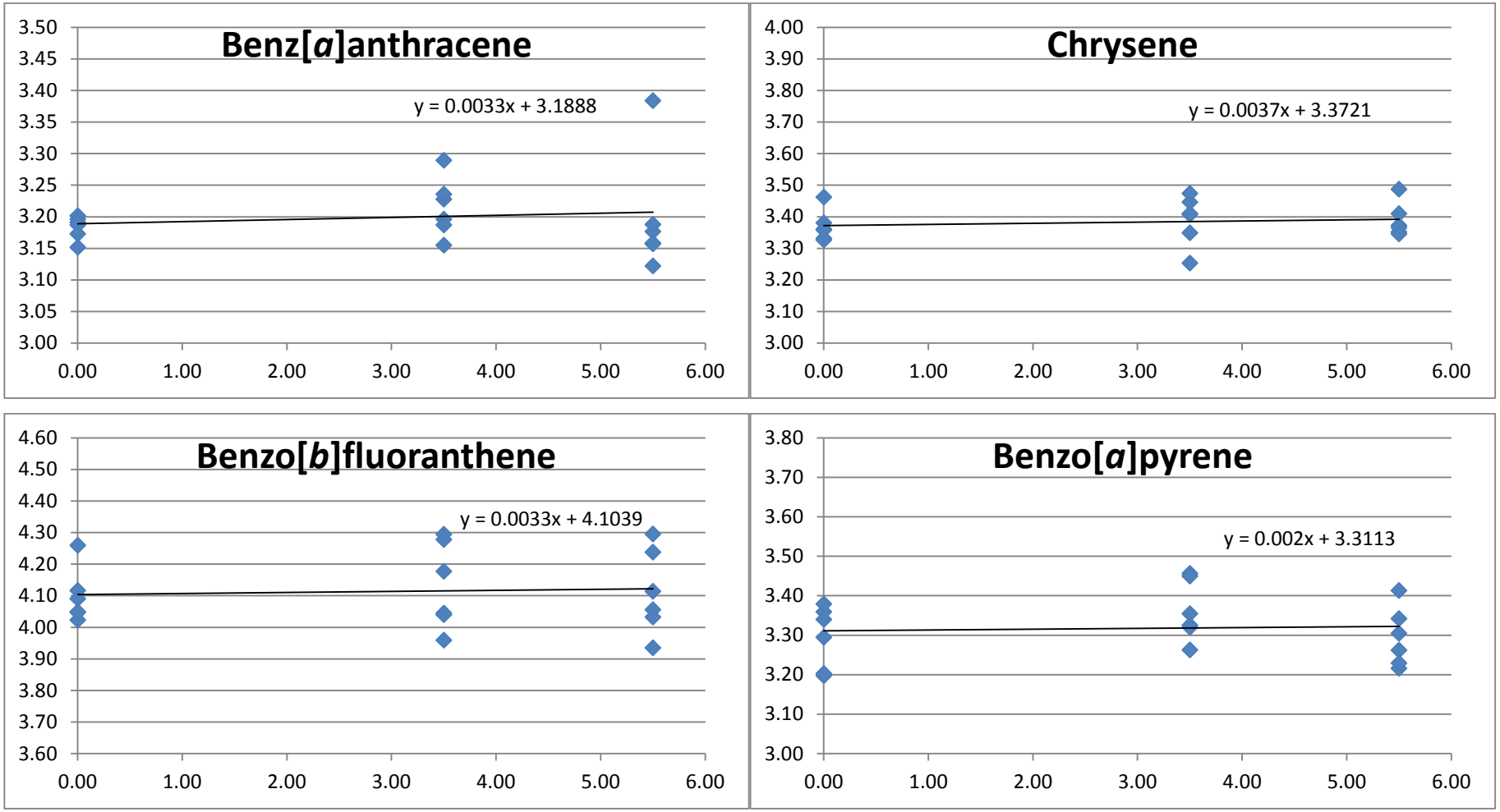
Bottle	Result a	Result b	diff	sum	avg
Ampoule 05	3.67	3.63	0.04	7.29	3.65
Ampoule 16	3.55	3.67	-0.12	7.23	3.61
Ampoule 27	3.68	3.67	0.01	7.35	3.68
Ampoule 39	3.60	3.64	-0.04	7.25	3.62
Ampoule 57	3.62	3.66	-0.04	7.27	3.64
Ampoule 63	3.55	3.68	-0.13	7.22	3.61
Ampoule 71	3.65	3.67	-0.02	7.32	3.66
Ampoule 85	3.66	3.65	0.00	7.31	3.65
Ampoule 98	3.71	3.65	0.06	7.36	3.68
Ampoule 113	3.63	3.65	-0.01	7.28	3.64



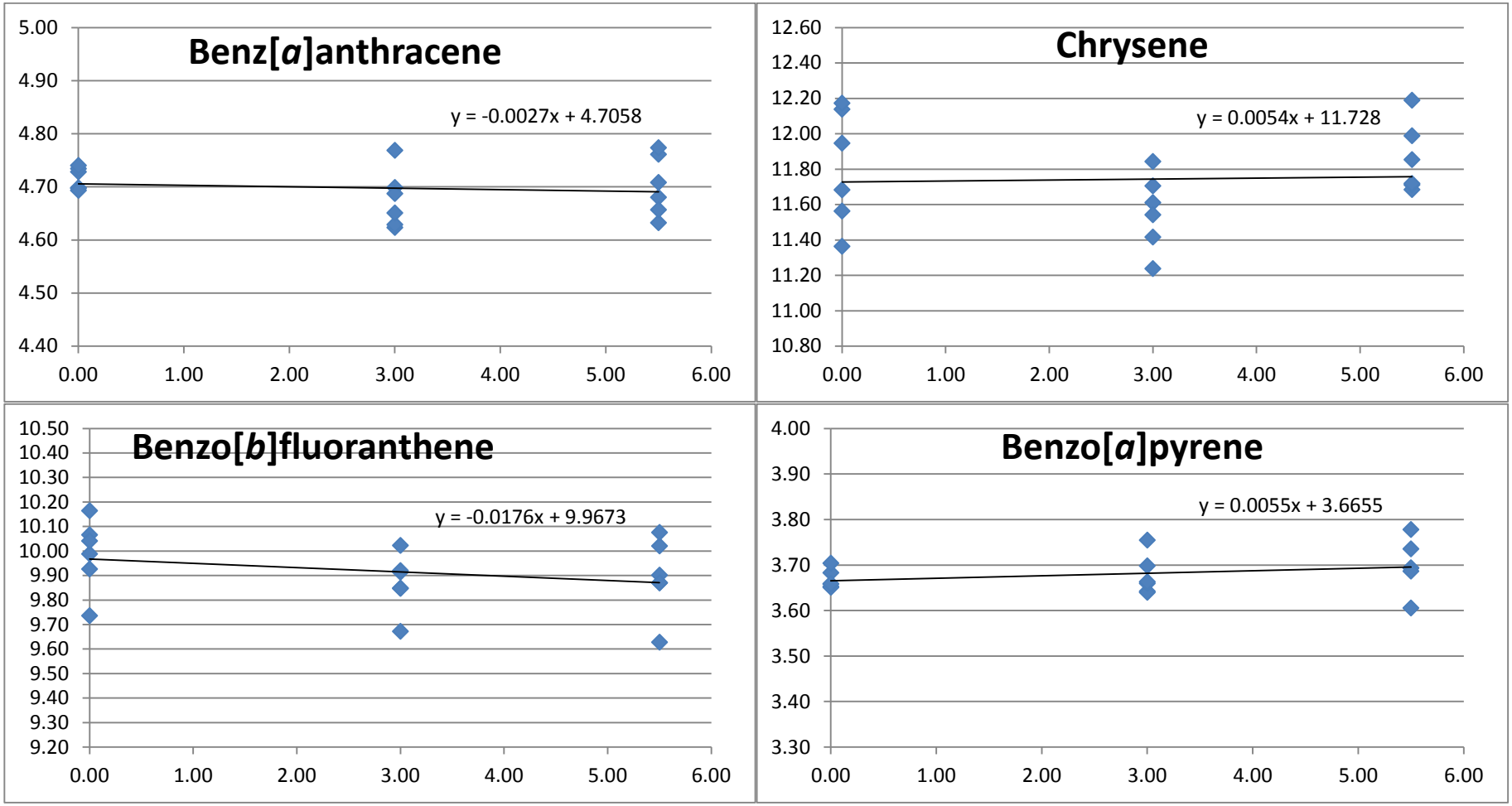
$\sum$**(diff)^2** = 0.040703

var(sum)/2 = 0.00120 =MSB

ANNEX 7.1.: Stability of the fish oil test material for the period of the study



ANNEX 7.2: Stability of the spirulina test material for the period of the study



ANNEX 8. Questionnaire and method performance characteristics

2014PT PAH in food supplements			
No.	Cue	Question	Answers
1	Level of confidence	What is the level of confidence (in %) reflected by the coverage (k) given by your results?	32 Answers
2	Recovery corrected	Are your results recovery corrected and how?	34 Answers
3	Uncertainty estimate	What is the basis of your unceratinty estimate?	32 Answers
4	Reporting uncertainty	Do you usually provide an uncertainty statment to your customers for this type of analysis?	33 Answers
5	Quality system	Does your laboratory have a quality system in place (ISO 17025, ISO 9000 series, other)?	33 Answers
6	Laboratory accredeted	Is your laboratory accredeted for analysis of PAHs in smoked meat?	33 Answers
7	Previous experience	How many samples/year do you analyse usually?	33 Answers
8	Sample amount	What is the sample amount you take per analysis?	34 Answers
9	Accredeted method	Have you analysed the samples following the procedure of an accredeted method for determination of PAHs?	33 Answers
10	Deviation of method	Did you deviate from the accredeted method in one or several steps and what are the deviations	31 Answers
11	Calibration	What type of calibration did you use - external calibration, internal calibration, standard addition	33 Answers
12	Recovery rate	What is the range of your recovery rates (apparent recovery, real recovery) ?	33 Answers
13	Problems sample prep	Did you experience problem during sample preparation?	33 Answers
14	Problems calibration	Did you experience problems during calibration?	33 Answers
15	Chrom.interference	Did you experience chromatographic interferences?	32 Answers
16	Comment	Do you have any comments? Please let us know ...	15 Answers

Lab Code	Level of confidence	Recovery corrected	Uncertainty estimate	Reporting uncertainty
101	95%, k=2	yes	data from reproducibility	
104	0,95	by internal standard		yes
105	2	no	valitation, EU Vo 401/2006	YES
106	95% K=2	YES USING A STANDARD ADDITION METHOD	COMBINED TYPE B UNCERTAINTY THAT IS NOT EXCEED THE Uf VALUE IN ALL CASES	yes
108	0,95	no	based on fit-for-purpose function (see Reg. 333/2007),	Yes
109	0,95		Yes, using spiked samples	On request.
111	95% & 2k	Yes. Stable Isotope dilution.	Expanded measurement uncertainty based on validation data and everyday ongoing QC	yes, in '± xx µg/kg' form
112	95	Yes, we use deuterised internal standards.	Validation and calculation with InterVal software	only if the result is above the regulatory limit
113	60	no, but not necessary as we do standard additions	Horwitz-equation	Yes
114		Yes (Isotopically labeled ISTD)	Control Charts	Yes
115	0,95	Yes, isotopic dilution	3 replicates	Yes. Relative expanded uncertainty in µg/kg.
116	2	Yes. Use of validated recovery correction factors.	Eurochem Guide 3rd Ed. 2012.	20%
117	0,95	no	0,2	YES
118	95	Recovery corrected automatically using mass-labelled internal standards		yes
119	95	no	certified ref material and inhouse ref material	yes
120	95% (k = 2)	Yes. Recoveries have been estimated from speaking results	We have taken into account both contributiona: internal reproducibility and recovery	yes
121	95	yes by calibration curve in matrix	metrological	yes
122	95	no	calculated from 3 parallel measurements	Yes
123	95%, k=2	Yes	repeatibility	No
124	k=2	Yes, the recoveries come from the validation data (6 day-to-day reproducibility)	oil: 2*RSD of the oil control chart // spirulina: 2*RSD of the "matrix with extraction" control chart	No
125	0,95	No	Uncertainty estimate is based on validation data	Yes
126	Satisfactory	Yes, using reference material	statistic	Yes
501	0,95	Yes, with ISTD	Horwitz/Horrat	yes
502	2	internal standard	at least duplicate analysis of each sample, multiple analysis at different concentration levels during validation,	Yes
503	95 % (k = 2)	Yes (internal standardisation)	SUM 4 PAHs: sums of the three determinations	yes
504		yes	triplicate	no customers
505	25	yes	method validation	yes, if the maximum level is exceeded
506	0,95	yes, corrected with internel standard benzo(b)chrysene	repeatability measured in our lab coverage factor 2 used	yes
508	0,1	yes	validation data	Yes
509	7% (k=2)	no, analyzed with deuterated ISTD	Std. dev. * 2	yes
510	17,5%	no	0,2	no
511	95%, k=2	no recovery corrected	Sample 6 times Measurand	only in case of exceeding MRL
513	95 %, k=2	ISTD used	calculated by multiple analysis of the same sample	only on request
515	k=2, 95% confidence	no	recovery, bias, inhomogeneity	only on request

Lab Code	Quality system	Laboratory accredited	Previous experience	Sample amount
101	yes	fish oil - yes, other food supplements - no	yes, 10 per year	5g
104				15 g
105	ISO 17025	yes	no	2 g
106	YES	YES	FOR SPIRULINA NONE FOR FISH OIL YES ABOUT 20 SAMPLES	2.5g
108	yes	laboratory is accredited with flexible scope including analysis of PAH, method validations did not include food supplements until now.	no	spirulina: 2.5 g, fish oil: 2.0 g
109	Yes	No	No	2g spirulina, 2,5g fish oil
111		ISO 17025	>100	
112	ISO 17025	The laboratory is accredited for analysis of PAH in food.	No experience.	0,5 g (fish oil), 1 g (spirulina)
113	yes, ISO 17025	yes	no, for none of these two matrices	15 gr
114	Yes	Yes	Spirulina - no, fish oil - yes (50 a year)	Spirulina 3 g, fish oil - 2 g
115	ISO 17025	Yes	No	5 g spirulina, 2 g fishoil
116	Yes ISO 17025.	Yes.	Yes.	5g.
117	ISO 17025	Yes	8 years	0,25 g oil, 1 g spirulina
118	Accreditation ISO 17025	YES	NO - We never analyse these type of matrixes	1,0 g
119	ISO 17025	yes	0 for spirulina and 10 samples of fish oil	4-5 g
120	yes, ISO 17025	yes	We have already analysed one of each sample	3 grames
121	yes	no	no	1 g for fish oil, 2,5 g for spirulina powder
122	ISO 17025	not for food supplements	no experience for spirulina, lot of experience with fish	1 g
123	ISO 17025	Yes	diet suplements in 2013 about 30 samples (some of them are the spirulina samples), fish oil - no experinces (vegetable oils - we have experience)	2 g
124	ISO 17025	Yes	spirulina : 1 experience (your 2011 PT) // fish oil : 1-10 samples /year + some PTs	2
125	Yes	Spirulina no -Fish oil yes	Spirulina no -Fish oil yes, >100	Spirulina 0,5g -Fish oil 0,3g
126	Yes, ISO 17025	No	No	1 gram
501	ISO 17025	Yes	No	1 g
502	yes, ISO 17025	yes	No. We just started experiments on spirulina (8 samples).	Spirulina: 3g, Fish oil: 2g
503	Yes	Yes	Yes (Spirulina: about 10 samples, fish oil: about 15 samples)	2-20 g (here: 4-5,5 g)
504	yes	yes	fishoil yes, , 20samples/annum	1g
505	yes	no	no	oil 1 g, spirulina 0,5 g
506	ISO 17025	yes	no	between 2.5 and 10 g, depends on matrice and analysis method
508	yes, ISO 17025	yes	yes	2 g
509	Yes	Yes	Yes, 50	2,5g for normal Matrices, 0,5g for Fat
510	ISO 17025	yes for benzo(a)pyrene	no	2-5g
511	ISO 17025	no	Fish Oil = 20 Samples, Spirulina not Measurand	5,0 g
513	yes	yes	no	generally 10 g, here 5 g
515	ISO 17025	yes in oil, not for solid matters (like spirulina)	spirulina is a new matrix for us, fish oil: >1000 samples before	0,5 g

Lab Code	Sample amount	Accredited method	Deviation of method	Deviation of method
101	5g	yes (fish analysis)	no	no
104	15 g			
105	2 g	yes	no	no
106	2.5g	YES	NO	NO
108	spirulina: 2.5 g, fish oil: 2.0 g	fish oil: analysed with method validated for vegetable oils, spirulina: analysed with method validated for PAH in food of plant origin	no	no
109	2g spirulina, 2,5g fish oil	No	No	No
111		2.5g & 2g (based on what the homogeneity was proven at). For routine samples we take ~5g fish oil and between 0.5g - 3g for spirulina. Sometimes they are extremely high!	No	No
112	0,5 g (fish oil), 1 g (spirulina)	Yes	Yes, in case of spirulina, we lowered the sample amount.	Yes, in case of spirulina, we lowered the sample amount.
113	15 gr	yes	no	no
114	Spirulina 3 g, fish oil - 2 g	Yes	No	No
115	5 g spirulina, 2 g fishoil	Yes	No	No
116	5g.	Yes.	No.	No.
117	0,25 g oil, 1 g spirulina	yes	no	no
118	1,0 g	YES	NO	NO
119	4-5 g	yes	further preparation steps were requiered for the spirulina sample	further preparation steps were requiered for the spirulina sample
120	3 grames	yes		
121	1 g for fish oil, 2,5 g for spirulina powder	no	no	no
122	1 g	yes	no	no
123	2 g	Yes	No	No
124	2	YES	2 successive centrifugations before SPE instead of 1 for spirulina	2 successive centrifugations before SPE instead of 1 for spirulina
125	Spirulina 0,5g -Fish oil 0,3g	Yes	No	No
126	1 gram	Yes	No	No
501	1 g	Yes		
502	Spirulina: 3g, Fish oil: 2g	yes	yes, for spirulina we added a clean-up by silica-SPE after GPC	yes, for spirulina we added a clean-up by silica-SPE after GPC
503	2-20 g (here: 4-5,5 g)	Yes	No	No
504	1g	yes	yes	yes
505	oil 1 g, spirulina 0,5 g	yes	yes for spiurulina, less sample than usual for other food	yes for spiurulina, less sample than usual for other food
506	between 2.5 and 10 g, depends on matrice and analysis method	yes for fish oil, no for spirulina	saponification under reflux	saponification under reflux
508	2 g	yes	no	no
509	2,5g for normal Matrices, 0,5g for Fat	Yes	No	No
510	2-5g	yes	no	no
511	5,0 g	Yes	no	no
513	generally 10 g, here 5 g	yes	no	no
515	0,5 g	yes	no	no

Lab Code	Calibration	Recovery rate	Problems sample prep
101	internal calibration	fish oil (80% to 100%), spirulina (70% to 90%)	no
104		50 - 120%	no
105	external calibration	90 - 100 %	NO
106	STANDARD ADDITION	75 TO 118% REAL RECOVERY	no
108	external calibration, isotopically labelled standards added to sample.	70 - 105%	No
109	External Calibration	70-120%	No
111		internal calibration	No
112	We use standards in solvents (not in matrix) for calibration. We add deuterised internal standards to the samples and to the calibration solutions as well.	90-110%	yes for spirulina, extreme colouring of the extract, and fluctuations of the internal standard BaP-D12
113	standard addition	real recovery: 60 - 70 %	in sufficient purity of spirulina extract
114	Internal calibration	50%	
115	Internal	apparent recovery ca. 60%	No
116	Internal calibration with isotopically labelled IS.	Validated recovery correction factors (apparent recovery against isotopically labelled IS) are between 95 - 100%. Yield of isotopically labelled IS generally between 75 - 90% is not used for result correction.	No.
117	ESTD	90-105 %	no
118	internal calibration	50-120 %	NO
119	internal calibration	60-70%	dificulties with the liquid/liquid separation for the spirulina sample
120	external calibration	99,3-110,7% for spirulin and 99,3-111,4% for fish oil	no
121	internal calibration, standard addition	84-102 %	no
122	external calibration	99-105%	no
123	External five points calibration	real recovery	No
124	calibration with internal standard in solvent	real recovery : oil 100% // spirulina 85%	NO
125	Internal	80-120 %	No
126	external	70 - 105% apparent	No
501	external calibration	97-104	No
502	external calibration	Apparent 86-99%, real recovery >80%	The addiotional clean-up for spirulina was the source of benzo(a)anthracene in our blank samples
503	Internal calibration	87-98 %	No
504	matrix matched	real recovery ~ 70%	spirulina: too much noise in the chromatogramm
505	internal calibration	oil 80 -90 %	after reducing the sample amount not
506	external calibration	of internal standard Benzo(b)chrysene between around 65 and 105 %	the sample amount was lower then expected so it was not possible to take the sample weight given in the analysis method
508	internal calibration	70 % to 110 % calculated over a recovery standard for the internal standards	no
509	internal calibration	>90% -110%	No
510	external calibration and internal standard	80-120%	no
511	Internal Calibrations	70 % - 120 %	no
513	external calibration		no
515	standard addition	75-110	no

Lab Code	Problems calibration	Chrom. interference	Comment
101	no	no	no
104			
105	no	no	
106	NO	SOME BUT NO SERIOUS PROBLEMS	NO COMMENTS
108	no	spirulina: chromatographic interference with peak of chrysene	uncertainty of measurement (MU%) is given as the expanded uncertainty (k=2)
109	No	Yes for spirulina. Too may matrix interfering peaks.	Spirulina is a difficult matrix.
111		No	
112	No	There was triphenylene in the samples.	Please note that I have modified the lab details. The RingDat application "froze" several times after I pushed the 'Save Data' button.
113	yes for spirulina, not absolutely linear (R2 < 0.98)	no	
114	No	No	
115	No	Interference on chrysene (with triphenylene?), peaks were seperated, but not on baseline level. More interference with spirulina than with fish oil	Spirulina: first ASE extraction with hexane/acetone 1:1
116	No.	No.	
117	no	Not known	no
118	NO	NO	
119	no	baseline interferences for the spirulina sample	
120	no	no, but the fish oil chromatograms were cleaner than the spirulin chromatograms	
121	no	yes	strong matrix interference did not allow chrysene determination in spirulina powder
122	no	minor with spirulina	no
123	No	Yes in case of chrysene	
124	NO	Yes for BaA (on each side), Chrysene (small blank contamination)	preparation for fish oil : DACC // preparation for spirulina : liquid/liquid + SPE + DACC
125	No	No	
126	No	benzo(a)anthracene and chrysene	This PT out of our real work
501	No	Yes	
502	Yes. At the moment we have to cope wirth sensitivity problems due to technical problems with the detector.	Without additional clean-up spirulina showed chrom. interferences	
503	No	No	No
504	no		spirulina no data given
505	no	yes	
506	no	interferences around the second internal standard Benzo(a)anthracene-D12, which could therefore not be used for the analysis of the compunds	their was nothing written on the packet, that the samples inside should be store cool, samples were not stored cool for some days, analysis method for spirulina: ASE and SPE, for fish oil: saponification, liquid/liquid-partioning and column chromatography on silica, sample amount was lower than 20 g (16 g fish oil and 19 g spirulina powder), standard solution was not send in acetonitrile but in toluol
508	no	no	

509	No	No	
510	no	no	
511	no	no	So, more then 20g from Test materials are greatfull because Sample measurand three times respond 15 g Test material. If the Sample makes Problem there were not enough material to complete the measurand.
513	no	the average noise in spirulina was bigger than in fish oil matrix	
515	no	no	Comment

METHOD PERFORMANCE LOD and LOQ

Method performance characteristics were assessed for compliance with Commission Regulation (EC) No 333/2007 as amended by Commission Regulation (EU) No 836/2011. Threshold values for the evaluation were LOD= 0.30 µg/kg, LOQ = 0.90 µg/kg.. Non-compliant values are marked in in bold red font.

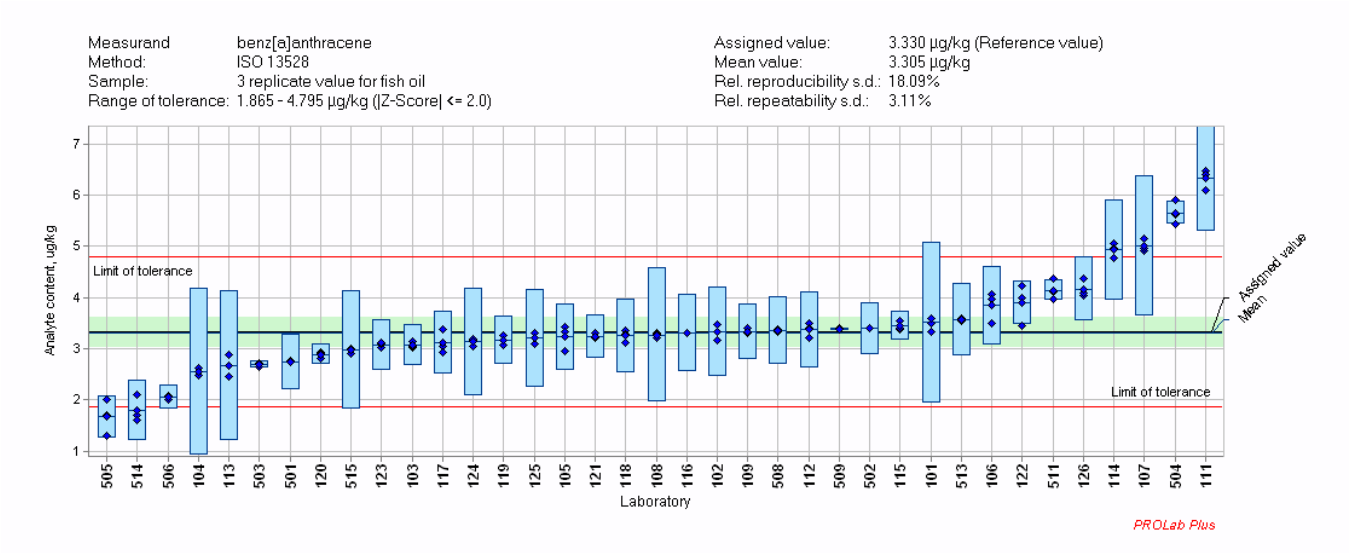
	BaA				BaP				BbF				CHR			
	Fish oil		Spirulina (if different)		Fish oil		Spirulina (if different)		Fish oil		Spirulina (if different)		Fish oil		Spirulina (if different)	
Lab Code	LOD [µg/kg	LOQ [µg/kg	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]:	LOQ [µg/kg]:	LOD [µg/kg]:	LOQ [µg/kg]:	LOD [µg/kg]:	LOQ [µg/kg]:
101	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1
102	0.025	0.05	0.025	0.05	0.025	0.05	0.025	0.05	0.05	0.1	0.05	0.1	0.025	0.05	0.025	0.05
103	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.3	0.1	0.2	0.1	0.3	0.1	0.2	0.1	0.3
104	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.2	0.5	0.2	0.5
105	0.07	0.21	0.01	0.03	0.08	0.24	0.008	0.024	0.15	0.45	0.015	0.045	0.04	0.12	0.004	0.012
106	0.2	0.6	0.2	0.6	0.1	0.3	0.1	0.3	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
107																
108	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
109	0.21	0.69			0.16	0.53			0.19	0.63			0.32	1.05		
110																
111	0.11	0.11	0.09	0.09	0.18	0.18	0.15	0.15	0.14	0.14	0.12	0.12	0.15	0.15	0.12	0.12
112	0.2	0.7	0.1	0.2	0.2	0.8	0.1	0.2	0.3	0.8	0.1	0.3	0.2	0.7	0.1	0.2
113	0.19	0.63	0.07	0.07	0.02	0.06	0.02	0.04	0.12	0.41	0.01	0.01	0.13	0.43	0.05	0.07
114	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
115	0.01	0.02	0.02	0.04	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.02	0.04
116	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
117		0.5		0.5		0.2		0.2		0.2		0.2		0.5		0.2
118	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03
119	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
120	0.008	0.51	0.006	0.012	0.004	0.51	0.003	0.005	0.024	0.51	0.017	0.034	0.007	0.51	0.005	0.01
121	0.07	0.2	0.3	0.7	0.07	0.2	0.3	0.8	0.07	0.2	0.2	0.5	0.07	0.2	0.6	1.3
122	0.1	0.5	0.1	0.5	0.2	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
123		0.4		0.4		0.2		0.2		0.3		0.3		0.64		0.64
124	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4
125	0.17	0.5	0.1	0.3	0.17	0.5	0.1	0.3	0.17	0.5	0.1	0.3	0.17	0.5	0.1	0.3
126	0.07	0.21	0.12	0.36	0.05	0.15	0.08	0.24	0.15	0.45	0.11	0.33	0.03	0.09	0.03	0.09
501	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
502	0.1	0.4	0.3	0.9	0.2	0.6	0.3	0.9	0.1	0.5	0.6	2	0.1	0.3	0.6	2
503	0.2	0.5	0.2	0.6	0.2	0.5	0.2	0.6	0.2	0.5	0.2	0.6	0.2	0.5	0.2	0.6
504	0.2	0.6			0.2	0.6			0.2	0.6			0.2	0.6		
505	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4
506	0.1	0.48	0.03	0.13	0.06	0.29	0.02	0.08	0.15	0.75	0.04	0.2	0.1	0.49	0.08	0.39
507																
508	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1
509	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5
510						0.5		0.5								
511	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
512																
513	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5
514		0.8				0.8				0.8				0.8		
515	0.26	0.3	0.16	0.3	0.29	0.5	0.13	0.5	0.26	0.3	0.07	0.3	0.19	0.2	0.11	0.2

ANNEX 9: Data reported by participants

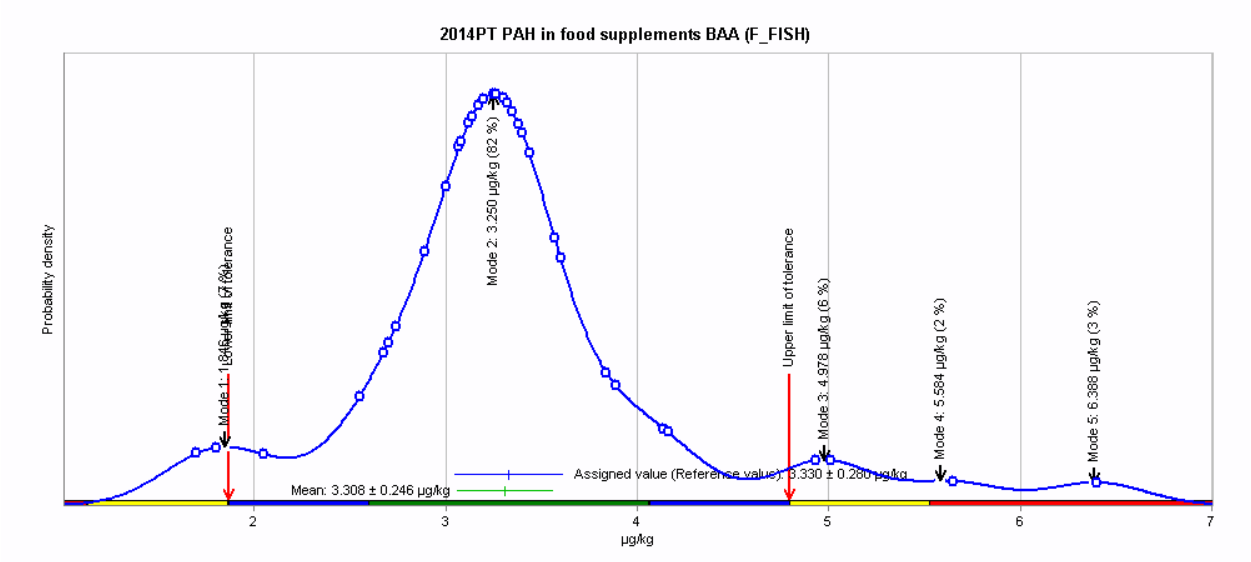
The data reported by the participants are compiled in the following tables. Uncertainty values that do not comply with the U_f thresholds (individual PAHs) are marked by bold red font. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores.

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the fish oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range



Kernel density plot of the reported values for proficiency assessment for the benz[*a*]anthracene (BAA) content of the fish oil test sample



Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA) in fish oil.

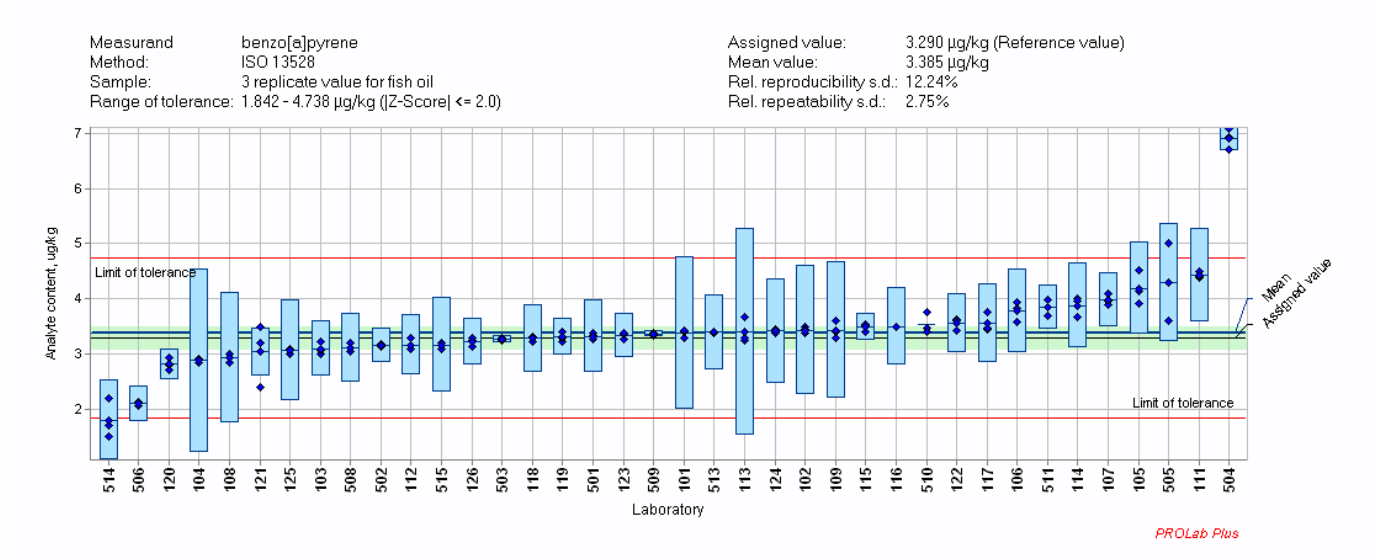
Assigned value is 3.33±0.28 µg/kg**.** The uncertainty refers to the value for proficiency assessment. Red cells indicate results for proficiency assessment, which deviate in terms of significant figures from the provision set in legislation.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	BAA	3.6	3.5	3.6	3.6	42	GC-MS
102	BAA	3.17	3.34	3.47	3.32	26	HPLC-FLD
103	BAA	3.03	3.05	3.15	3.08	6	GC-MS
104	BAA	2.54	2.62	2.47	2.55	64	HPLC-FLD
105	BAA	2.943	3.416	3.331	3.2	20	HPLC-FLD
106	BAA	3.50	4.07	3.96	3.84	20	HPLC-FLD
107	BAA	4.92	5.15	4.97	5.01	27.3	n.r.
108	BAA	3.30	3.22	3.28	3.26	40	GC-MS
109	BAA	3.4	3.3	3.3	3.3	16.5	HPLC-FLD
110	BAA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	BAA	6.48	6.09	6.40	6.40	16.25	GC-MS
112	BAA	3.5	3.2	3.4	3.4	22	GC-MS/MS
113	BAA	2.457	2.658	2.874	2.677	55	GC-MS/MS
114	BAA	5.05	4.78	4.95	4.93	20	GC-MS/MS
115	BAA	3.367	3.409	3.538	3.438	8.3	GC-HRMS
116	BAA	3.3	3.3	3.3	3.3	22.9	GC-MS
117	BAA	3.05	2.92	3.38	3.12	20	HPLC-FLD
118	BAA	3.35	3.11	3.29	3.25	22.3	GC-MS/MS
119	BAA	3.08	3.17	3.25	3.17	15	GC-MS
120	BAA	2.93	2.91	2.82	2.89	6.9	HPLC-FLD
121	BAA	3.3	3.2	3.2	3.2	13	GC-MS
122	BAA	3.44	4.00	4.22	3.89	11	GC-MS
123	BAA	3.01	3.09	3.12	3.07	16	HPLC-FLD
124	BAA	3.159	3.198	3.051	3.136	33.6	HPLC-FLD
125	BAA	3.3	3.2	3.1	3.2	30	GC-MS/MS
126	BAA	4.36	4.03	4.09	4.16	15	HPLC-FLD
501	BAA	2.74	2.73	2.75	2.74	20	HPLC-FLD
502	BAA	3.39	3.39	3.40	3.4	15	HPLC-FLD
503	BAA	2.72	2.65	2.69	2.7	2.6	HPLC-FLD
504	BAA	5.90	5.44	5.62	5.65	4	HPLC-FLD
505	BAA	1.3	1.7	2.0	1.7	25	n.r.
506	BAA	2.07	2.08	2.01	2.05	11.8	HPLC-FLD
507	BAA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	BAA	3.34	3.34	3.38	3.35	20	GC-MS/MS
509	BAA	3.39	3.39	3.37	3.38	0.6	GC-MS/MS
510	BAA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
511	BAA	4.37	3.96	4.10	4.14	4.7	GC-MS
512	BAA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	BAA	3.58	3.53	3.60	3.57	20	GC-MS
514	BAA	2.1	1.7	1.6	1.8	33	HPLC-FLD
515	BAA	3.0	2.9	3.0	3.0	39	HPLC-FLD

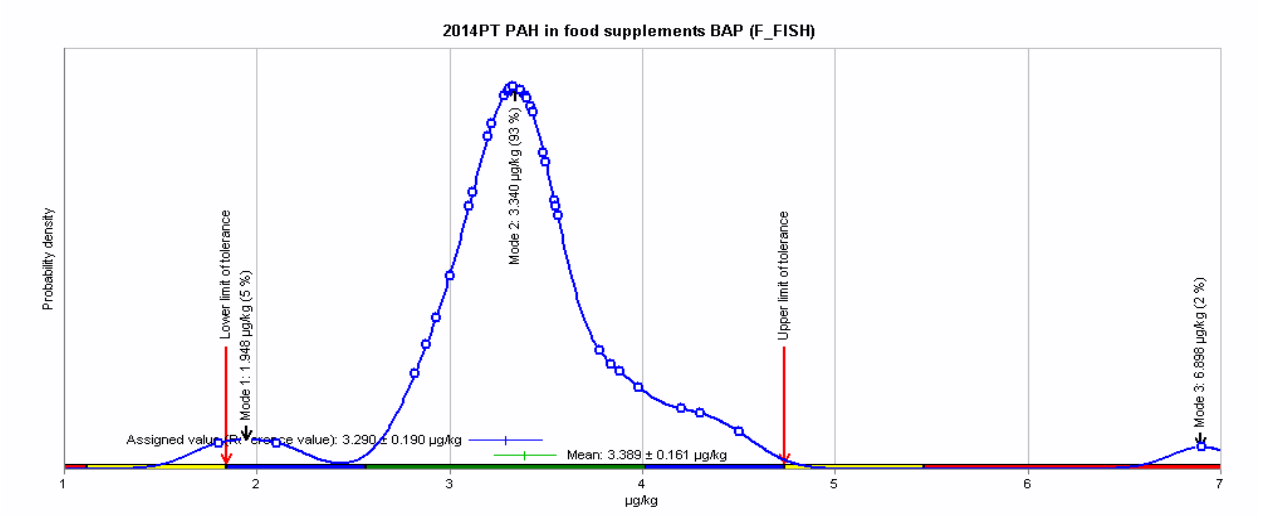
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benzo[*a*]pyrene (BAP) content of the fish oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the benzo[*a*]pyrene (BAP) content of the fish oil test sample



Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP) in fish oil test material.

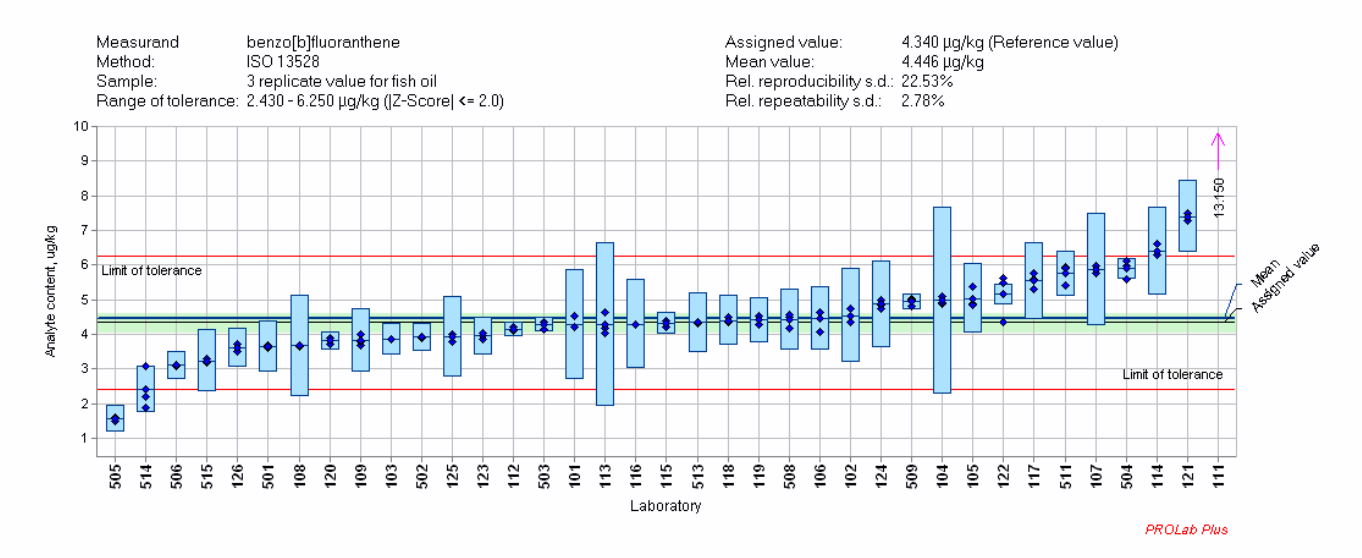
Assigned value is 3,29±0.19 µg/kg**.** The uncertainty refers to the final value. Red cells indicate results for proficiency assessment, which deviate in terms of significant figures from the provision set in legislation.

LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	BAP	3.4	3.3	3.4	3.4	41	GC-MS
102	BAP	3.38	3.48	3.44	3.43	34	HPLC-FLD
103	BAP	3.00	3.06	3.23	3.10	13	GC-MS
104	BAP	2.85	2.89	2.90	2.88	58	HPLC-FLD
105	BAP	4.509	3.917	4.144	4.2	20	HPLC-FLD
106	BAP	3.59	3.94	3.82	3.78	20	HPLC-FLD
107	BAP	4.1	3.95	3.89	3.98	12.5	n.r.
108	BAP	3.01	2.94	2.85	2.93	40	GC-MS
109	BAP	3.4	3.3	3.6	3.4	36.2	HPLC-FLD
110	BAP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	BAP	4.39	4.40	4.50	4.50	18.7	GC-MS
112	BAP	3.1	3.1	3.3	3.2	17	GC-MS/MS
113	BAP	3.254	3.662	3.298	3.394	55	GC-MS/MS
114	BAP	4.00	3.68	3.95	3.88	20	GC-MS/MS
115	BAP	3.523	3.401	3.542	3.488	7	GC-HRMS
116	BAP	3.5	3.5	3.5	3.5	20	GC-MS
117	BAP	3.45	3.47	3.75	3.56	20	HPLC-FLD
118	BAP	3.22	3.30	3.32	3.28	19	GC-MS/MS
119	BAP	3.23	3.30	3.40	3.31	10	GC-MS
120	BAP	2.94	2.80	2.72	2.82	10	HPLC-FLD
121	BAP	2.4	3.2	3.5	3	14	GC-MS
122	BAP	3.42	3.63	3.61	3.55	15	GC-MS
123	BAP	3.27	3.35	3.37	3.33	12	HPLC-FLD
124	BAP	3.452	3.412	3.387	3.417	27.8	HPLC-FLD
125	BAP	3.1	3.1	3.0	3.1	30	GC-MS/MS
126	BAP	3.24	3.13	3.30	3.22	13	HPLC-FLD
501	BAP	3.26	3.33	3.38	3.33	20	HPLC-FLD
502	BAP	3.13	3.18	3.15	3.2	10	HPLC-FLD
503	BAP	3.30	3.24	3.27	3.3	2	HPLC-FLD
504	BAP	7.08	6.70	6.92	6.90	3	HPLC-FLD
505	BAP	3.6	5.0	4.3	4.3	25	n.r.
506	BAP	2.11	2.12	2.07	2.10	15.2	HPLC-FLD
507	BAP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	BAP	3.11	3.05	3.20	3.12	20	GC-MS/MS
509	BAP	3.33	3.38	3.39	3.37	1.78	GC-MS/MS
510	BAP	3.47	3.75	3.41	3.543		HPLC-FLD
511	BAP	3.85	3.98	3.69	3.84	10.5	GC-MS
512	BAP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	BAP	3.40	3.39	3.41	3.40	20	GC-MS
514	BAP	2.2	1.7	1.5	1.8	40	HPLC-FLD
515	BAP	3.2	3.1	3.2	3.2	27	HPLC-FLD

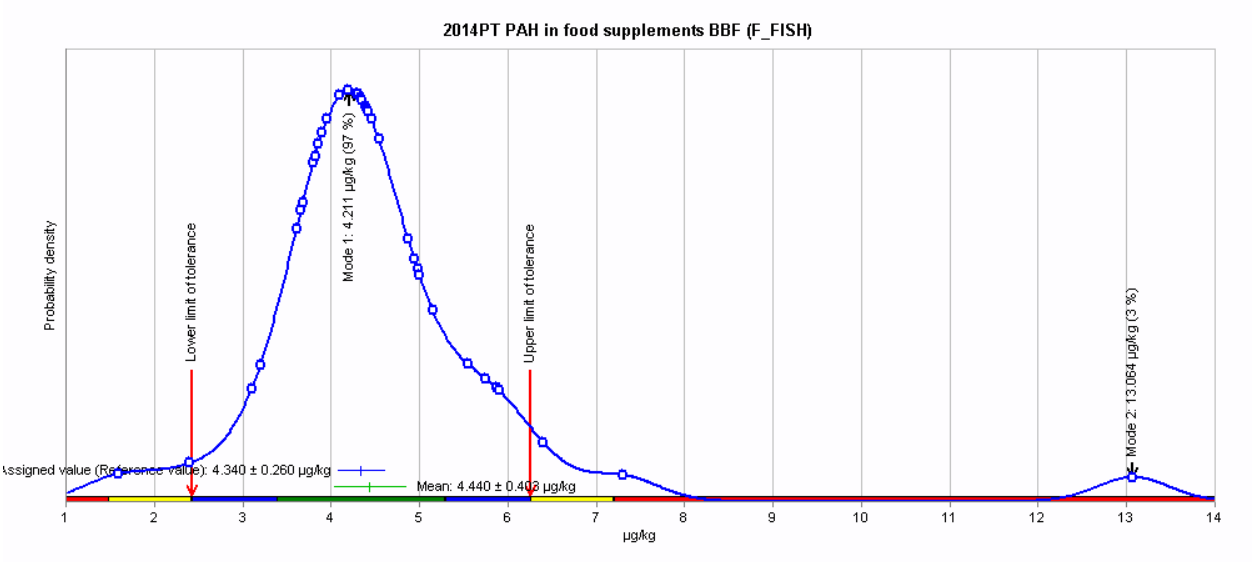
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content of the fish oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the benzo[*b*]fluoranthene (BBF) content of the fish oil test sample



Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF) in fish oil test material.

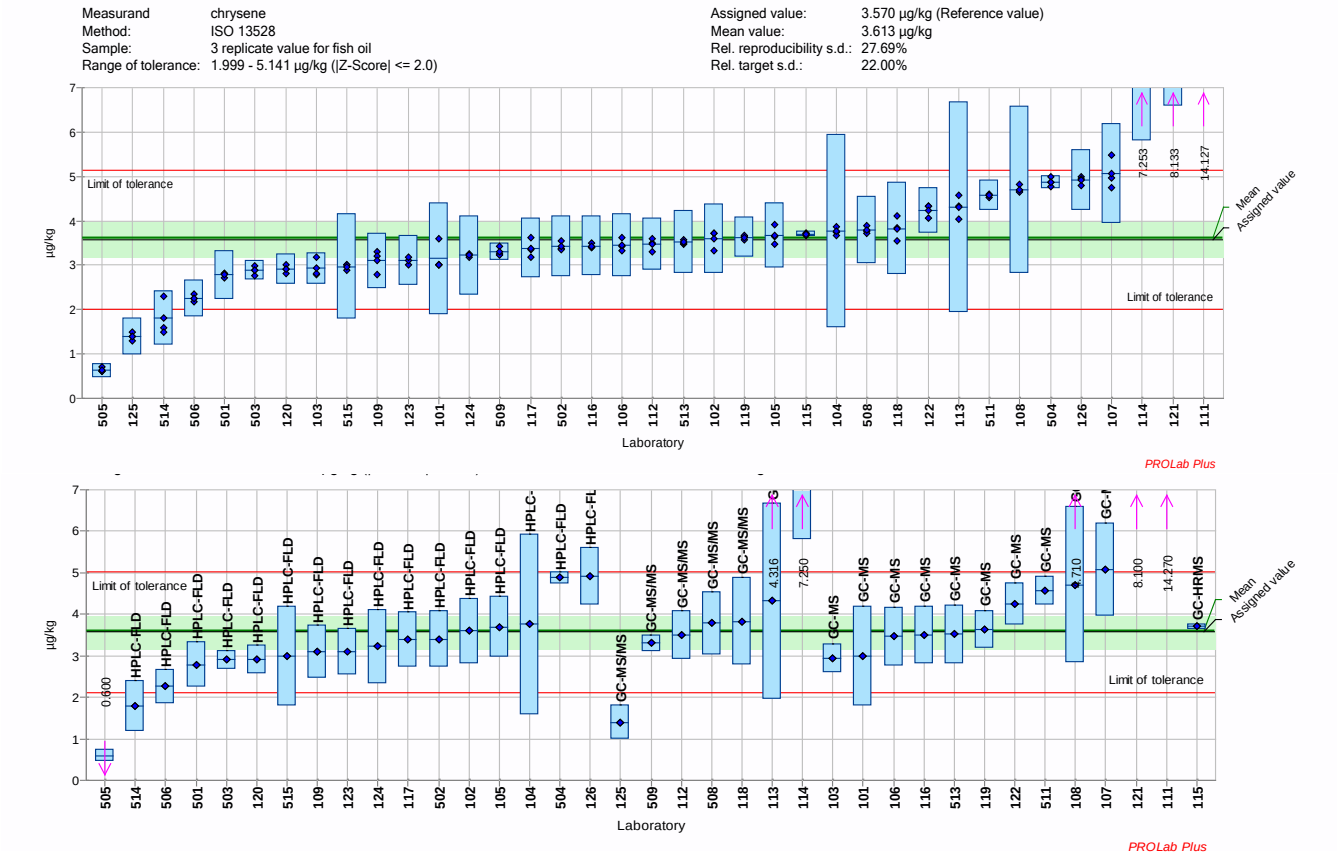
Assigned value is 4,34±0.26 µg/kg. The uncertainty refers to the final value. Red cells indicate results for proficiency assessment, which deviate in terms of significant figures from the provision set in legislation.

LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	BBF	4.2	4.2	4.2	4.2	40.5	GC-MS
102	BBF	4.36	4.52	4.74	4.54	30	HPLC-FLD
103	BBF	3.85	3.86	3.86	3.86	16	GC-MS
104	BBF	5.11	4.90	4.92	4.98	54.0	HPLC-FLD
105	BBF	5.391	4.872	4.832	5.0	20	HPLC-FLD
106	BBF	4.09	4.65	4.64	4.46	20.3	HPLC-FLD
107	BBF	5.98	5.89	5.75	5.87	27.5	n.r.
108	BBF	3.65	3.7	3.67	3.68	40	GC-MS
109	BBF	4.0	3.7	3.8	3.8	24.1	HPLC-FLD
110	BBF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	BBF	13.38	13.00	13.07	13.07	17.1	GC-MS
112	BBF	4.2	4.1	4.1	4.1	5	GC-MS/MS
113	BBF	4.187	4.024	4.654	4.297	55	GC-MS/MS
114	BBF	6.63	6.30	6.28	6.40	20	GC-MS/MS
115	BBF	4.392	4.378	4.216	4.329	7.2	GC-HRMS
116	BBF	4.3	4.3	4.3	4.3	30.1	GC-MS
117	BBF	5.32	5.58	5.76	5.55	20	HPLC-FLD
118	BBF	4.36	4.35	4.48	4.39	16.5	GC-MS/MS
119	BBF	4.3	4.41	4.53	4.41	15	GC-MS
120	BBF	3.90	3.82	3.73	3.82	7.08	HPLC-FLD
121	BBF	7.4	7.5	7.3	7.3	14	GC-MS
122	BBF	4.35	5.63	5.47	5.15	6	GC-MS
123	BBF	3.87	3.95	4.05	3.96	14	HPLC-FLD
124	BBF	4.994	4.867	4.757	4.872	25.8	HPLC-FLD
125	BBF	3.8	4.0	4.0	3.9	30	GC-MS/MS
126	BBF	3.61	3.72	3.51	3.61	16	HPLC-FLD
501	BBF	3.67	3.61	3.67	3.66	20	HPLC-FLD
502	BBF	3.91	3.93	3.91	3.9	10	HPLC-FLD
503	BBF	4.37	4.16	4.28	4.3	4.9	HPLC-FLD
504	BBF	6.12	5.58	5.99	5.90	5	HPLC-FLD
505	BBF	1.6	1.6	1.5	1.6	25	n.r.
506	BBF	3.09	3.11	3.11	3.10	13.4	HPLC-FLD
507	BBF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	BBF	4.51	4.19	4.56	4.42	20	GC-MS/MS
509	BBF	4.81	5.03	4.99	4.94	4.6	GC-MS/MS
510	BBF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
511	BBF	5.93	5.92	5.40	5.75	11.6	GC-MS
512	BBF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	BBF	4.33	4.37	4.34	4.35	20	GC-MS
514	BBF	3.1	2.2	1.9	2.4	28	HPLC-FLD
515	BBF	3.2	3.2	3.3	3.2	28	HPLC-FLD

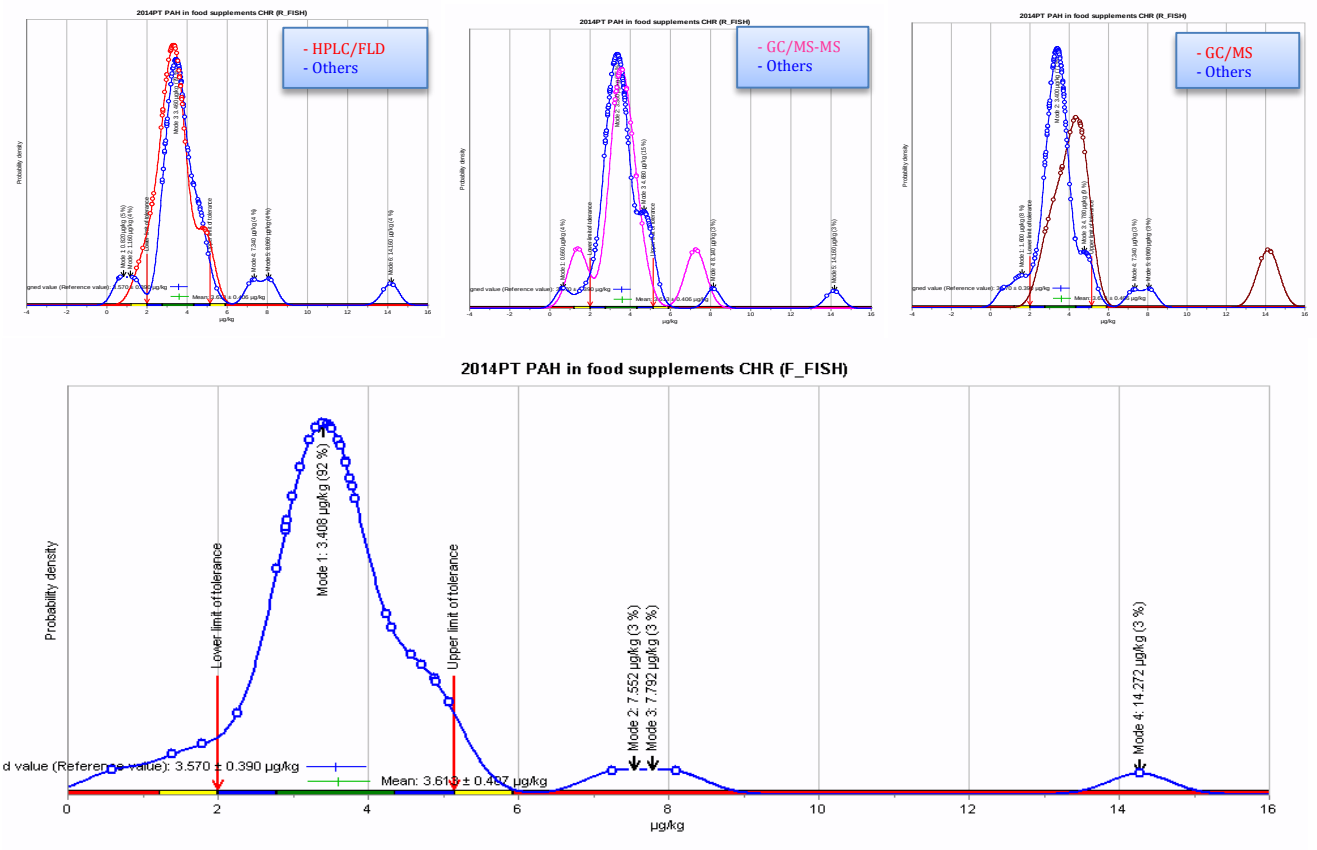
n.r.: not reported

Distribution of individual results of replicate determinations reported for the chrysene (CHR) content of the fish oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the chrysene (CHR) content of the fish oil test sample



Results, as reported by the participants, for the content of chrysene (CHR) in fish oil test material.

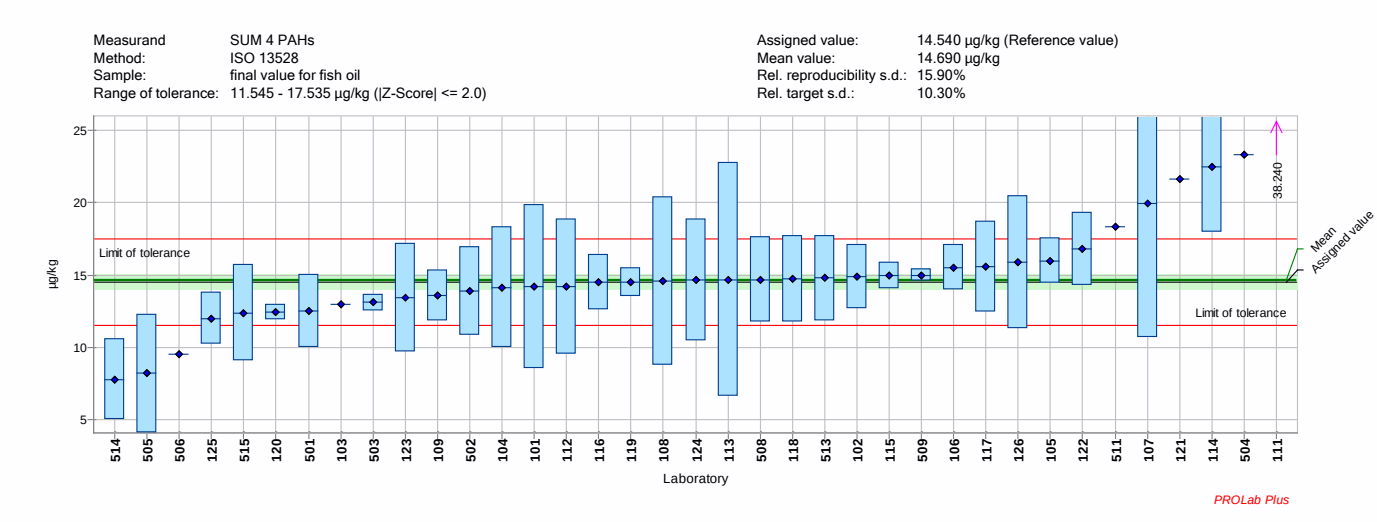
Assigned value is 3.57±0.39 µg/kg. The uncertainty refers to the final value. Red cells indicate results for proficiency assessment, which deviate in terms of significant figures from the provision set in legislation.

LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	CHR	3.0	3.0	3.0	3.0	40	GC-MS
102	CHR	3.34	3.73	3.73	3.60	22	HPLC-FLD
103	CHR	2.78	2.82	3.19	2.93	12	GC-MS
104	CHR	3.74	3.68	3.86	3.76	58	HPLC-FLD
105	CHR	3.636	3.476	3.912	3.7	20	HPLC-FLD
106	CHR	3.62	3.43	3.33	3.46	20.5	GC-MS
107	CHR	4.74	5.49	4.97	5.07	22	n.r.
108	CHR	4.67	4.65	4.81	4.71	40	GC-MS
109	CHR	3.3	3.2	2.8	3.1	20.4	HPLC-FLD
110	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	CHR	14.3	13.81	14.27	14.27	16	GC-MS
112	CHR	3.5	3.3	3.6	3.5	17	GC-MS/MS
113	CHR	4.587	4.042	4.321	4.316	55	GC-MS/MS
114	CHR	7.3	7.08	7.38	7.25	20	GC-MS/MS
115	CHR	3.713	3.683	3.718	3.705	1.6	GC-HRMS
116	CHR	3.5	3.4	3.4	3.5	20	GC-MS
117	CHR	3.35	3.18	3.63	3.39	20	HPLC-FLD
118	CHR	3.84	3.55	4.10	3.83	27.4	GC-MS/MS
119	CHR	3.57	3.65	3.66	3.63	12.5	GC-MS
120	CHR	3.01	2.92	2.82	2.91	12	HPLC-FLD
121	CHR	8.1	8.1	8.2	8.1	19	GC-MS
122	CHR	4.32	4.34	4.06	4.24	12	GC-MS
123	CHR	3.02	3.10	3.19	3.10	18	HPLC-FLD
124	CHR	3.254	3.229	3.192	3.225	28	HPLC-FLD
125	CHR	1.5	1.4	1.3	1.4	30	GC-MS/MS
126	CHR	4.99	4.80	4.95	4.91	14	HPLC-FLD
501	CHR	2.72	2.81	2.81	2.79	20	HPLC-FLD
502	CHR	3.37	3.36	3.54	3.4	20	HPLC-FLD
503	CHR	2.99	2.77	2.89	2.9	7.6	HPLC-FLD
504	CHR	5.00	4.87	4.77	4.88	3	HPLC-FLD
505	CHR	0.7	0.6	0.6	0.6	25	n.r.
506	CHR	2.34	2.26	2.18	2.26	18.4	HPLC-FLD
507	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	CHR	3.78	3.71	3.89	3.79	20	GC-MS/MS
509	CHR	3.26	3.42	3.24	3.31	6	GC-MS/MS
510	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
511	CHR	4.54	4.58	4.60	4.57	7.6	GC-MS
512	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	CHR	3.48	3.50	3.58	3.52	20	GC-MS
514	CHR	2.3	1.6	1.5	1.8	34	HPLC-FLD
515	CHR	3.0	2.9	3.0	3.0	40	HPLC-FLD

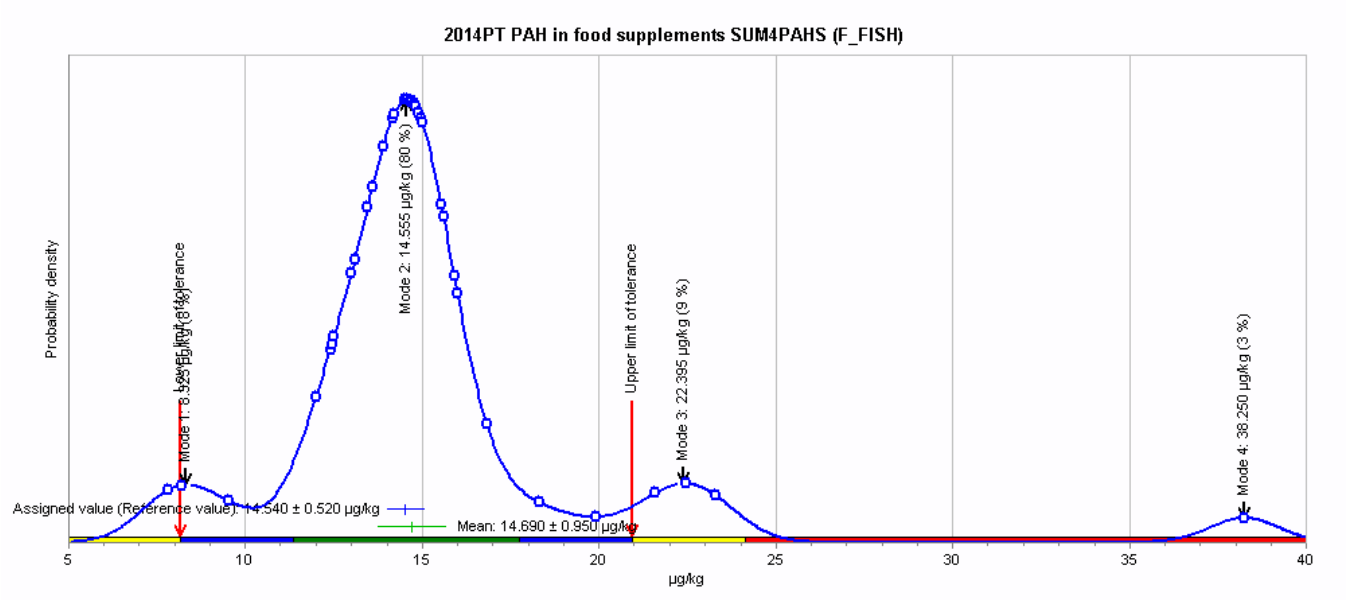
n.r.: not reported

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content of the fish oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the SUM4PAH content of the fish oil test sample.



Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH) in fish oil test material.

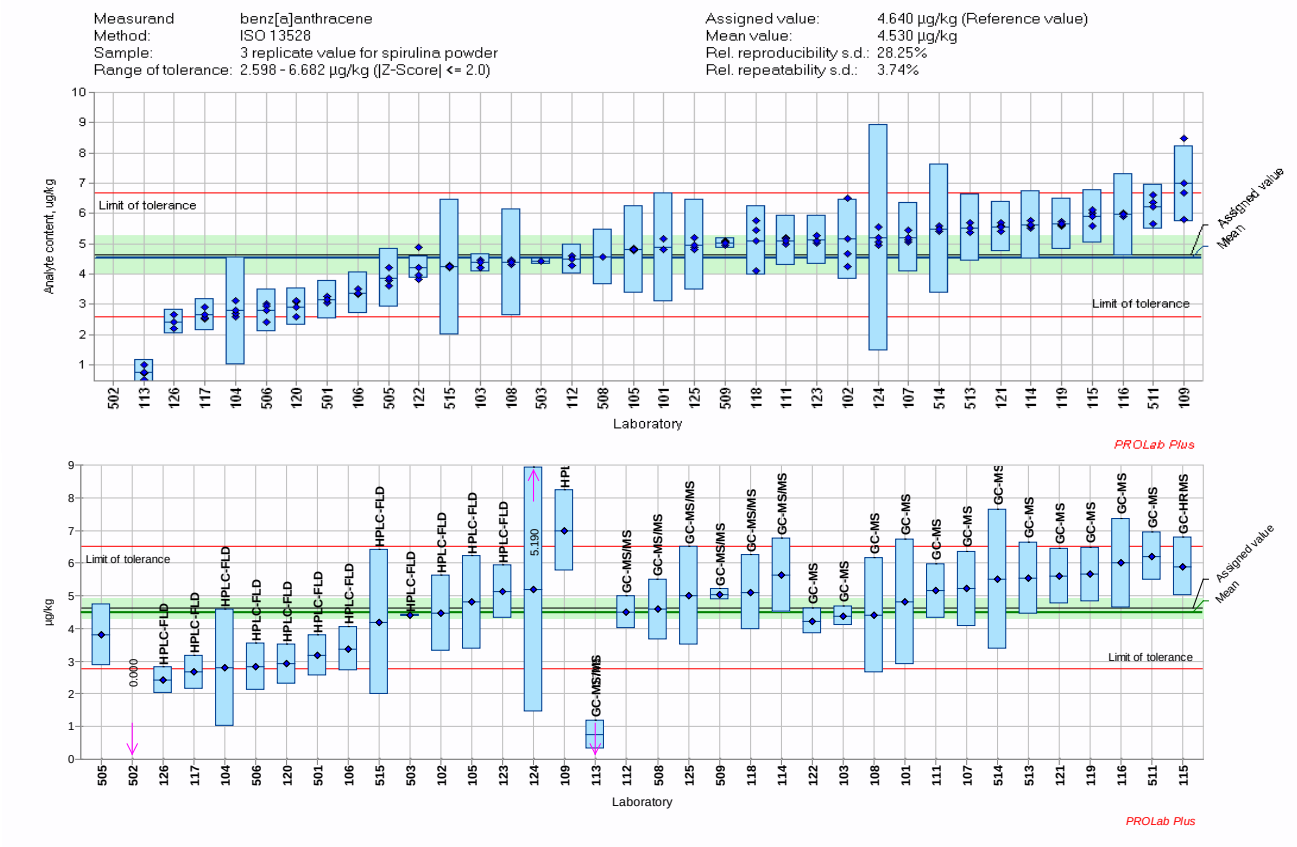
Assigned value is 14.54±0.58 µg/kg. Red cells indicate results for proficiency assessment, which deviate in terms of significant figures from the provision set in legislation.

LCode	Measurant	Final value, µg/kg	Uncertainty, %	Analytical technique
101	SUM 4PAH	14.2	40	GC-MS
102	SUM 4PAH	14.89	15	HPLC-FLD
103	SUM 4PAH	13.0	n.r.	GC-MS
104	SUM 4PAH	14.16	29.5	HPLC-FLD
105	SUM 4PAH	16	10	HPLC-FLD
106	SUM 4PAH	15.54	10	n.r.
107	SUM 4PAH	19.93	46.3	n.r.
108	SUM 4PAH	14.6	40	GC-MS
109	SUM 4PAH	13.6	12.8	HPLC-FLD
110	SUM 4PAH	n.r.	n.r.	n.r.
111	SUM 4PAH	38.24	9.0	GC-MS
112	SUM 4PAH	14.2	33	GC-MS/MS
113	SUM 4PAH	14.685	55	GC-MS/MS
114	SUM 4PAH	22.45	20	GC-MS/MS
115	SUM 4PAH	14.96	6.1	GC-HRMS
116	SUM 4PAH	14.5	13.0	GC-MS
117	SUM 4PAH	15.6	20	HPLC-FLD
118	SUM 4PAH	14.76	20.1	GC-MS/MS
119	SUM 4PAH	14.52	7	GC-MS
120	SUM 4PAH	12.44	4.5	HPLC-FLD
121	SUM 4PAH	21.6	n.r.	n.r.
122	SUM 4PAH	16.83	15	GC-MS
123	SUM 4PAH	13.46	28	HPLC-FLD
124	SUM 4PAH	14.651	28.7	HPLC-FLD
125	SUM 4PAH	12	15	GC-MS/MS
126	SUM 4PAH	15.91	29	HPLC-FLD
501	SUM 4PAH	12.51	20	HPLC-FLD
502	SUM 4PAH	13.9	22	n.r.
503	SUM 4PAH	13.1	4.6	HPLC-FLD
504	SUM 4PAH	23.3	n.r.	HPLC-FLD
505	SUM 4PAH	8.2	50	n.r.
506	SUM 4PAH	9.51	n.r.	HPLC-FLD
507	SUM 4PAH	n.r.	n.r.	n.r.
508	SUM 4PAH	14.7	20	GC-MS/MS
509	SUM 4PAH	15.00	2.9	GC-MS/MS
510	SUM 4PAH	n.r.	n.r.	n.r.
511	SUM 4PAH	18.31	n.r.	GC-MS
512	SUM 4PAH	n.r.	n.r.	n.r.
513	SUM 4PAH	14.8	20	GC-MS
514	SUM 4PAH	7.8	36	HPLC-FLD
515	SUM 4PAH	12.4	27	HPLC-FLD

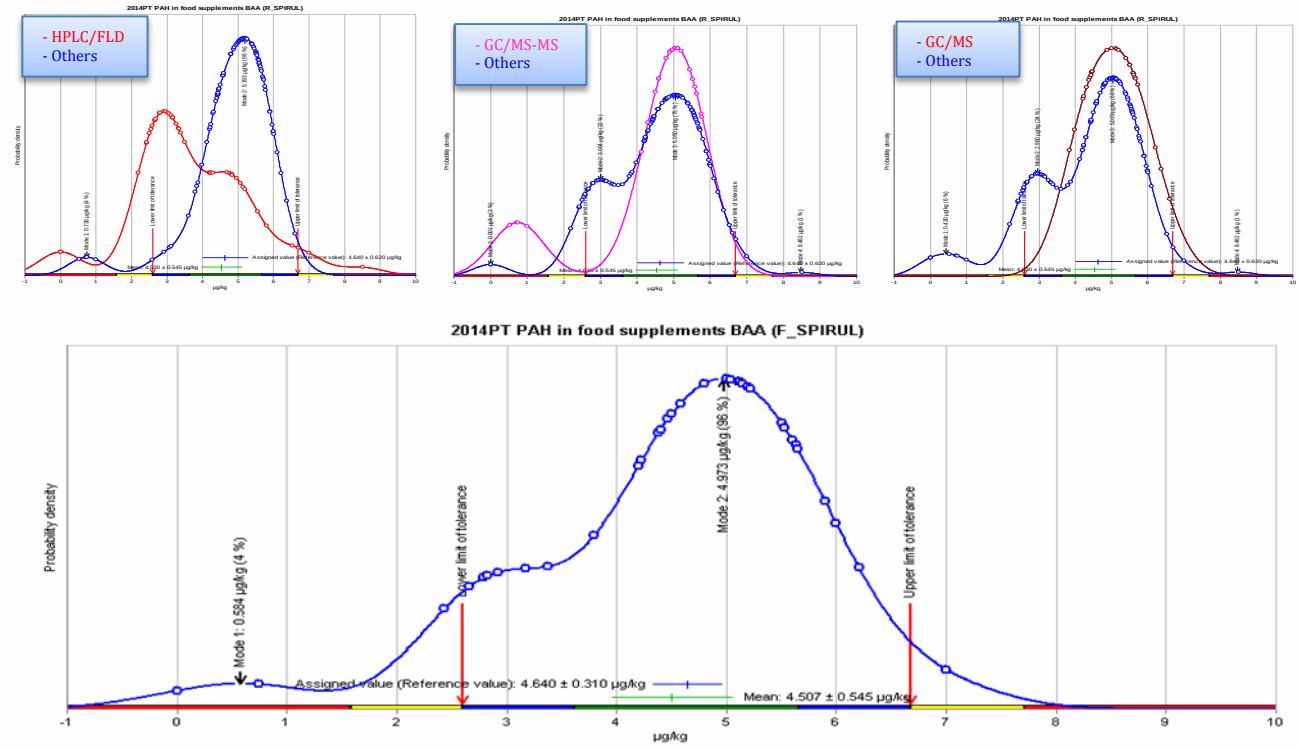
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the spirulina test material.

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for benz[*a*]anthracene (BAA) content of spirulina test sample



Results, as reported by participants, for the content of benz[*a*]anthracene (BAA) in the spirulina test material.

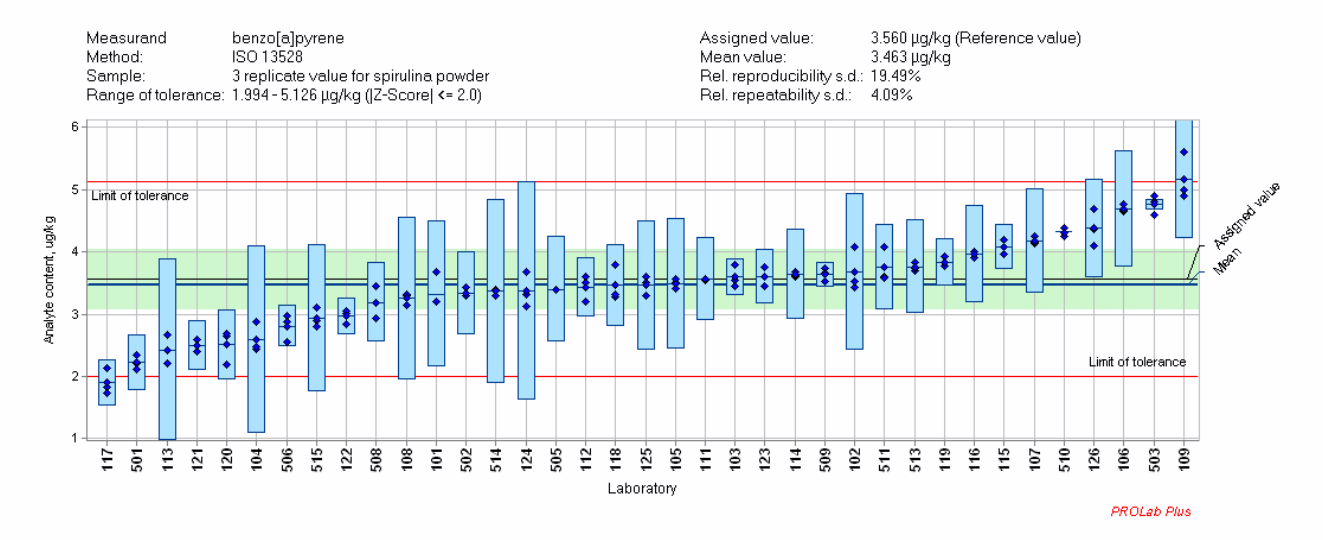
Assigned value is 4.64±0.31 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	BaA	4.8	4.8	4.8	4.8	40	GC-MS
102	BaA	4.24	4.69	6.52	4.47	26	HPLC-FLD
103	BaA	4.46	4.21	4.47	4.38	6.8	GC-MS
104	BaA	3.11	2.59	2.68	2.79	64.2	HPLC-FLD
105	BaA	4.831	4.837	4.765	4.8	30	HPLC-FLD
106	BaA	3.5	3.32	3.33	3.38	20.2	HPLC-FLD
107	BaA	5.46	5.07	5.12	5.22	22	n.r.
108	BaA	4.43	4.31	4.47	4.4	40	GC-MS
109	BaA	6.7	5.8	8.5	7.0	18	HPLC-FLD
110	BaA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	BaA	5.19	5.00	5.15	5.15	16	GC-MS
112	BaA	4.3	4.6	4.6	4.5	11	GC-MS/MS
113	BaA	0.715	0.994	0.52	0.748	60	GC-MS/MS
114	BaA	5.52	5.78	5.58	5.63	20	GC-MS/MS
115	BaA	6.012	5.576	6.105	5.90	15	GC-HRMS
116	BaA	6.0	6.0	5.9	6.0	22.9	GC-MS
117	BaA	2.51	2.55	2.92	2.66	20	HPLC-FLD
118	BaA	5.44	5.76	4.12	5.11	22.3	GC-MS/MS
119	BaA	5.60	5.72	5.62	5.65	15	GC-MS
120	BaA	2.58	3.07	3.11	2.92	20.8	HPLC-FLD
121	BaA	5.4	5.6	5.7	5.6	15	GC-MS
122	BaA	3.84	3.98	4.87	4.23	9	GC-MS
123	BaA	5.02	5.09	5.26	5.12	16	HPLC-FLD
124	BaA	4.956	5.549	5.067	5.190	72	HPLC-FLD
125	BaA	5.2	4.9	4.8	5.0	30	GC-MS/MS
126	BaA	2.42	2.19	2.66	2.43	17	HPLC-FLD
501	BaA	3.26	3.15	3.06	3.17	20	HPLC-FLD
502	BaA	0	0	0	0	20	HPLC-FLD
503	BaA	4.43	4.44	4.42	4.4	0.5	HPLC-FLD
504	BaA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
505	BaA	3.6	4.2	3.8	3.8	25	n.r.
506	BaA	3.03	2.96	2.43	2.83	25	HPLC-FLD
507	BaA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	BaA	4.58	4.58	4.58	4.58	20	GC-MS/MS
509	BaA	5.11	4.94	5.06	5.04	3.37	GC-MS/MS
510	BaA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
511	BaA	6.61	5.66	6.37	6.21	12	GC-MS
512	BaA	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	BaA	5.38	5.51	5.71	5.53	20	GC-MS
514	BaA	5.4	5.5	5.6	5.5	39	GC-MS
515	BaA	4.3	4.2	4.2	4.2	53	HPLC-FLD

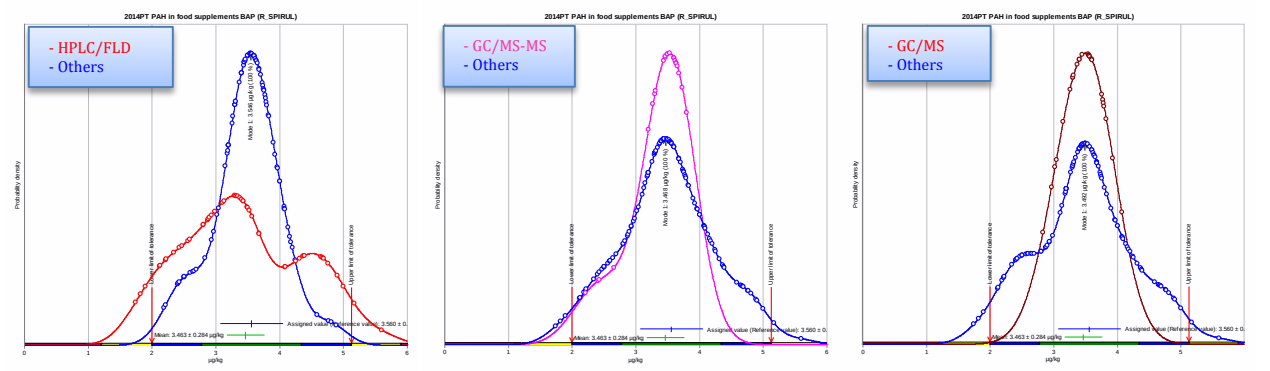
n.r.: not reported

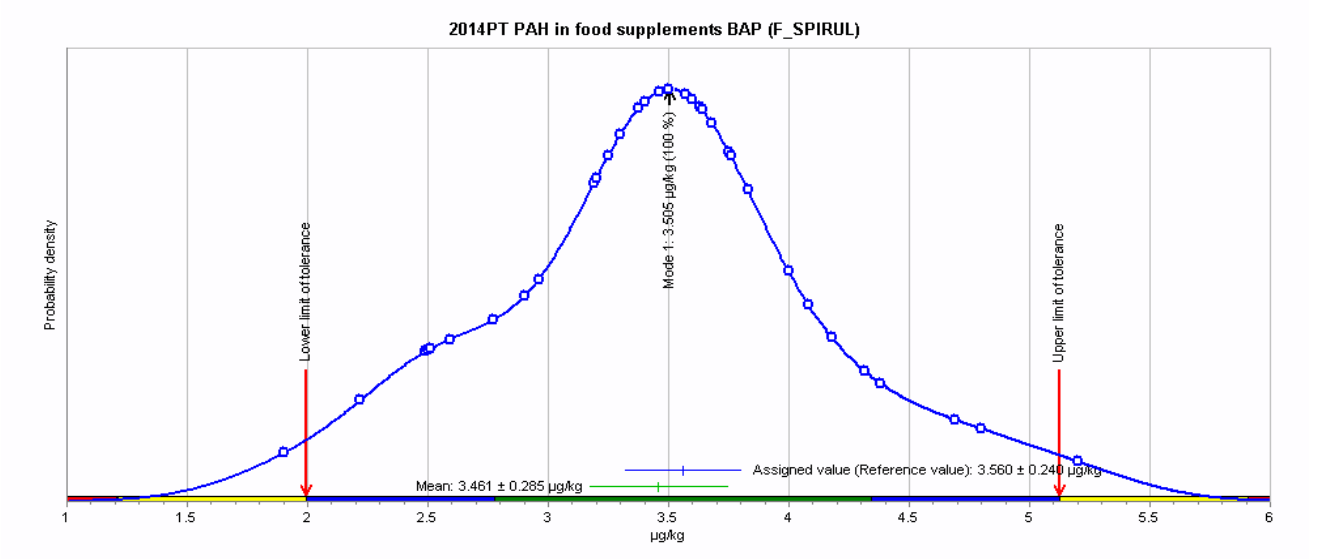
Distribution of individual results of replicate determinations reported for the benzo[*a*]pyrene (BAP) content of the spirulina test material..

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for benzo[*a*]pyrene (BAP) content of spirulina test sample





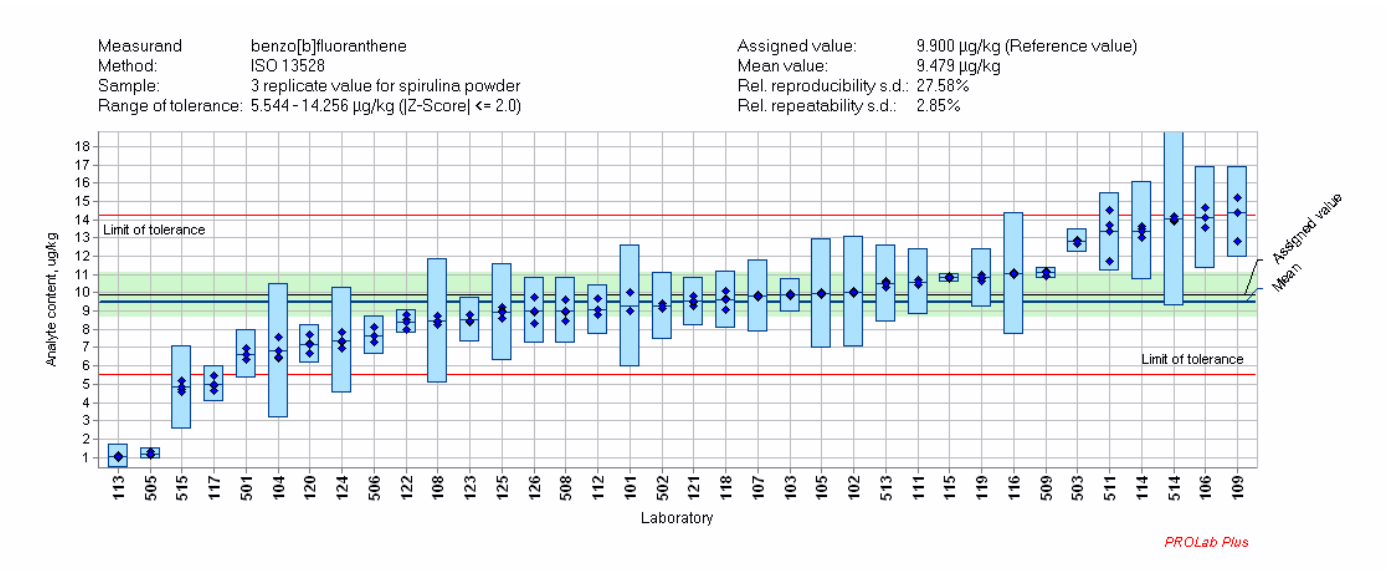
Results, as reported by participants, for the content of benzo[*a*]pyrene (BAP) in the spirulina test material.
Assigned value is 3.56±0.24 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Ref 1	Ref 2	Ref 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	BaP	3.2	3.2	3.2	3.2	40	GC-MS
102	BaP	3.43	3.52	4.08	3.68	34	HPLC-FLD
103	BaP	3.55	3.45	3.79	3.60	8.2	GC-MS
104	BaP	2.87	2.43	2.47	2.59	58	HPLC-FLD
105	BaP	3.499	3.567	3.407	3.5	30	HPLC-FLD
106	BaP	4.76	4.65	4.66	4.69	20	HPLC-FLD
107	BaP	4.24	4.13	4.16	4.18	22	n.r.
108	BaP	3.15	3.3	3.31	3.25	40	GC-MS
109	BaP	4.9	5.0	5.6	5.2	18.4	HPLC-FLD
110	BaP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	BaP	3.54	3.56	3.57	3.57	18.7	GC-MS
112	BaP	3.6	3.2	3.5	3.4	14	GC-MS/MS
113	BaP	2.411	2.214	2.658	2.488	60	GC-MS/MS
114	BaP	3.60	3.68	3.62	3.63	20	GC-MS/MS
115	BaP	4.196	3.963	4.075	4.08	9.1	GC-HRMS
116	BaP	4.0	4.0	3.9	4.0	20	GC-MS
117	BaP	1.82	1.74	2.13	1.90	20	HPLC-FLD
118	BaP	3.27	3.31	3.80	3.46	18.8	GC-MS/MS
119	BaP	3.78	3.93	3.77	3.83	10	GC-MS
120	BaP	2.19	2.64	2.69	2.51	22.6	HPLC-FLD
121	BaP	2.4	2.5	2.6	2.5	16	GC-MS
122	BaP	3.02	3.04	2.83	2.96	10	GC-MS
123	BaP	3.45	3.60	3.75	3.60	12	HPLC-FLD
124	BaP	3.130	3.681	3.317	3.376	52	HPLC-FLD
125	BaP	3.6	3.5	3.3	3.5	30	GC-MS/MS
126	BaP	4.09	4.36	4.68	4.38	18	HPLC-FLD
501	BaP	2.34	2.21	2.12	2.22	20	HPLC-FLD
502	BaP	3.29	3.43	3.3	3.3	20	HPLC-FLD
503	BaP	4.81	4.89	4.59	4.8	6.5	HPLC-FLD
504	BaP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
505	BaP	3.4	3.4	3.4	3.4	25	n.r.
506	BaP	2.98	2.88	2.56	2.77	11.7	HPLC-FLD
507	BaP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	BaP	2.93	3.18	3.45	3.19	20	GC-MS/MS
509	BaP	3.53	3.73	3.65	3.64	5.5	GC-MS/MS
510	BaP	4.25	4.39	4.31	n.r.	n.r.	HPLC-FLD
511	BaP	4.07	3.60	3.59	3.75	18.2	GC-MS
512	BaP	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	BaP	3.70	3.74	3.83	3.76	20	GC-MS
514	BaP	3.3	3.4	3.4	3.4	44	GC-MS
515	BaP	3.1	2.9	2.8	2.9	40	HPLC-FLD

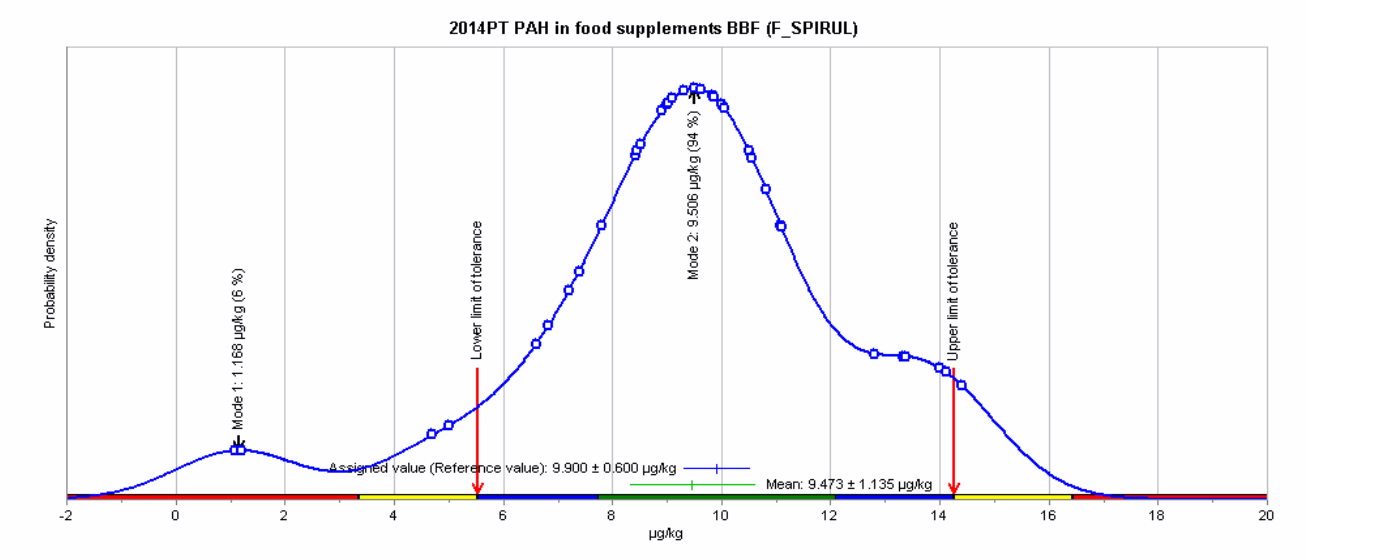
n.r.: not reported

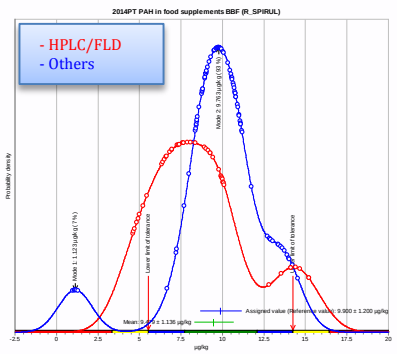
Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content of the spirulina test material..

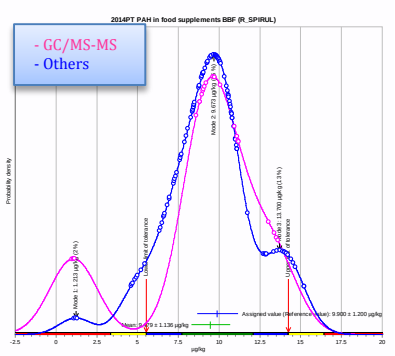
blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;

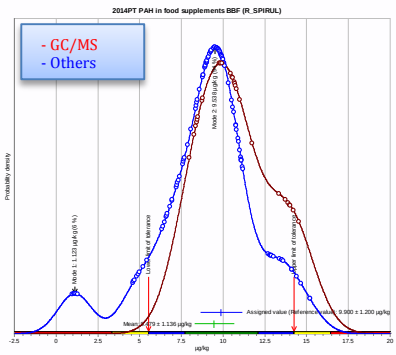


Kernel density plot of the reported values for proficiency assessment for benzo[*b*]fluoranthene (BBF) content of spirulina test sample









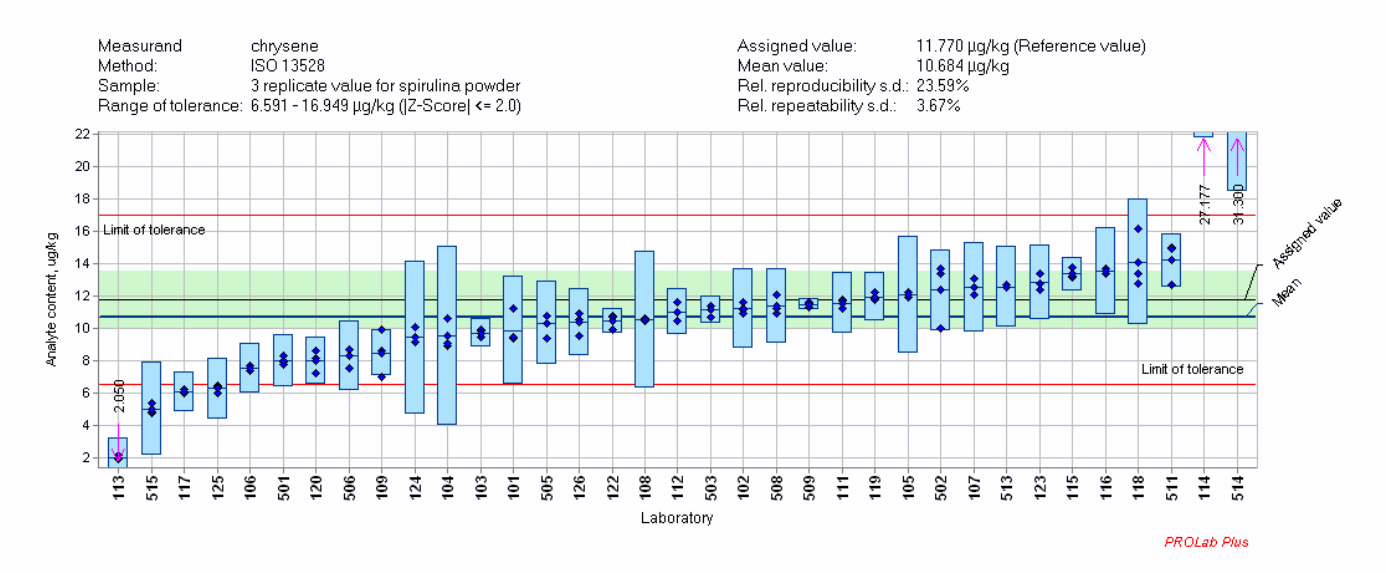
Results, as reported by participants, for the content of benzo[*b*]fluoranthene (BBF) in the spirulina test material.
Assigned value is 9.9±0.6 µg/kg**.** The uncertainty refers to the final value.

LCode	Measurand	Ref 1	Ref 2	Ref 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BbF	9.0	9.0	9.0	9.0	40	GC-MS
102	BbF	10.10	9.99	10.06	10.05	30	HPLC-FLD
103	BbF	9.79	9.84	9.94	9.86	9	GC-MS
104	BbF	7.59	6.39	6.49	6.82	54	HPLC-FLD
105	BbF	9.937	9.916	10.051	10	30	HPLC-FLD
106	BbF	14.67	13.54	14.11	14.11	20	HPLC-FLD
107	BbF	9.9	9.88	9.74	9.84	22	n.r.
108	BbF	8.37	8.26	8.74	8.46	40	GC-MS
109	BbF	12.8	15.2	15.2	14.4	17.2	HPLC-FLD
110	BbF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	BbF	10.70	10.46	10.56	10.56	17	GC-MS
112	BbF	8.8	8.8	9.7	9.1	15	GC-MS/MS
113	BbF	1.14	0.978	1.1	1.078	60	GC-MS/MS
114	BbF	13.60	13.52	13.03	13.38	20	GC-MS/MS
115	BbF	10.768	10.766	10.892	10.81	2.1	GC-HRMS
116	BbF	11.1	11.0	11.1	11.1	30.1	GC-MS
117	BbF	4.92	4.65	5.44	5.00	20	HPLC-FLD
118	BbF	9.71	10.08	9.04	9.61	16.5	GC-MS/MS
119	BbF	10.75	11.01	10.67	10.81	15	GC-MS
120	BbF	6.67	7.24	7.69	7.20	14.9	HPLC-FLD
121	BbF	9.3	9.5	9.8	9.5	14	GC-MS
122	BbF	7.98	8.5	8.78	8.42	8	GC-MS
123	BbF	8.39	8.43	8.77		14	HPLC-FLD
124	BbF	6.961	7.879	7.323	7.387	39	HPLC-FLD
125	BbF	9.2	9.0	8.6	8.9	30	GC-MS/MS
126	BbF	8.92	8.35	9.78	9.02	20	HPLC-FLD
501	BbF	6.94	6.61	6.33	6.60	20	HPLC-FLD
502	BbF	9.12	9.43	9.25	9.3	20	HPLC-FLD
503	BbF	12.91	12.70	12.90	12.8	1.8	HPLC-FLD
504	BbF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
505	BbF	1.1	1.3		1.2	25	
506	BbF	8.09	7.63	7.28	7.80	13.6	HPLC-FLD
507	BbF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	BbF	8.47	9.65	8.95	9.02	20	GC-MS/MS
509	BbF	11.16	11.18	10.92	11.09	2.6	GC-MS/MS
510	BbF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
511	BbF	13.73	11.74	14.54	13.34	16.2	GC-MS
512	BbF	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	BbF	10.33	10.64	10.59	10.5	20	GC-MS
514	BbF	13.9	14.0	14.2	14.0	34	GC-MS
515	BbF	5.2	4.7	4.6	4.7	47	HPLC-FLD

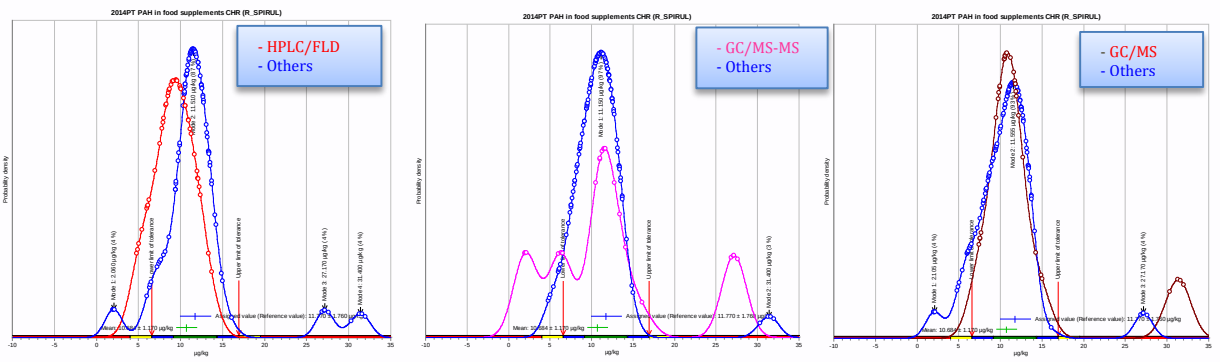
n.r.: not reported

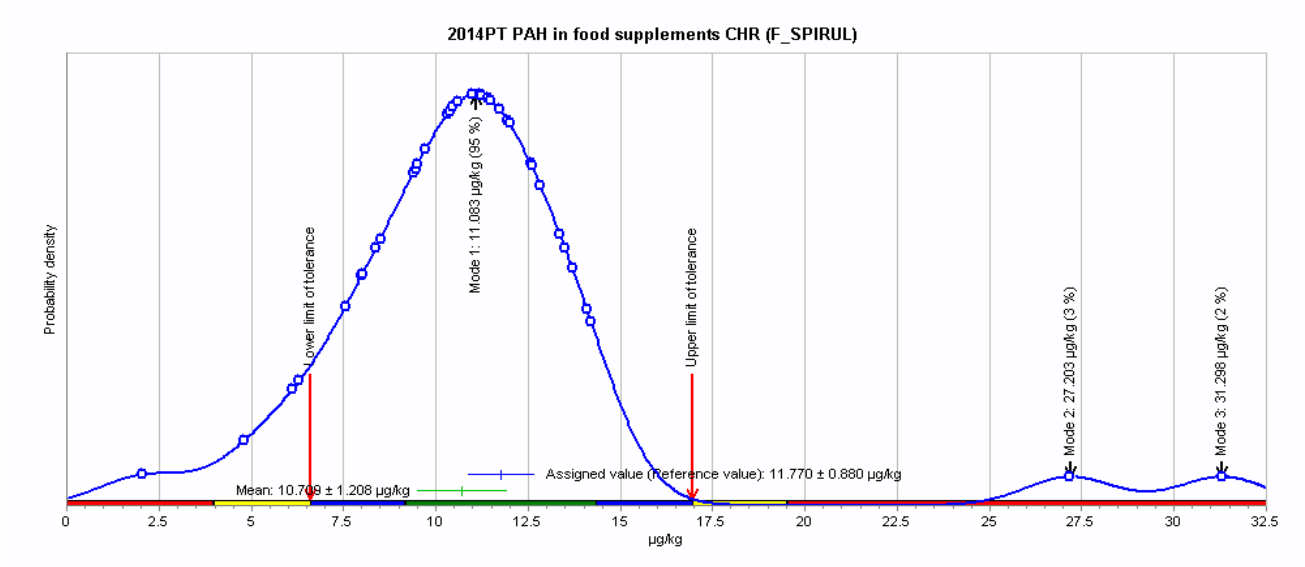
Distribution of individual results of replicate determinations, reported for the chrysene (CHR) content of the spirulina test material.

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for chrysene (CHR) content of spirulina test sample





Results, as reported by participants, for the content of chrysene (CHR) in the spirulina test material.

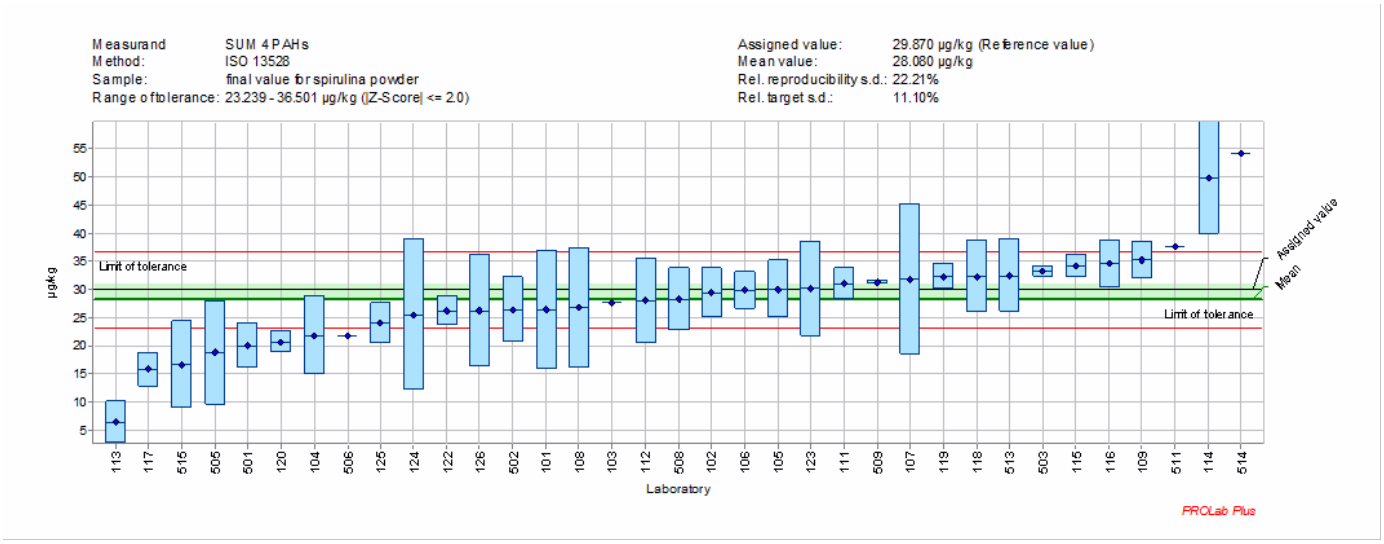
Assigned value is 11.77± 0.88 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Ref 1	Ref 2	Ref 3	Final value, µg/kg	Uncertainty, %	Analytical technique
101	CHR	9.4	9.4	9.5	9.4	40	GC-MS
102	CHR	11.14	10.95	11.65	11.24	22	HPLC-FLD
103	CHR	9.47	9.82	9.90	9.73	9.2	GC-MS
104	CHR	10.59	8.90	9.06	9.52	58	HPLC-FLD
105	CHR	12.224	12.074	11.958	12	30	HPLC-FLD
106	CHR	7.57	7.69	7.43	7.56	20.1	GC-MS/MS
107	CHR	13.06	12.1	12.52	12.56	22	n.r.
108	CHR	10.6	10.6	10.48	10.6	40	GC-MS
109	CHR	7.0	9.9	8.6	8.5	16.5	HPLC-FLD
110	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
111	CHR	11.77	11.22	11.72	11.72	16	GC-MS
112	CHR	10.5	11.0	11.6	11.0	13	GC-MS/MS
113	CHR	2.04	1.94	2.17	2.054	60	GC-MS/MS
114	CHR	26.83	27.07	27.63	27.18	20	GC-MS/MS
115	CHR	13.155	13.208	13.739	13.37	7.7	GC-HRMS
116	CHR	13.7	13.5	13.4	13.5	20	GC-MS
117	CHR	6.02	6.27	6.08	6.12	20	HPLC-FLD
118	CHR	13.38	16.11	12.77	14.09	27.4	GC-MS/MS
119	CHR	11.88	12.20	11.77	11.95	12.5	GC-MS
120	CHR	7.23	8.17	8.63	8.00	18	HPLC-FLD
121	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
122	CHR	9.92	10.75	10.73	10.47	7	GC-MS
123	CHR	12.37	12.74	13.38	3.60	18	HPLC-FLD
124	CHR	9.151	10.063	9.144	9.453	50	HPLC-FLD
125	CHR	6	6.5	6.4	6.3	30	GC-MS/MS
126	CHR	10.94	10.58	9.58	10.37	20	HPLC-FLD
501	CHR	8.28	7.93	7.81	8.02	20	HPLC-FLD
502	CHR	13.36	10.01	13.71	13.7	20	HPLC-FLD
503	CHR	11.40	11.38	10.72	11.2	6.9	HPLC-FLD
504	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
505	CHR	10.8	9.4	10.8	10.3	25	n.r.
506	CHR	8.67	8.72	7.53	8.37	25.6	HPLC-FLD
507	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
508	CHR	10.9	12.1	11.2	11.4	20	GC-MS/MS
509	CHR	11.29	11.52	11.64	11.48	3.1	GC-MS/MS
510	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
511	CHR	15.03	12.70	14.89	14.21	11.6	GC-MS
512	CHR	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
513	CHR	12.51	12.52	12.67	12.6	20	GC-MS
514	CHR	30.3	31.6	32.0	31.3	41	GC-MS
515	CHR	5.4	4.8	4.9	4.8	57	HPLC-FLD

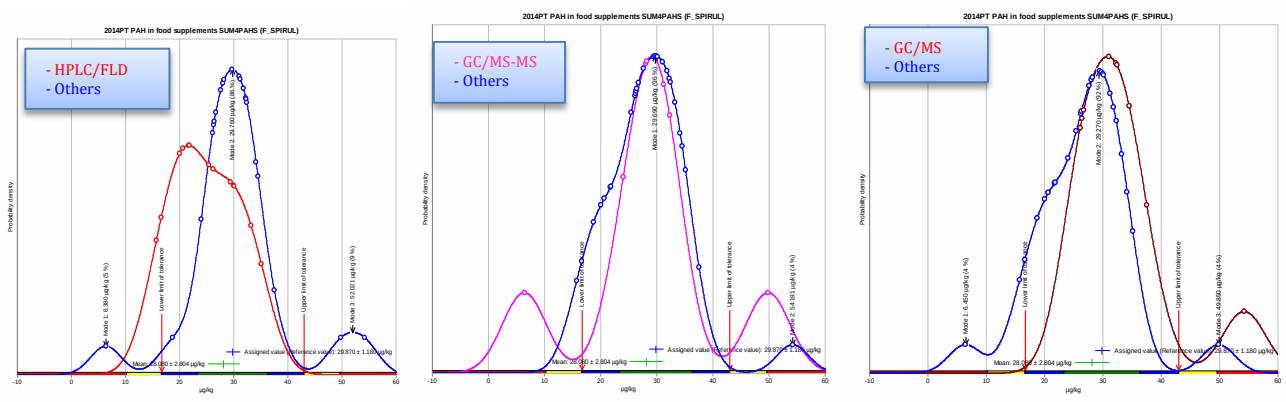
n.r.: not reported

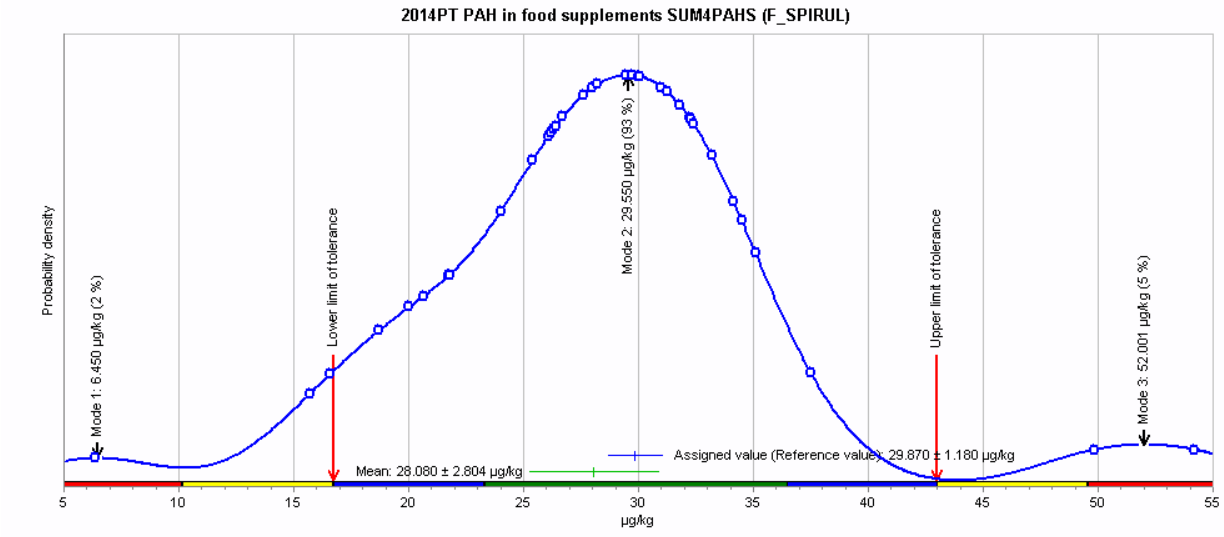
Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content of the spirulina test material.

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the sum of the 4 marker PAHs (SUM4PAH) content of spirulina test sample





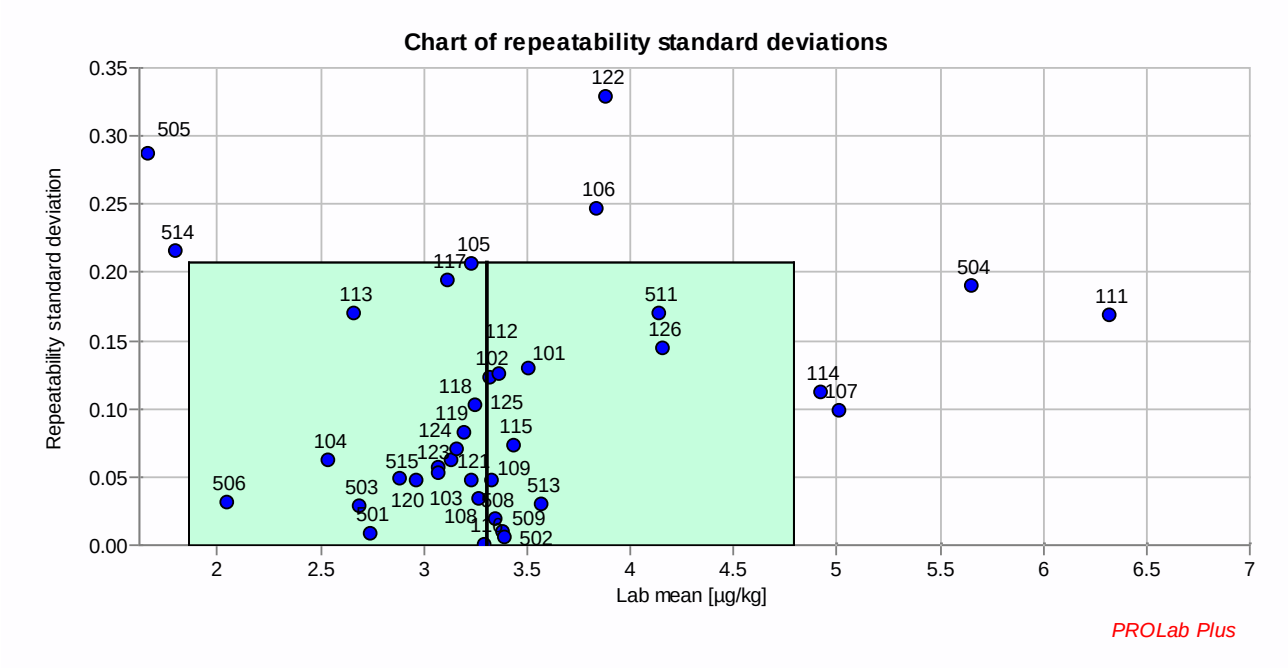
Results, as reported by participants, for the sum of the four markers PAHs (SUM4PAH) in the spirulina test material.
Assigned value is 29.87±1.13 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Final value, µg/kg	Uncertainty, %	Analytical technique
101	SUM 4 PAHs	26.4	40	GC-MS
102	SUM 4 PAHs	29.44	15	HPLC-FLD
103	SUM 4 PAHs	27.6	n.r.	n.r.
104	SUM 4 PAHs	21.72	32.4	HPLC-FLD
105	SUM 4 PAHs	30	17	HPLC-FLD
106	SUM 4 PAHs	29.75	12	n.r.
107	SUM 4 PAHs	n.r.	n.r.	n.r.
108	SUM 4 PAHs	26.7	40	GC-MS
109	SUM 4 PAHs	35.1	9.3	HPLC-FLD
110	SUM 4 PAHs	n.r.	n.r.	n.r.
111	SUM 4 PAHs	31.00	9.06	GC-MS
112	SUM 4 PAHs	28.0	27	GC-MS/MS
113	SUM 4 PAHs	6.369	60	GC-MS/MS
114	SUM 4 PAHs	49.82	20	GC-MS/MS
115	SUM 4 PAHs	34.15	6.1	GC-HRMS
116	SUM 4 PAHs	34.5	12.4	GC-MS
117	SUM 4 PAHs	15.7	20	HPLC-FLD
118	SUM 4 PAHs	32.26	20.1	GC-MS/MS
119	SUM 4 PAHs	32.23	7	GC-MS
120	SUM 4 PAHs	20.63	9.55	HPLC-FLD
121	SUM 4 PAHs	n.r.	n.r.	n.r.
122	SUM 4 PAHs	26.08	10	GC-MS
123	SUM 4 PAHs	n.r.	n.r.	n.r.
124	SUM 4 PAHs	25.407	53	HPLC-FLD
125	SUM 4 PAHs	24	15	GC-MS/MS
126	SUM 4 PAHs	26.19	38	HPLC-FLD
501	SUM 4 PAHs	20.02	20	HPLC-FLD
502	SUM 4 PAHs	26.3	22	n.r.
503	SUM 4 PAHs	33.2	3	HPLC-FLD
504	SUM 4 PAHs	n.r.	n.r.	n.r.
505	SUM 4 PAHs	18.7	50	n.r.
506	SUM 4 PAHs	21.77	n.r.	HPLC-FLD
507	SUM 4 PAHs	n.r.	n.r.	n.r.
508	SUM 4 PAHs	28.2	20	GC-MS/MS
509	SUM 4 PAHs	31.24	0.9	GC-MS/MS
510	SUM 4 PAHs	n.r.	n.r.	n.r.
511	SUM 4 PAHs	37.51	n.r.	GC-MS
512	SUM 4 PAHs	n.r.	n.r.	n.r.
513	SUM 4 PAHs	32.4	20	GC-MS
514	SUM 4 PAHs	54.2	n.r.	GC-MS
515	SUM 4 PAHs	16.6	47	HPLC-FLD

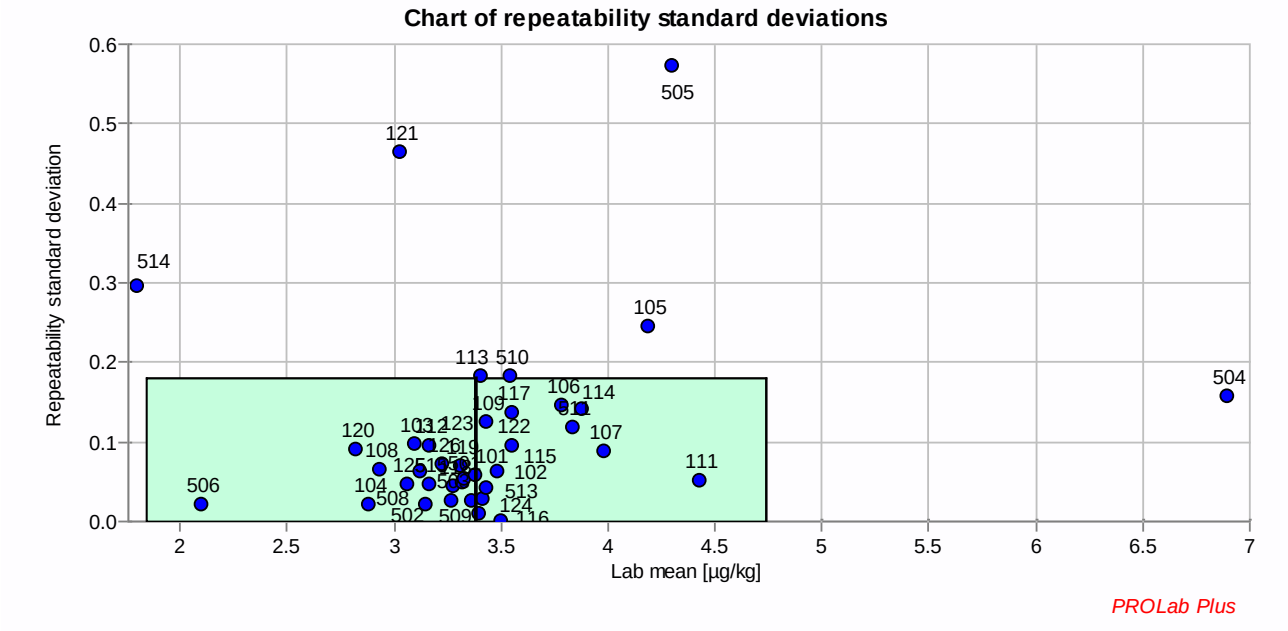
n.r: not reported

ANNEX 10: Laboratory means and repeatability standard deviation

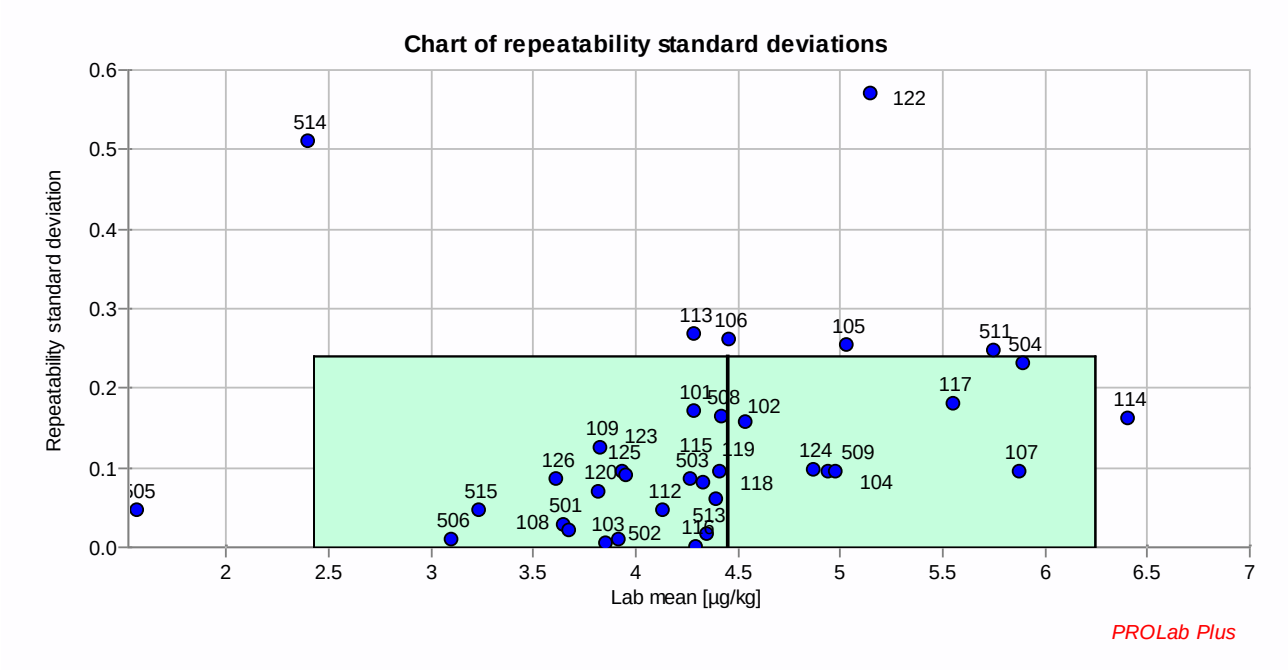
Lab means and repeatability standard deviation for the determination of BAA in the fish oil test material



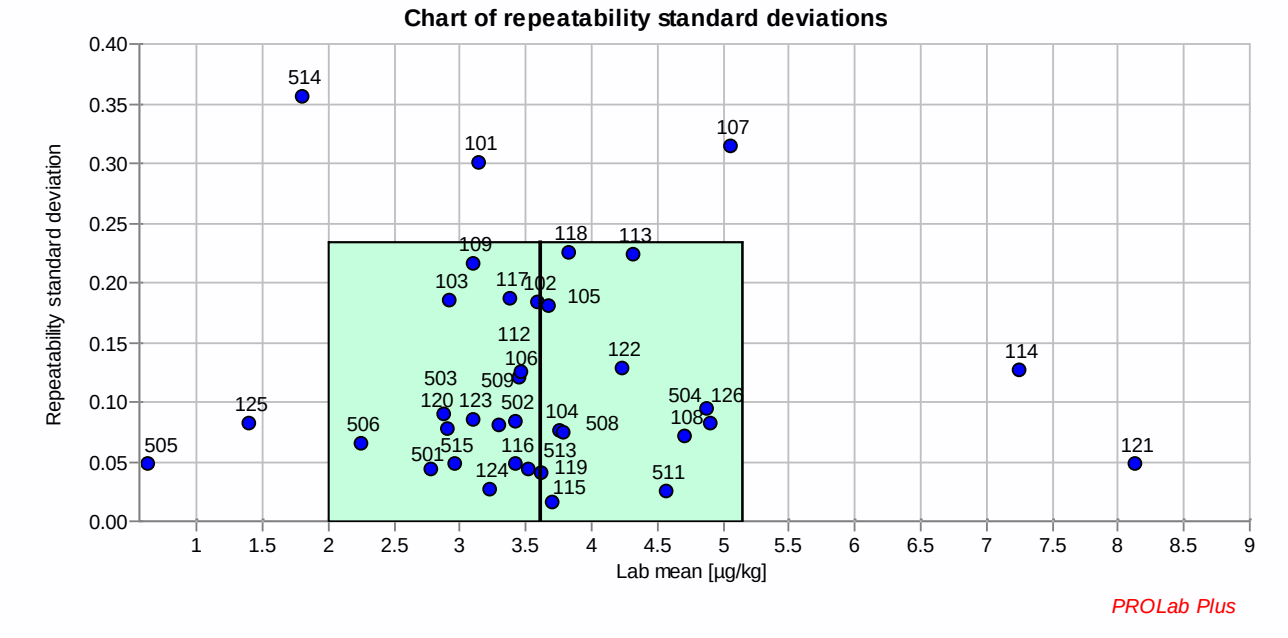
Lab means and repeatability standard deviation for the determination of BAP in the fish oil test material



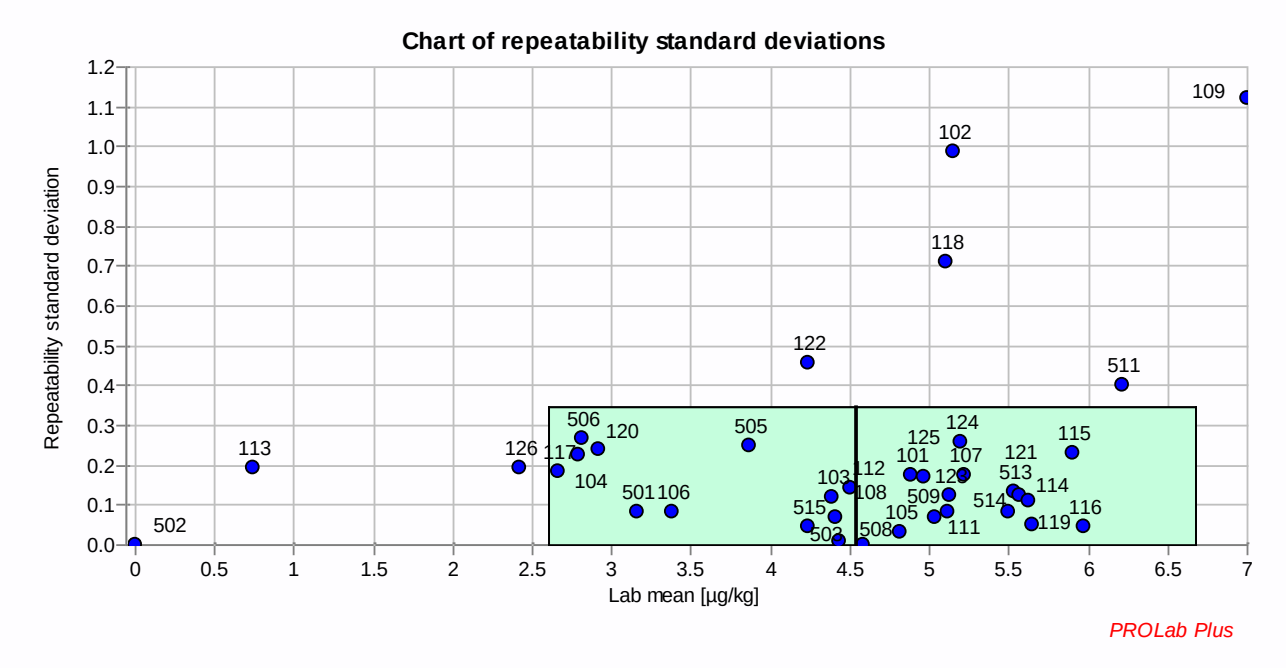
Lab means and repeatability standard deviation for the determination of BBF in the fish oil test material



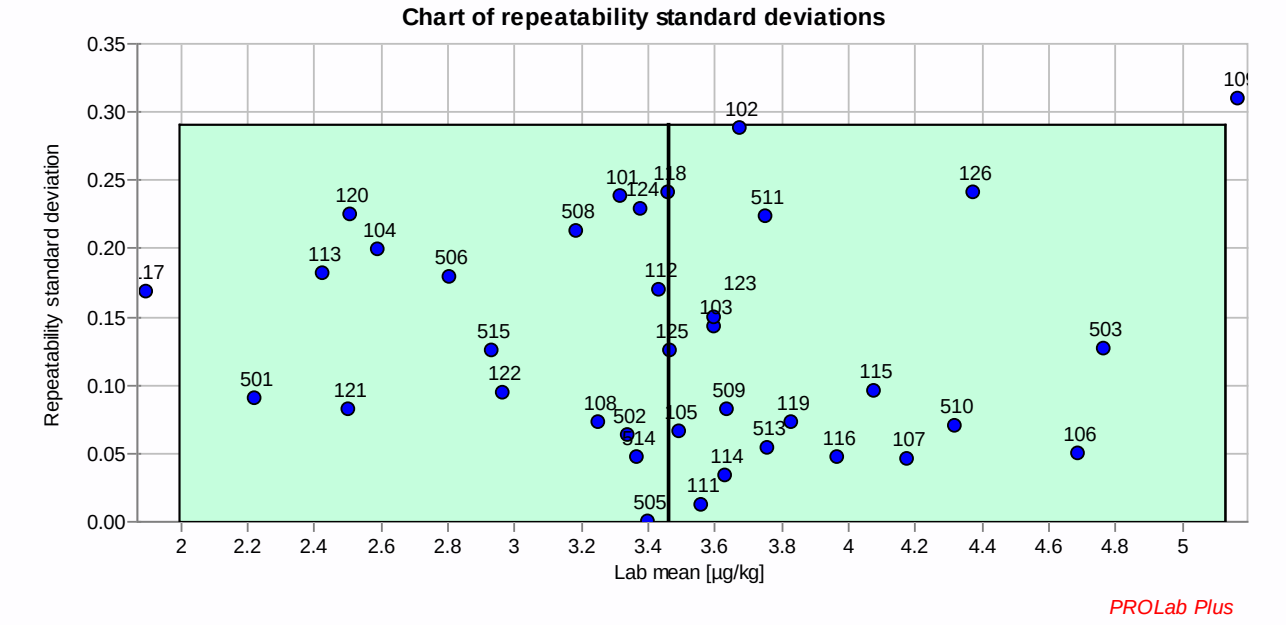
Lab means and repeatability standard deviation for the determination of CHR in the fish oil test material



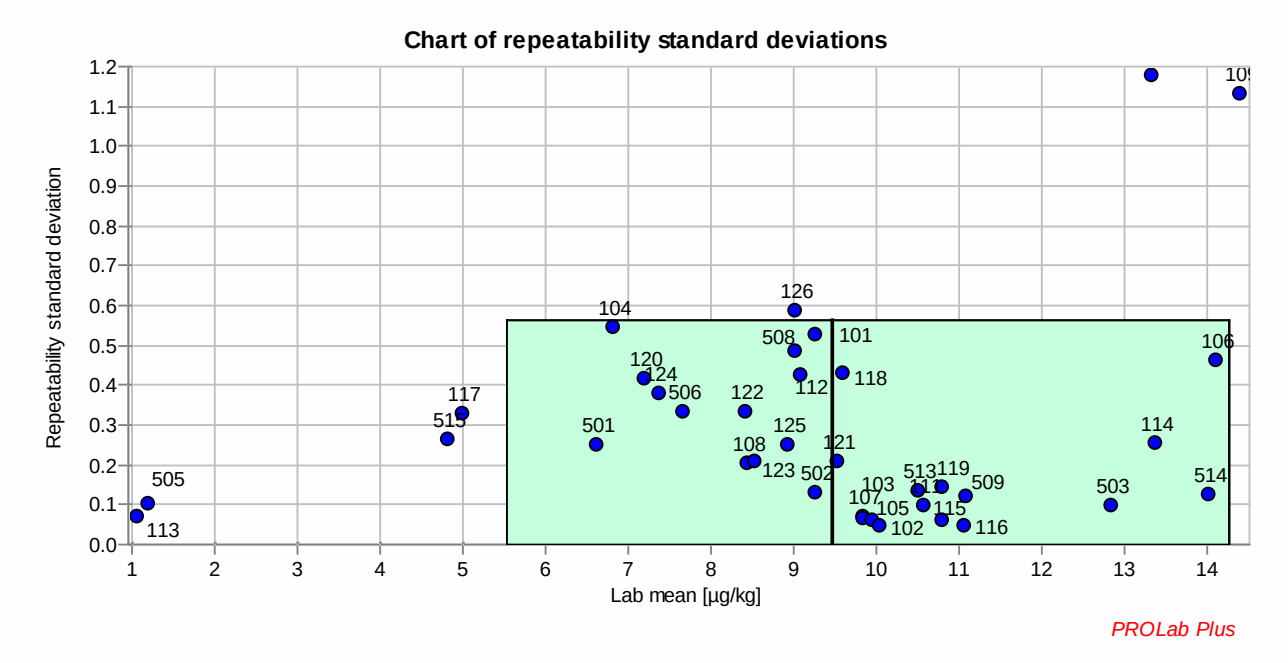
Lab means and repeatability standard deviation for the determination of BAA in the spirulina powder test material



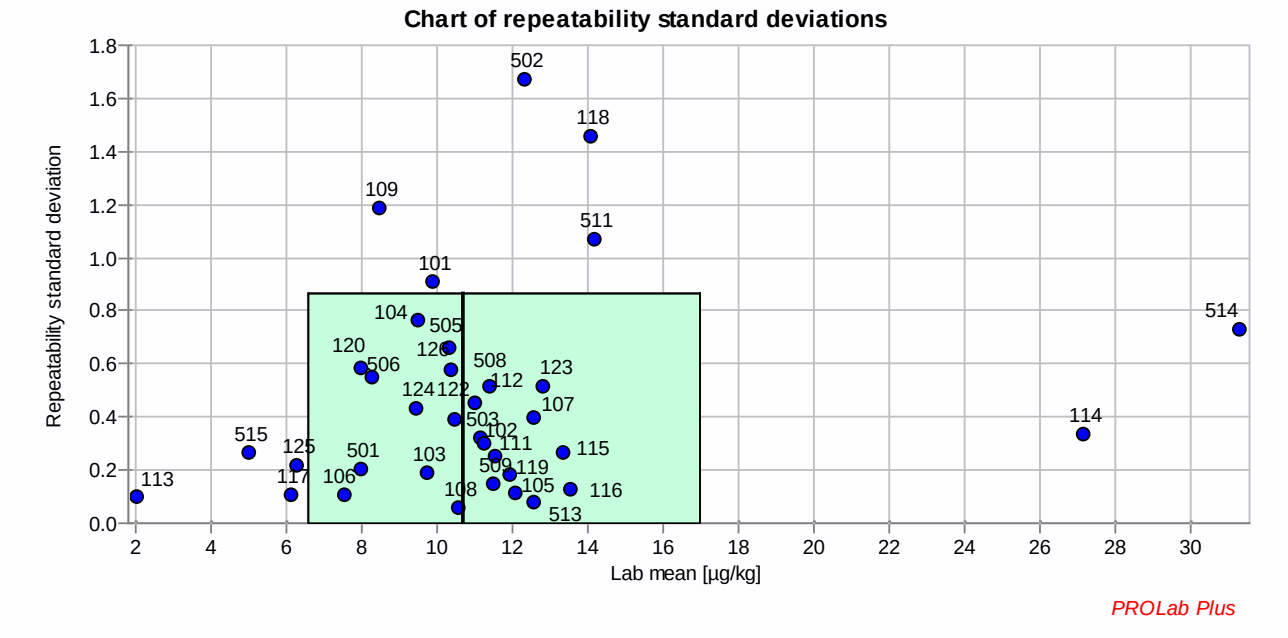
Lab means and repeatability standard deviation for the determination of BAP in the spirulina powder test material



Lab means and repeatability standard deviation for the determination of BBF in the spirulina powder test material



Lab means and repeatability standard deviation for the determination of CHR in the spirulina powder test material



European Commission
EUR 26847 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: **Report on the 14th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons - Four marker PAHs in food supplements**

Authors: Stefanka Bratinova, Zuzana Zelinkova, Thomas Wenzl

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