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Report on the 12th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in bivalve molluscs

Stefanka Bratinova, Zuzana Zelinkova, Lubomir Karasek and Thomas Wenzl

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1 Executive summary

This report presents the results of the twelfth inter-laboratory comparison (ILC) organised as a proficiency test (PT) by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAHs) 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 bivalve molluscs. It was conducted under ISO Standard 17043 accreditation and the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.

In agreement with the National Reference Laboratories, the test materials used in this exercise were lyophilised as well as frozen mussels. Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with disclosed PAH content for the verification of their instrument calibration.

Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States were admitted as participants. Twenty-six NRLs and 19 OCLs subscribed for participation.

The assigned values and their uncertainty were determined from in-house measurements by the EURL PAH applying bracketing calibration on two different days.

Participants were free to choose the method of analysis. The four EU marker PAHs were chosen as target analytes as limits for their sum were recently introduced in European legislation. The performance of the participating laboratories in the determination of the target PAHs in the test materials was expressed by z-scores. Additionally, the compliance of reported method performance characteristics was checked against specifications given in legislation.

This proficiency test demonstrated the competence of the participating laboratories in the analysis of regulated PAHs in a bivalve molluscs matrix. More than 70 % of the reported test results were graded with z-scores that were below an absolute value of 2, 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.

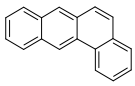
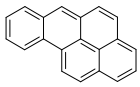
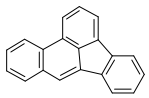
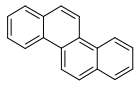
In 2002 the European Commission's Scientific Committee on Food identified 15 individual PAHs as being of major concern for human health. These 15 EU priority PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene (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 bivalve molluscs. 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 ILC was 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	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

All 26 NRLs registered for participation reported results.

Table 3: List of participating Official Food Control Laboratories

Institute	*Country*
Institut für Umwelt und Lebensmittelsicherheit	AUSTRIA
IDAC	FRANCE
LDA 22	FRANCE
LDA 56	FRANCE
LEAV - Laboratoire de l'environnement et de l'alimentation de Vendée	FRANCE
SCL MASSY	FRANCE
Laboratoire Départemental de la Sarthe	FRANCE
LUFA-ITL GmbH	GERMANY
Chemisches Untersuchungsamt Hagen	GERMANY
CVUA-MEL	GERMANY
Thüringer Landesamt für Verbraucherschutz	GERMANY
Chemisches und Veterinäruntersuchungsamt Freiburg	GERMANY
Landesbetrieb Hessisches Landeslabor	GERMANY
Chemisches und Veterinäruntersuchungsamt Rheinland	GERMANY
Istituto Zooprofilattico Sperimenatle delle Venezie	ITALY
Istituto Zooprofilattico Sperimentale del Mezzogiorno	ITALY
Istituto Zooprofilattico sperimentale reg. Lazio e Toscana	ITALY
Food & Consumer Products Safety Authority	NETHERLANDS
GV.CONSELLERIA SANIDAD. Centro Salud Pública	SPAIN

All 19 registered for participation OCLs reported results.

5 Time frame

The design of the ILC was agreed with the NRLs at the EURL PAH workshop in Prague on the 14-15th of May 2013. It was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on the 29th of May 2013 (see ANNEX 2). Test samples were dispatched (see ANNEX 3) on the 08th of July 2013 and the deadline for reporting of results was set to the 9th of September 2013. The documents sent to the participants 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 freeze dried (lyophilized) mussels and fresh frozen mussels. This matrices are representative for the food category 6.1.6 " Smoked sprats and canned smoked sprats (sprattus sprattus); bivalve molluscs (fresh, chilled or frozen); heat treated meat and heat treated meat products sold to the final consumer" specified in Commission Regulation (EC) No 835/2011, with a maximum level for BAP and for the sum of the four PAHs (in the following indicated as SUM4PAH) of 5.0 µg/kg and 30.0 µg/kg respectively.

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.

The freeze dried mussel material was purchased from the International Atomic Energy Agency (IAEA) provided with a provisional certificate for the assessed "reference values" according to several criteria [10]. It has been used in the Interlaboratory comparison (IAEA-432), organized by the Marine Environment Laboratory, Monaco. The material was tested for homogeneity and stability at IAEA. The values listed in the certificate were established on the basis of statistically valid results submitted by the laboratories which participated in the ILC. The details concerning the criteria for qualification as recommended or information value can be found in the report IAEA/AL/146 (10).

The frozen mussel test item was prepared by the EURL PAH laboratory starting from three kilos of mussels, acquired at a local supermarket. The mussels were ground in a slurry and homogenized. Subsample is separated for blank sample. The rest of the slurry is spiked with a PAH standard solution containing the four EU marker PAHs at the levels given in table 5. After spiking, the test sample was homogenized over night by intensive stirring. Aliquots of about 30 g of the slurry were packed into amber glass screw cap vials and stored in the freezer.

The standard solution was 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 substance on a microbalance and solution 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 under inert atmosphere and flame sealed in 2 ml amber glass ampoules.

7.2 Homogeneity and stability

Homogeneity of the freeze dried mussels was not evaluated by the EURL PAH as it was assumed homogeneous on the basis of the information given in the certificate by IAEA.

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

Homogeneity experiments included duplicate analysis of 10 samples randomly selected among the ampoules prepared for dispatch along the packing sequence. The duplicate analysis were performed in random order. The test material was rated sufficiently homogenous and no trend was observed. Details of the homogeneity tests are given in ANNEX 6.

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 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 was stored at the recommended condition - freezer (~ -20C°) for frozen mussels and room temperature (22C°) for frieze dried mussels. The second set of 3 samples was stored at better conditions for the whole period of the study - freezer (~ -80C°) and fridge (~ 4 C°) respectively. The third set of 3 samples was stored at both temperatures (recommended and more favourable conditions) for the half of the period. At the end of the test period, all 9 samples were analysed in duplicate.

No significant difference of the analyte contents among the test samples was found. Hence stability of the samples over the whole period can be assumed under the recommended conditions (ANNEX 6)

7.3 Assigned value and standard deviation for proficiency assessment

As for the freeze dried mussels (IAEA-432) the values reported in the Reference sheet [10] are recommended values, they were not considered as assigned values (Annex 7).

The assigned values and their associated uncertainties for both materials were determined by the EURL PAH applying bracketing calibration in two different analysis sessions with two bracketing standards from totally independent sources - NIST SRM 2260a and neat certified reference materials BCR® from IRMM. The analytical method applied was fully validated by ILC study accredited method [12] (WI-0344), which is presented to CEN for standardization and will become EN standard in a short time. All the results showed good agreements among them within their associated uncertainties.

The assigned values for the individual analytes in the frozen mussels were in good correlations with the gravimetrical preparation concentrations, corrected for the purity of the reference materials and the content of the PAHs measured in blank mussels (Table 5).

The assigned value for the sum of PAH 4 was calculated from the individual assigned values, and its corresponding uncertainty was calculated from the uncertainties of the individual assigned values according to equation 1

Equation 1 $$u_{sum} = \sqrt{u_{BAA}^2 + u_{BAP}^2 + u_{BBF}^2 + u_{CHR}^2}$$ [13]

where u_{sum} refers to the standard uncertainty associated to the sum of the four PAHs and u_{BAA}, u_{BAP}, u_{BBF}, and u_{CHR} refer to the standard uncertainty of the individual analytes

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 lyophilised mussels test item, expressed on product basis.

		Assigned value	U	σ_P	
Analyte	**Analyte short name**	**µg/kg**	**µg/kg**	**µg/kg**	**%**
Benz[*a*]anthracene	BAA	**3.12**	**0.35**	**0.64**	20.6
Chysene	CHR	**5.66**	**0.54**	**1.14**	20.2
Benzo[*b*]fluoranthene	BBF	**4.91**	**0.57**	**0.99**	20.2
Benzo[*a*]pyrene	BAP	**0.77**	**0.12**	**0.21**	27.9
Sum of the four marker PAHs	SUM4PAH	**14.46**	**0.87**	**1.66**	11.5

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

	Spiking level	Blank [1]	Assigned value	U	σ_P	
Analyte	**µg/kg**	**µg/kg**	**µg/kg**	**µg/kg**	**µg/kg**	**%**
BAA	3.51	0.11	**3.66**	**0.25**	**0.75**	20.41
CHR	4.99	0.30	**5.28**	**0.29**	**1.07**	20.20
BBF	4.77	0.17	**4.85**	**0.42**	**0.98**	20.24
BAP	3.89	-	**3.99**	**0.34**	**0.81**	20.35
SUM4PAH	17.15	0.58	**17.78**	**0.66**	**1.82**	10.24

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 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 frozen mussels test sample as well as the lyophilized mussels test material. The test materials were shipped in 4 kg parcels full with dry ice.

[1] The values are in the range of LODs and are only indicative for the presence of the analytes in the blank

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.

Some results were reported as smaller than a certain threshold value. However some of the threshold values (often LOQ) didn't comply with the legislative requirements. In those cases the results were not evaluated. For cases where reported threshold values were close to the legislative requirements, results were rated assuming the threshold value as content value.

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. In contrast to z-scores, 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. For the SUM parameter the agreement between reported standard measurement uncertainties and the combined standard uncertainty of the four EU marker PAHs was evaluated. The latter was derived via the law of uncertainty propagation from the

uncertainties reported for the individual analytes. 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 45 reporting participants was 1530. They submitted in total 1526 results, which equals to 99.7 %. 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 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 8) for some of the parameters (CHR and SUM4PAHs in both matrices) fall outside the confidence interval for the assigned value, while for the other parameters (BAA in lyophilized mussels, BAP in frozen mussels) they are exactly on the lower limit. Robust standard deviations of the PT for 4 markers PAHs in frozen mussels are significantly lower than target standard deviations, while for PAHs in lyophilized mussels the robust SDs are higher than the target level. The difference in the robust standard deviations for both test items could be explained with the fact that the 4 markers PAHs were spiked in frozen mussels, while for freeze dried mussels they were naturally incurred.

82 % of the results reported by the participants obtained a satisfactory z-score (81% for NRLs and 84% for OCLs). 20 participants have 100% (10) of satisfactory z-scores, while 13 participants (29%) have less than 80% satisfactory z-scores.

Figure 1 and Figure 2 provide overviews of the z-scores assigned to the results for freeze dried and frozen mussels 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 questionable and unsatisfactory scores, the corresponding score values are presented next to the triangles.

The numerical values of the calculated z-scores are compiled in Table 6 for both mussels 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.

Some laboratories had major problems with the determination of the target PAHs in both matrices, e.g. participants 109, 115 underestimated the analyte contents for all measurands in frozen mussels and for most of the measurands in lyophilized mussels. Other participants experienced problems only with one of the matrices, overestimating the content of all of the 4 markers PAHs only in the frozen mussels sample (lab.118) or only in freeze dried sample (lab 112). It should be noted that for the four labs (109, 112, 115, 118) the results were equally biased for all measurands, with the exception of BAP in the lyophilized sample for lab 112,

where the bias is one order of magnitude higher. Hence these participants shall scrutinize their analysis procedure for systematic error, which might be caused by biased instrument calibration, by wrong aliquotation, calculation errors, wrong recovery estimation etc.

Comparing both matrices, the percentage of successful z-score is higher for frozen mussels (85%) then for lyophilized mussels (80%). However the number of unsatisfactory z-scores is equal for both matrices, whereas the number of attributed questionable z-scores was higher for results reported for lyophilized mussels.

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 less favourable picture. 70.7 % for NRLs and 69.5% for OCLs of the zeta-scores assigned for the four individual analytes and for the SUM4PAH were within the satisfactory performance range. 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.

Consequently the laboratories perform according to internationally agreed standards, which form the basis for the z-scores, but seem to have difficulties in estimating realistic measurement uncertainty values. The establishment of proper measurement uncertainty values caused problems especially for the SUM parameter. Twenty two out of 46 participants reported for this parameter values much higher than the value which is derived by the law of uncertainty propagation.

Hence the EURL PAHs will continue to pay special attention to this parameter, in the ILCs to come, as it has major implications on the assessment of compliance of food with European 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.

As could be seen from the Kernel density plots the distribution of results are typically Gaussian only for BAP in both matrices. For other analytes the distributions were closed to Gaussian but with visible shoulders corresponding to mass fractions lower than the reported by the majority of participants. In most of the cases the major modes are closer to the assigned (reference) value, than the robust mean, which demonstrates an underestimation from some participants.

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. It would be very much appreciated if they would report back to the EURL PAH the identified reason for the deviations

Figure 1: 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 frozen and freeze dried mussels test material.

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 performance categories.

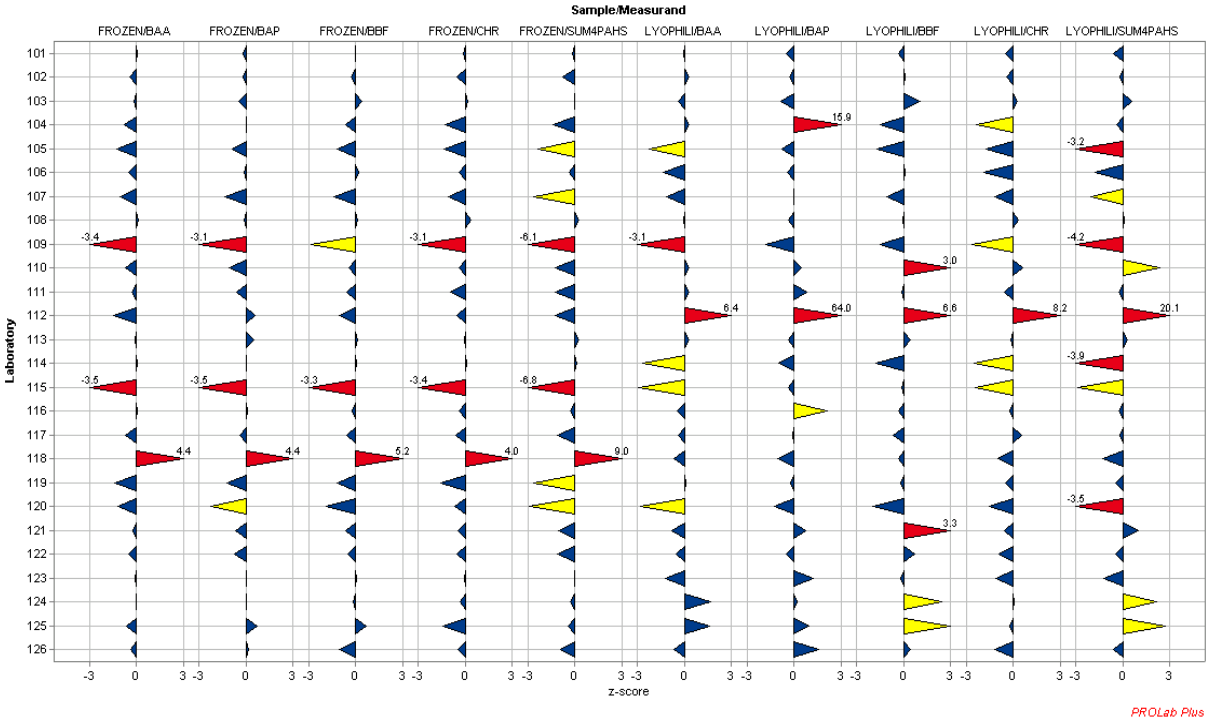


Figure 2: Graphical presentation of **z-scores** corresponding to the "final values for proficiency assessment" reported by the OCLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the frozen and freeze dried mussels test material.

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.

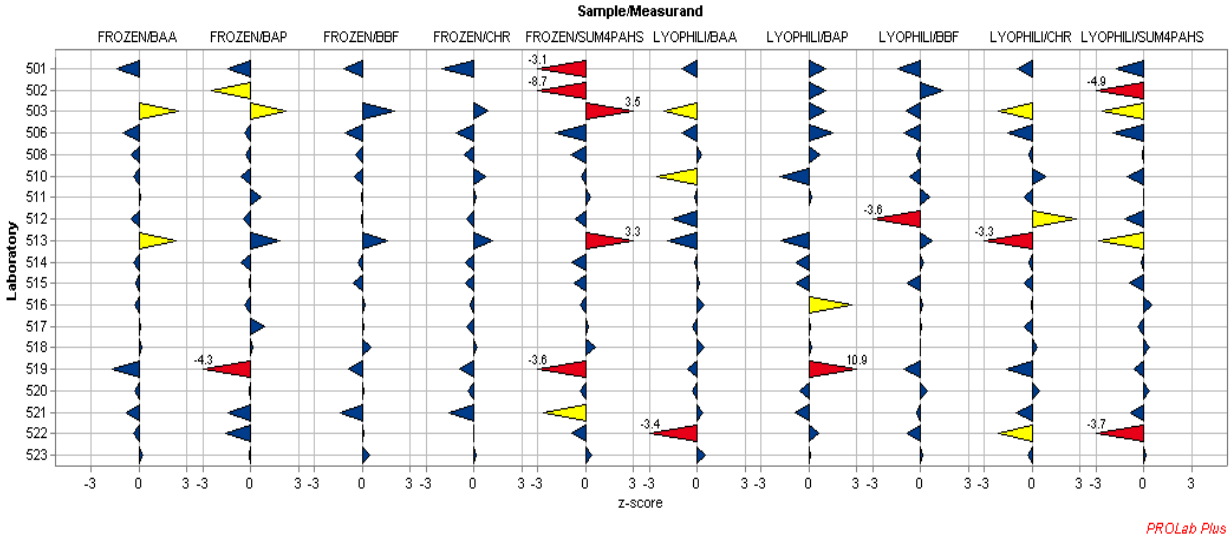


Table 6: Compilation of z-scores calculated from the "final values" reported by the participants for test material the two test items: *z-scores outside the satisfactory range (|z| > 2) are indicated by red (unsatisfactory) and yellow (questionable) background; empty cells - z-score not calculated*

	Sample/Measurand									
Lab Code	FROZEN / BAA	FROZEN / BAP	FROZEN / BBF	FROZEN / CHR	FROZEN/ SUM4PAHS	LYOPHILI / BAA	LYOPHILI / BAP	LYOPHILI / BBF	LYOPHILI / CHR	LYOPHILI/ SUM4PAHS
	NATIONAL REFERENCE LABORATORIES (NRLs)									
101	0.0	-0.2	0.0	-0.1	-0.1	0.0	-0.4	-0.3	-0.5	-0.6
102	-0.5	-0.2	-0.3	-0.6	-0.8	0.3	-0.3	0.1	-0.4	-0.2
103	-0.2	-0.5	0.4	0.1	0.0	-0.4	-0.8	1.1	0.3	0.6
104	-0.7	0.0	-0.6	-1.3	-1.4	0.3	16.0	-1.6	-2.4	-0.4
105	-1.3	-0.9	-1.2	-1.3	-2.3	-2.3	-0.8	-1.7	-1.8	-3.2
106	-0.5	-0.1	0.2	-0.4	-0.4	-1.3	-0.4	0.1	-1.9	-1.8
107	-1.0	-1.3	-1.4	-1.1	-2.6	-1.1	0.0	-1.1	-1.2	-2.1
108	0.1	-0.2	0.1	0.3	0.3	0.0	-0.4	-0.1	0.3	0.1
109	-3.4	-3.1	-2.8	-3.1	-6.1	-3.1	-1.8	-1.5	-2.7	-4.2
110	-0.7	-1.1	-0.5	-0.4	-1.2	0.3	0.4	3.0	0.6	2.4
111	-0.3	-0.6	-0.6	-1.0	-1.2	0.3	0.8	-0.1	-0.6	-0.3
112	-1.5	0.6	-1.1	-0.5	-1.2	6.4	64.1	6.6	8.2	20.1
113	-0.1	0.5	0.2	-0.1	0.2	0.3	-0.2	0.4	-0.1	0.3
114	0.0	0.1	0.0	0.1	0.1	-2.7	-1.0	-1.8	-2.5	-3.9
115	-3.5	-3.5	-3.3	-3.4	-6.8	-2.9	-0.4	-0.1	-2.4	-2.9
116	0.1	0.1	-0.2	-0.4	-0.3	-0.5	2.1	-0.3	-0.3	-0.3
117	-0.7	-0.4	-0.6	-0.6	-1.1	-0.4	-0.1	-0.7	0.5	-0.2
118	4.4	4.5	5.2	4.0	9.0	-0.7	-1.0	-0.4	-1.0	-1.3
119	-1.4	-1.2	-1.2	-1.5	-2.6	0.1	-0.2	-0.2	-0.5	-0.5
120	-1.2	-2.2	-1.9	-0.7	-2.9	-2.8	-1.3	2.0	-1.5	-3.5
121	-0.2	-0.7	-0.1	-0.5	-1.0	0.0	1.8	3.3	-0.9	1.0
122	-0.5	-0.7	-0.5	-0.5	-1.1	-0.6	-0.5	0.7	-0.9	-0.5
123	-0.1	0.1	0.1	-0.1	0.0	-1.2	-1.2	-0.2	-1.2	-1.2
124	0.0	0.0	-0.1	-0.4	-0.3	1.7	0.2	2.4	0.0	2.1
125	-0.7	0.7	0.6	-1.4	-0.5	1.6	0.9	3.0	-0.2	2.7
126	-0.4	0.1	-1.1	-0.4	-0.9	-0.6	1.5	0.4	-1.2	-0.6
	OFFICIAL CONTROL LABORATORIES (OCLs									
501	-1.4	-1.5	-1.2	-2.0	-3.1	-0.9	1.1	-1.4	-0.9	-1.7
502		-2.5			-8.7		1.1	1.4		-4.9
503	2.5	2.2	2.0	0.9	3.5	-2.1	1.1	-0.9	-2.2	-2.6
506	-1.0	-0.4	-1.1	-1.2	-1.9	-1.0	1.5	-1.1	-1.6	-1.9
508	-0.5	-0.4	-0.5	-0.6	-1.0	0.3	0.7	-0.2	-0.2	-0.1
510	-0.4	-0.7	-0.5	0.7	-0.3	-2.5	-1.9	-0.7	0.8	-1.1
511	0.1	0.7	0.0	0.1	0.3	-0.2	0.1	0.6	-0.5	0.0
512	-0.5	-0.5	0.0	-0.5	-0.6	-1.6	-1.3	-3.6	2.8	-1.2
513	2.4	1.8	1.6	1.1	3.3	-2.0	-1.6	0.7	-3.3	-2.8
514	-0.4	-0.6	-0.3	-0.5	-0.9	-0.2	-0.8	0.2	-0.2	-0.2
515	-0.2	-0.1	-0.5	-0.5	-0.8	0.1	-0.7	-0.8	-0.5	-0.9
516	-0.3	-0.4	0.2	-0.3	-0.4	0.4	2.7	0.1	-0.1	0.5
517	0.1	0.6	0.1	-0.4	0.2	-0.2	0.1	0.0	-0.4	-0.4
518	0.2	0.2	0.6	0.2	0.6	0.4	0.3	0.0	0.3	0.4
519	-1.6	-4.3	-0.9	-0.9	-3.6	-0.6	10.9	-1.1	-1.6	-0.6
520	-0.4	-0.1	0.1	-0.4	-0.3	-0.3	-0.6	0.4	0.5	0.4
521	-0.8	-1.5	-1.4	-1.6	-2.6	0.3	-0.9	-0.2	-1.0	-0.8
522	-0.3	-1.6	0.1	-0.1	-0.9	-3.4	0.6	-0.8	-2.1	-3.7
523	0.2	-0.1	0.5	0.1	0.4	0.5	0.1	0.2	-0.3	0.1

Table 7: Compilation of zeta-scores calculated from the "final values" reported by the NRLs and OCLs for test item frozen mussels, the combined reported standard measurement uncertainty of the assigned value, and the uncertainty of the analyte content of the test item:

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	3.66	±	0.25	3.99	±	0.34	4.85	±	0.42	5.28	±	0.29	17.78	±	0.66
	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score
Lab code	µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg	
	National Reference Laboratories (NRLs)														
101	3.68	0.58	0.1	3.86	0.67	-0.3	4.87	0.83	0.0	5.12	0.81	-0.3	17.53	1.47	-0.3
102	3.32	0.5	-1.0	3.83	0.57	-0.4	4.57	0.69	-0.5	4.69	0.59	-1.4	16.41	1.18	-1.5
103	3.53	0.48	-0.4	3.61	0.38	-1.0	5.21	0.68	0.7	5.43	0.61	0.4	17.78	1.1	0.0
104	3.1	1.2	-0.9	4	1.6	0.0	4.2	1.7	-0.7	3.9	1.6	-1.6	15.2	6.1	-0.8
105	2.72	0.46	-2.8	3.3	0.59	-1.5	3.68	0.74	-2.1	3.84	0.77	-3.0	13.54	1.3	-4.6
106	3.29	0.5	-1.0	3.89	0.59	-0.2	5.07	0.77	0.4	4.86	0.74	-0.9	17.11	3.34	-0.4
107	2.9	0.88	-1.5	2.9	0.88	-2.0	3.5	1	-2.1	4.1	1.2	-1.8	13	2	-4.0
108	3.78	0.76	0.3	3.9	0.78	-0.2	4.95	0.99	0.2	5.65	1.13	0.6	18.29	3.66	0.3
109	1.09	0.16	-9.8	1.47	0.2	-7.1	2.07	0.28	-6.3	1.95	0.26	-10.5	6.6	0.9	-14.0
110	3.16	0.63	-1.2	3.09	0.62	-2.0	4.41	0.88	-0.7	4.86	0.98	-0.7	15.52	1.59	-2.2
111	3.47	0.9	-0.4	3.49	0.59	-1.1	4.31	0.91	-0.9	4.25	0.98	-1.8	15.52	1.71	-2.1
112	2.57	0.3	-3.7	4.46	0.4	1.2	3.81	0.4	-2.2	4.71	0.4	-1.6	15.55	1.5	-2.2
113	3.6	0.9	-0.1	4.4	0.8	0.8	5	1.6	0.2	5.2	1.1	-0.1	18.2	2.2	0.3
114	3.69	0.2	0.1	4.03	0.37	0.1	4.89	0.59	0.1	5.34	0.12	0.2	17.95	0.7	0.2
115	1.05	0.26	-9.3	1.14	0.29	-7.7	1.58	0.4	-7.0	1.64	0.41	-10.2	5.41	1.35	-13.1
116	3.72	0.75	0.1	4.05	0.81	0.1	4.64	0.94	-0.3	4.84	0.98	-0.8	17.25	1.75	-0.5
117	3.13	0.78	-1.1	3.67	0.73	-0.6	4.3	0.63	-1.0	4.61	0.63	-1.6	15.7	3.9	-1.0
118	6.98	1.56	4.1	7.59	1.43	4.5	9.97	1.64	5.6	9.57	2.62	3.2	34.11	6.86	4.7
119	2.61	0.6	-2.7	3	0.7	-2.0	3.7	0.7	-2.1	3.64	0.7	-3.6	12.96	1.4	-5.0
120	2.78	0.56	-2.3	2.18	0.29	-4.9	3.02	0.51	-3.7	4.53	0.91	-1.4	12.51	2.5	-3.7
121	3.5	0.3	-0.5	3.47	0.3	-1.4	4.23	0.4	-1.3	4.75	0.5	-1.4	15.9	0.5	-2.7
122	3.27	0.37	-1.3	3.4	0.4	-1.5	4.36	0.66	-0.9	4.71	0.62	-1.3	15.8	1.06	-2.3
123	3.59	0.93	-0.1	4.03	1.37	0.1	4.92	1.48	0.1	5.21	1.15	-0.1	17.75	2.5	0.0
124	3.63	0.69	-0.1	4.02	0.8	0.1	4.72	1	-0.2	4.9	1	-0.7	17.26	1.77	-0.5
125	3.172	0.673	-1.2	4.568	0.412	1.5	5.482	0.91	1.0	3.739	0.772	-3.2	16.961	2.768	-0.5
126	3.4	1.02	-0.5	4.1	1.23	0.2	3.8	1.14	-1.5	4.8	1.45	-0.6	16.1	2.44	-1.2
	Official Control Laboratories (OCLs)														
501	2.6	0.1	-4.2	2.8	0.1	-3.5	3.7	0.1	-2.7	3.1	0.1	-7.4	12.2	0.8	-7.2
502	<5	n.r.		2	n.r.		<5	n.r.		<5	n.r.		2	n.r.	
503	5.5	n.r.		5.8	n.r.		6.8	n.r.		6.2	n.r.		24.2	n.r.	
506	2.9	1.27	-1.1	3.64	1.6	-0.4	3.78	1.66	-1.2	4.03	1.77	-1.3	14.35	3.17	-2.0
510	3.37	1.01	-0.5	3.46	1.04	-0.9	4.33	1.3	-0.7	6.07	1.82	0.8	17.24	5.2	-0.2
508	3.3	0.7	-0.8	3.7	0.7	-0.6	4.4	0.9	-0.7	4.6	0.9	-1.3	16	3.2	-1.0
511	3.7	1.6	0.0	4.5	2	0.5	4.8	2.1	0.0	5.4	2.4	0.1	18.4	2.4	0.5
512	3.3	0.3	-1.2	3.6	0.4	-1.0	4.8	0.7	-0.1	4.8	0.3	-1.5	16.6	3.4	-0.6
513	5.4	0.8	3.7	5.5	0.9	2.7	6.4	1	2.4	6.5	1	2.1	23.8	3.7	3.1
514	3.366	1.01	-0.5	3.517	1.055	-0.8	4.593	1.378	-0.3	4.703	1.411	-0.8	16.179	4.854	-0.6
515	3.5	0.7	-0.4	3.9	0.6	-0.2	4.3	0.6	-1.1	4.7	0.9	-1.1	16.4	3.3	-0.8
516	3.43	0.69	-0.5	3.65	0.73	-0.7	5.01	1	0.2	4.99	1	-0.5	17.08	1.73	-0.6
517	3.72	0.93	0.1	4.69	1.03	1.1	4.92	0.54	0.1	4.8	0.53	-1.2	18.13	4.17	0.2
518	3.8	1.7	0.2	4.1	1.8	0.1	5.4	2.4	0.4	5.5	2.5	0.2	18.9	8.3	0.3
519	2.4	0.5	-3.6	0.5	0.1	-10.2	3.96	0.7	-1.6	4.3	0.8	-2.0	11.2	2.2	-5.1
520	3.43	0.33	-0.8	3.92	0.47	-0.2	4.94	0.71	0.2	4.87	0.31	-1.2	17.16	1.79	-0.6
521	3.06	0.2	-2.2	2.8	0.05	-3.5	3.51	0.19	-3.1	3.59	0.27	-5.3	12.96	0.71	-6.4
522	3.4	1.02	-0.5	2.69	0.81	-2.5	4.92	1.48	0.1	5.23	1.57	-0.1	16.23	4.87	-0.6
523	3.84	0.09	0.7	3.91	0.12	-0.2	5.3	0.95	0.7	5.42	0.25	0.4	18.47	1.29	0.7

Table 8: Compilation of zeta-scores calculated from the "final values" reported by the NRLs and OCLs for test item freeze dried (lyophilized) mussels, the combined reported standard measurement uncertainty of the assigned values and the uncertainty of the analyte content of the test item**:**

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	3.12	±	0.35	0.77	±	0.12	4.91	±	0.57	5.66	±	0.54	14.46	±	0.87
	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score
Lab code	µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg	
	National Reference Laboratories (NRLs)														
101	3.1	0.49	0.0	0.67	0.21	-0.6	4.6	0.8	-0.4	5.1	0.83	-0.8	13.47	1.27	-0.9
102	3.31	0.5	0.4	0.71	0.09	-0.5	4.99	0.75	0.1	5.18	0.65	-0.8	14.19	1.12	-0.3
103	2.86	1.32	-0.3	0.59	0.27	-1.0	5.96	2.86	0.7	5.97	2.6	0.2	15.38	4.09	0.4
104	3.3	1.3	0.2	4.1	1.6	4.1	3.4	1.4	-1.7	3	1.2	-3.3	13.8	5.5	-0.2
105	1.68	0.28	-3.8	0.6	0.11	-1.3	3.22	0.64	-2.6	3.63	0.73	-3.1	9.13	1.02	-5.3
106	2.27	0.34	-2.2	0.68	0.1	-0.7	5.01	0.76	0.1	3.54	0.54	-3.5	11.49	2.24	-2.1
107	2.4	0.73	-1.4	0.77	0.23	0.0	3.8	1.1	-1.4	4.3	1.3	-1.6	11	1.9	-2.7
108	3.1	0.62	0.0	0.7	0.14	-0.5	4.83	0.97	-0.1	6.02	1.2	0.4	14.64	2.93	0.1
109	1.12	0.03	-5.7	0.394	0.02	-3.1	3.4	0.45	-2.5	2.63	0.05	-5.6	7.56	0.39	-7.7
110	3.3	0.66	0.4	0.86	0.17	0.6	7.9	1.58	3.1	6.35	1.27	0.8	18.41	2.14	2.9
111	3.3	0.86	0.3	0.94	0.17	1.2	4.8	1.01	-0.1	4.97	1.14	-0.9	14.02	1.76	-0.4
112	7.2	0.7	8.2	14.22	1.5	17.7	11.43	1	8.6	14.96	1.5	10.1	47.81	4	15.3
113	3.3	0.8	0.3	0.7	0.1	-0.5	5.3	1.6	0.4	5.5	1.1	-0.2	14.9	2.1	0.3
114	1.42	0.12	-4.8	0.56	0.05	-1.7	3.18	0.33	-2.9	2.84	0.48	-4.8	8	0.6	-7.0
115	1.25	0.31	-4.9	0.693	0.173	-0.5	4.79	1.2	-0.1	2.9	0.73	-4.2	9.63	2.41	-3.2
116	2.81	0.57	-0.7	1.21	0.25	2.5	4.61	0.93	-0.4	5.38	1.09	-0.4	14.02	1.56	-0.4
117	2.86	0.64	-0.5	0.75	0.18	-0.1	4.25	0.58	-1.0	6.23	0.83	0.8	14.09	3.3	-0.2
118	2.69	0.6	-0.9	0.55	0.1	-1.7	4.55	0.75	-0.5	4.52	1.24	-1.4	12.31	2.47	-1.4
119	3.17	0.7	0.1	0.72	0.2	-0.3	4.72	0.9	-0.3	5.06	0.9	-0.9	13.68	1.5	-0.7
120	1.34	0.27	-4.7	0.5	0.09	-2.1	2.96	0.5	-3.1	3.91	0.78	-2.6	8.61	1.72	-4.8
121	2.62	0.2	-1.4	0.92	0.1	1.2	8.13	0.8	4.6	5.02	0.5	-1.1	16.1	0.5	1.8
122	2.76	0.31	-0.9	0.66	0.08	-0.9	5.6	0.85	1.0	4.64	0.61	-1.6	13.7	1.1	-0.7
123	2.35	0.61	-1.7	1.03	0.35	1.2	4.7	1.41	-0.2	4.34	0.96	-1.8	12.43	1.84	-1.6
124	4.2	0.8	2.0	0.81	0.29	0.2	7.29	1.54	2.5	5.7	1.16	0.1	18	2.11	2.6
125	4.143	0.879	1.8	0.963	0.087	1.5	7.864	1.305	3.4	5.405	1.117	-0.3	18.95	3.388	2.4
126	2.7	0.82	-0.8	1.1	0.32	1.7	5.3	1.59	0.4	4.3	1.28	-1.6	13.4	2.22	-0.8
	Official Control Laboratories (OCLs)														
501	2.5	1	-1.0	1	0.4	1.0	3.5	1.2	-1.7	4.6	1.9	-1.0	11.6	0.2	-3.3
502	<5	n.r.		<1	n.r.		6.3	n.r.		<5	n.r.		6.3	n.r.	
503	1.8	n.r.		1	n.r.		4	n.r.		3.2	n.r.		10.1	n.r.	
506	2.5	1.1	-1.0	1.08	0.47	1.2	3.84	1.69	-1.0	3.88	1.71	-1.8	11.3	2.69	-2.0
508	3.3	0.7	0.4	0.91	0.18	0.9	4.7	0.9	-0.3	5.4	1.1	-0.3	14.3	2.8	-0.1
510	1.49	0.45	-3.9	0.38	0.11	-3.0	4.21	1.26	-0.8	6.61	1.98	0.8	12.7	3.8	-0.8
511	3	1.3	-0.2	0.8	0.4	0.1	5.5	2.4	0.4	5.1	2.2	-0.5	14.4	2.4	0.0
512	2.1	0.2	-2.8	<0.5	n.r.		1.3	0.2	-6.2	8.8	0.6	5.1	12.5	2.6	-1.3
513	1.9	0.3	-3.2	0.4	0.06	-3.0	5.6	0.9	1.0	1.9	0.3	-6.7	9.8	2.3	-3.2
514	3.021	0.906	-0.2	0.611	0.183	-1.1	5.096	1.529	0.2	5.44	1.632	-0.2	14.168	4.25	-0.1
515	3.2	0.6	0.2	0.6	0.1	-1.3	4.1	0.6	-1.3	5.1	1	-0.8	13	2.6	-0.9
516	3.38	0.68	0.5	1.33	0.27	3.1	5.03	1	0.2	5.61	1.12	-0.1	15.35	1.67	0.7
517	2.94	0.73	-0.4	0.79	0.17	0.1	4.97	0.55	0.1	5.11	0.56	-0.9	13.81	3.18	-0.4
518	3.4	1.5	0.3	0.8	0.4	0.1	4.9	2.2	0.0	6	2.7	0.2	15.1	6.7	0.2
519	2.73	0.5	-0.9	3.05	0.6	7.1	3.85	0.7	-1.6	3.83	0.8	-2.7	13.47	2.6	-0.6
520	2.94	0.28	-0.5	0.65	0.08	-0.9	5.3	0.76	0.6	6.22	0.53	0.9	15.11	1.58	0.6
521	3.34	0.3	0.6	0.58	0.05	-1.6	4.68	0.33	-0.4	4.5	0.46	-2.0	13.1	1.14	-1.3
522	0.95	0.29	-5.7	<0.9	n.r.		4.1	0.82	-1.2	3.28	0.98	-3.3	8.33	1.67	-5.1
523	3.45	0.28	0.9	0.79	0.01	0.2	5.07	0.12	0.3	5.37	0.22	-0.5	14.69	0.64	0.2

9.4 Evaluation of compliance with legislation

The performance characteristics of the methods used by the participants are listed in ANNEX 8.

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]. Non compliant values for LOD, LOQ, and recovery are indicated by bold red font.

One NRL and 2 OCLs reported non-compliant LOD/LOQ and two participants (1NRLs and 1 OCL) didn't report any LOD/LOQ values.

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 %.

Consequently all participants reporting method performance characteristics that do not comply with the minimum performance characteristics specified in legislation shall identify and implement for their analytical methods possibilities for improvement, or shall apply a different, more appropriate analysis procedure.

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

9.5 Additional information extracted from the questionnaire

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

Eight participants (5 NRLs and 3OCLs) reported that the applied method was not accredited. 18 participants (13 NRLs and 5 OCLs) in total declared that mussels are not within the scope of their accreditation.

Regarding the experience of the laboratories with this kind of analysis, 16 NRLs and 7 OCLs, which is 50% of the participants, don't analysed more than 10 samples per year, indicating that they do not perform the analysis on a routine basis (Figure 3).

More than half of the participants (NRLs and OCLs) used HPLC/FLD and 1 lab LC/MS for determination of PAHs (Figure 4). The rest of participants used GC with different types of mass spectrometric detection. The analysis of all data revealed that laboratory performance was not linked to any analytical technique or sample preparation method used.

A survey on the instrument calibration reveal that 10 participant didn't use internal standards. However those are mainly laboratories applying HPLC/FLD as measurement technique and only one laboratory using GC-MS/MS, applying matrix matched calibration. Ten participants reported the application of standard addition technique.

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.

The EURL will set up follow-up measures in due time for all NRLs that received for at least one of the four PAHs (BAA, BAP, BBF, and CHR) z-scores > |3| as required by Regulation (EC) 882/2004, and by the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with European Union Reference Laboratories (EURLs) activities". These laboratories shall perform as an immediate

action root-cause-analysis, and shall report to the EURL PAH in writing the identified cause for their underperformance as well as the corrective actions that they are going to take. Additionally, EURL strongly recommend their participation to an independent (non-EURL) proficiency test on the determination of PAHs in food and further communication to the EURL PAH of the outcome of this exercise.

Figure 3. Experience of the participants in the analysis of PAH in mussels expressed as number of analyses per years

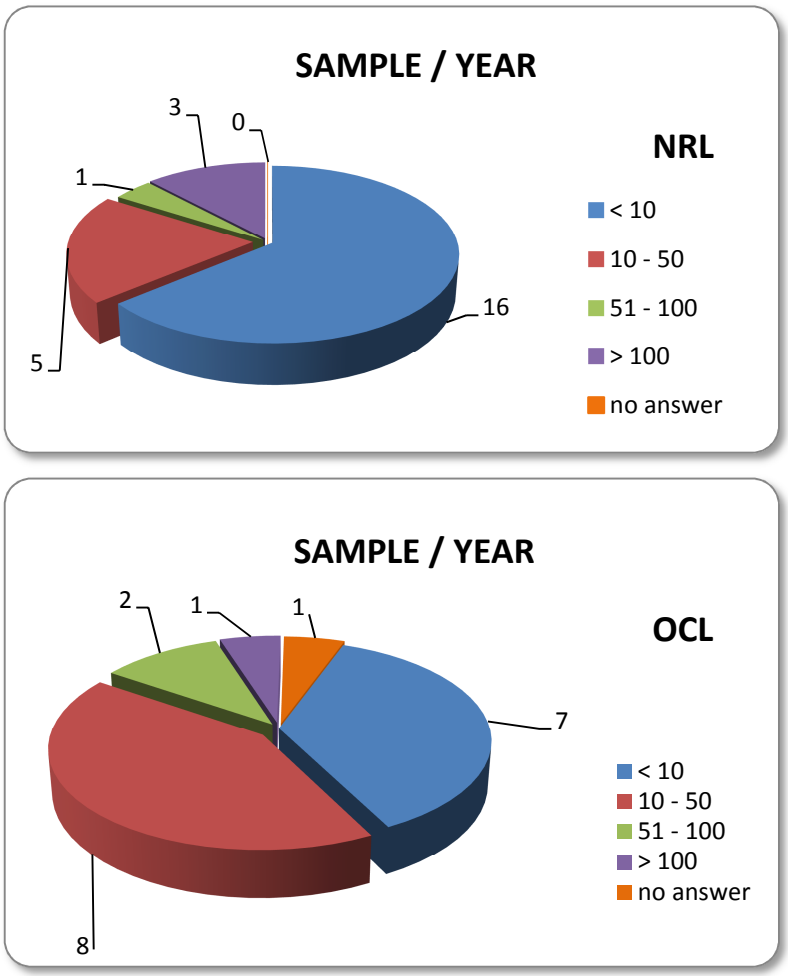
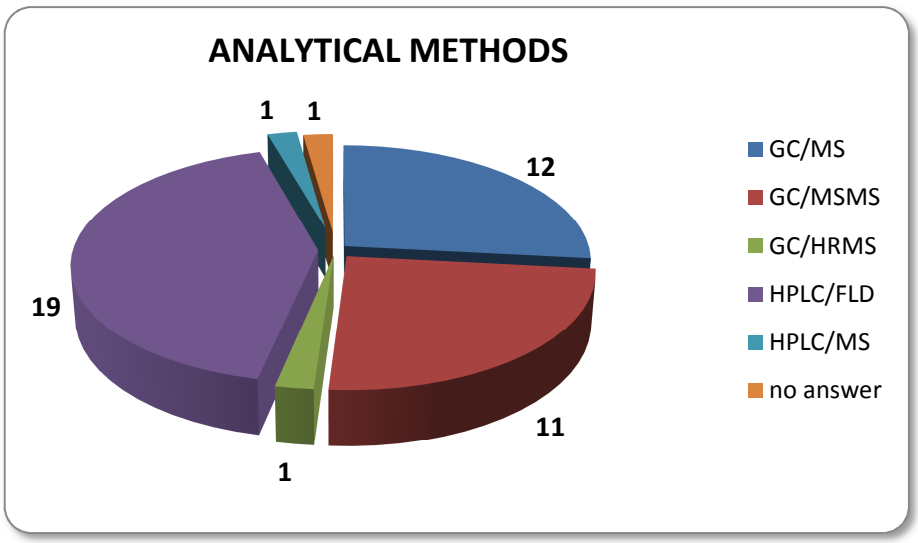


Figure 4. Application of different instrumental techniques for determination of PAH in mussels.



11 Conclusions

Forty-five participants reported analysis results. The performance of most participants was satisfactory. In total 81% and 82% of the results reported by NRLs and OCLs respectively obtained a satisfactory z-score. However, significant bias can be concluded from the pattern of performance indicators of some laboratories.

A few laboratories from OCLs did not report measurement uncertainties. They are urged to improve in this respect as this parameter is essential for compliance assessment and required by the accreditation bodies.

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 encouraged to verify the compliance to legislation of both the method and the modality of data reporting in use at their laboratory.

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 and all NRLs and OCLs for their cooperation.

13 References

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

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10. *REFERENCE SHEET REFERENCE MATERIAL IAEA-432 ORGANOCHLORINE COMPOUNDS AND PETROLEUM HYDROCARBONS IN A MUSSEL HOMOGENATE, 2004, IAEA, Marine Environmental Laboratory, Monaco*. http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/ Organic_Contaminants_/IAEA-432.htm

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 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

14 ANNEXES

ANNEX 1 – Announcement of the PT on the IRMM webpage

ANNEX 2 – Announcement via e-mail and invitation

ANNEX 3 – Announcement of material dispatch

ANNEX 4 – Documents sent to participants

ANNEX 5 – Technical specifications of the calibration solutions

ANNEX 6 – Homogeneity of the test material

ANNEX 7 - Reference sheet of the IAEA-432

ANNEX 8 – Questionnaire and method performance data

ANNEX 9 – Data reported by participants

ANNEX 10 - Laboratory means and repeatability standard deviation

ANNEX 1: Announcement of the PT on the IRMM webpage

EU-RL PT 1060: PAHs in bivalve molluscs

Proficiency Test on the determination of 4 marker PAHs in mussels

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

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 bivalve molluscs and to perform compliance assessment according to the corresponding legislative limits.

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 300 (three hundred) per registration for OCLs, which do not have NRL status

Test material and analytes

The set of test samples will consist of:

a) an amber glass vial containing about 15 g of lyophilized mussels sample, and
b) an amber glass vial containing about 30 g of frozen mussels,

for the determination of the EU marker PAHs (see Table 1).

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.

Table 1: The target analytes of the comparison:

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

General outline

Participants are requested to perform three independent analyses of the edible oil. 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.

At the end participants will be ask to perform compliance assessment according to the corresponding legislative limits.

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

Performance assessment:

The performance of the participants in the determination of PAHs in bivalve molluscs 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 P - values of the individual analytes, applying the law of uncertainty propagation.

Registration

Registration shall be done via https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=1060

Schedule

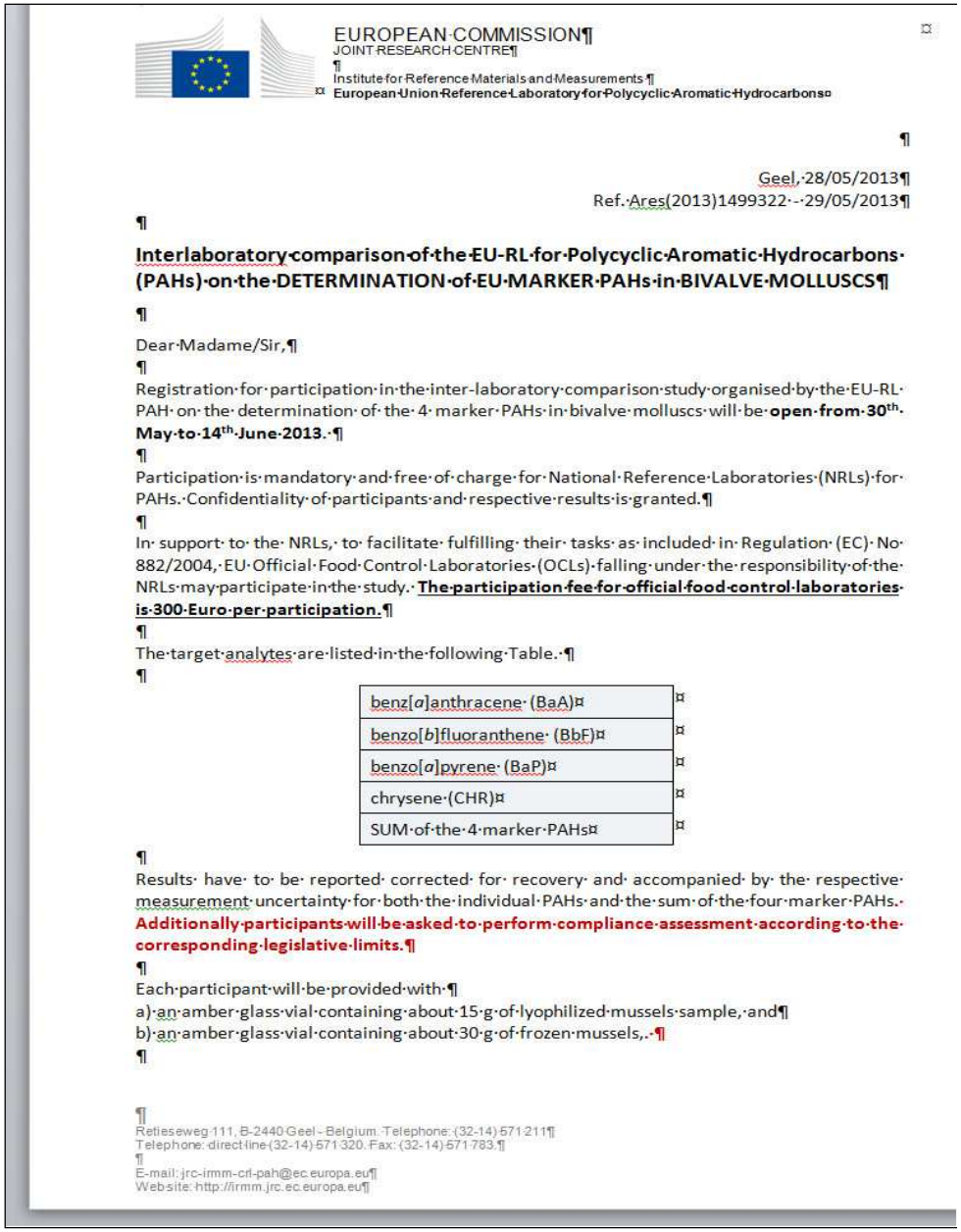
Registration deadline	Sample dispatch	Reporting of results	Report
14 June 2013	Beginning July 2013	Beginning of September 2013	December 2013

Contacts

Jrc-irmm-eurl-pah@ec.europa.eu

Latest update 31 May, 2013

ANNEX 2: Announcement of the PT via e-mail



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 28/05/2013
Ref. Ares(2013)1499322 - 29/05/2013

Interlaboratory comparison of the EU-RL for Polycyclic Aromatic Hydrocarbons (PAHs) on the DETERMINATION of EU MARKER PAHs in BIVALVE MOLLUSCS

Dear Madame/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EU-RL PAH on the determination of the 4 marker PAHs in bivalve molluscs will be **open from 30th May to 14th June 2013.**

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 300 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. **Additionally participants will be asked to perform compliance assessment according to the corresponding legislative limits.**

Each participant will be provided with
a) an amber glass vial containing about 15 g of lyophilized mussels sample, and
b) an amber glass vial containing about 30 g of frozen mussels,

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
Website: http://irmm.jrc.ec.europa.eu

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

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: 14 June 2013**
- Dispatch of samples: **beginning of July.** 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: **beginning of September.** You will receive the link for entering the results upon reception of the PT samples

Registration procedure:
Participants shall register via this link:
https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=1060

In order to register, laboratories must:

1. **Enter** the details on line:
2. **Print** the completed form (approved and confirmed version) when the system asks to do so, sign it and stamp it with your company stamp
3. **Send** it to the EU-RL PAHs members indicated below, either via FAX or via e-mail

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

Participants will be 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 to the OCLs under their responsibility, and to assist the EU-RL in identifying laboratories that are eligible to participate in the study.

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
Website: http://irmm.jrc.ec.europa.eu

¶

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

1) → *NRL enrols OCLs and covers participation fee.¶*
NRL submits to EU-RL 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 EU-RL for PAHs a letter of consent.¶

¶

¶

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

¶

JRC-IRMM-EURL-PAH@ec.europa.eu ¶

¶

¶

¶

With kind regards,¶

¶

Stefanka Bratinova¶

¶

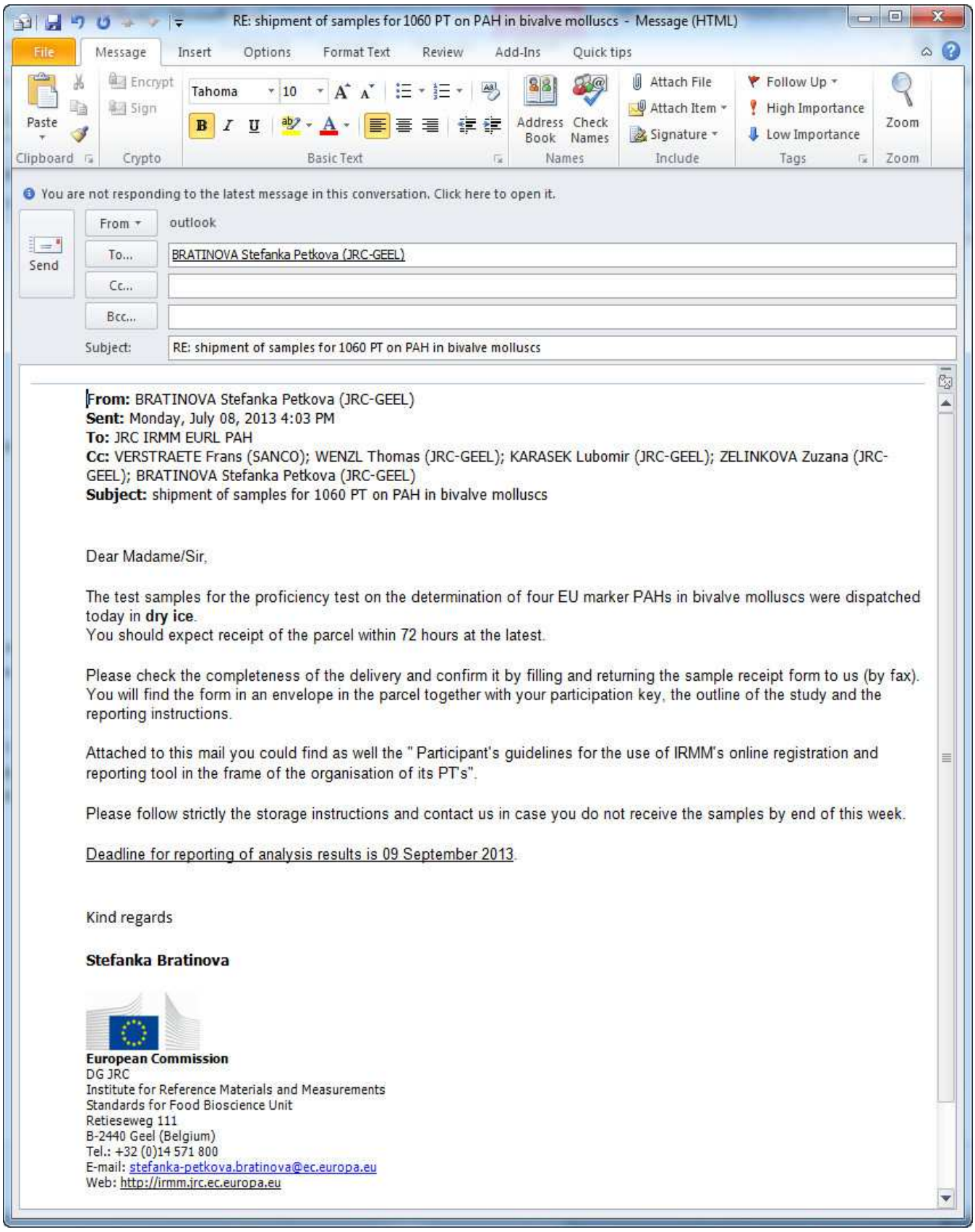
¶

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-crl-pah@ec.europa.eu¶
Website: http://irmm.jrc.ec.europa.eu¶

ANNEX 3: Announcement of material dispatch



RE: shipment of samples for 1060 PT on PAH in bivalve molluscs - Message (HTML)

File | Message | Insert | Options | Format Text | Review | Add-Ins | Quick tips

Paste | Encrypt | Sign | Tahoma | 10 | Address Book | Check Names | Attach File | Attach Item | Signature | Follow Up | High Importance | Low Importance | Zoom

Clipboard | Crypto | Basic Text | Names | Include | Tags | Zoom

You are not responding to the latest message in this conversation. Click here to open it.

Send

From: outlook

To: BRATINOVA Stefanka Petkova (JRC-GEEL)

Cc:

Bcc:

Subject: RE: shipment of samples for 1060 PT on PAH in bivalve molluscs

From: BRATINOVA Stefanka Petkova (JRC-GEEL)
Sent: Monday, July 08, 2013 4:03 PM
To: JRC IRMM EURL PAH
Cc: VERSTRAETE Frans (SANCO); WENZL Thomas (JRC-GEEL); KARASEK Lubomir (JRC-GEEL); ZELINKOVA Zuzana (JRC-GEEL); BRATINOVA Stefanka Petkova (JRC-GEEL)
Subject: shipment of samples for 1060 PT on PAH in bivalve molluscs

Dear Madame/Sir,

The test samples for the proficiency test on the determination of four EU marker PAHs in bivalve molluscs were dispatched today in **dry ice**.
You should expect receipt of the parcel within 72 hours at the latest.

Please check the completeness of the delivery and confirm it by filling and returning the sample receipt form to us (by fax). You will find the form in an envelope in the parcel together with your participation key, the outline of the study and the reporting instructions.

Attached to this mail you could find as well the " Participant's guidelines for the use of IRMM's online registration and reporting tool in the frame of the organisation of its PT's".

Please follow strictly the storage instructions and contact us in case you do not receive the samples by end of this week.

Deadline for reporting of analysis results is 09 September 2013.

Kind regards

Stefanka Bratinova

European Commission
DG JRC
Institute for Reference Materials and Measurements
Standards for Food Bioscience Unit
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Tel.: +32 (0)14 571 800
E-mail: stefanka-petkova.bratinova@ec.europa.eu
Web: http://irmm.jrc.ec.europa.eu

ANNEX 4: Documents sent to participants - <u>OUTLINE</u>

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 03 July 2013

ILC-1060

Twelfth inter-laboratory comparison study organised by the EU-RL PAHs

Analysis of four EU marker PAHs in BIVALVE MOLLUSCS

Dear Madame/Sir,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of four EU marker PAHs in bivavles molluscs 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 the participants are requested to report results on all of them.

Each participant will be provided with two crimp cap amber vials containing a portion of frozen mussels, a freeze dried mussels sample 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 **<u>09 September 2013 at the latest</u>** via a web-based interface. Your participation/password key (required for reporting of results) is shipped together with the test samples (in the same parcel).

The participants are requested to report for both samples the results obtained from three replicate analyses. They also have to report for each sample both a single content value per analyte ("final value"), and the sum of the contents of the four analytes, on which the performance of the laboratory will be assessed. The "final value" for the mussel samples shall be reported on product basis, as received by the laboratory.

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.

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Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

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

Test materials and analytes

1. One crimp cap amber vial, labelled as "EU-RL PAHs, Interlaboratory comparison 1060, 4 PAHs in freeze dried mussels", <u>containing about 15 g of a *freeze dried (lyophilized) mussels*</u>. 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 <u>triplicate</u>. 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 webpage for reasons of simplicity "final value". The homogeneity is proven at the level of 2 g test portion

   Store the freeze dried mussel sample refrigerated below 10°C.
   Be aware of <u>hygroscopicity!</u>

2. One crimp cap amber vial, labelled as "EU-RL PAHs, <u>Interlaboratory</u> comparison 1060, 4 PAHs in <u>frozen mussels</u>", <u>containing about 30 g of a *frozen commercial spiked and homogenised mussels*</u>. The concentration of the individual analytes is in the range of 0.5 µg/kg <u>to 10 µg/kg</u>. The analyte content shall be determined in <u>triplicate</u>. 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 webpage for reasons of simplicity "final value". The homogeneity is proven at the level of 5 g test portion.

   Store the frozen mussel sample in a freezer below – 10°C

3. Depending of your preference, one ampoule, labelled as "ACN-10/2012-K, PAH4 in <u>acetonitril</u>", or "TOL-10/2012-K, 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 *<u>do not contain any internal standard</u>*. The standard solution in acetonitrile contains small amounts of toluene, which stem from the preparation of stock solution from neat materials.

Contact person

Thomas <u>Wenzl</u>

Institute for Reference Materials and Measurements (IRMM)
<u>Retieseweg</u> 111, B-2440 <u>Geel</u>, Belgium
<u>Tel</u>: +32-14-571 320, <u>FAX</u>: +32-14-571 783

<u>E-mail</u>: jrc-irmm-crl-pah@ec.europa.eu

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

With kind regards,

Thomas <u>Wenzl</u>

(Operating Manager of the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons)

Cc: Franz VERSTRAETE, Franz <u>Ulberth</u>, Stefanka <u>Bratinova</u>

SAMPLE RECEIPT

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

ILC-1060

Twelfth Inter-laboratory comparison study organised by the EU-RL PAHs

Analysis of the four EU marker PAHs in bivalve molluscs

Confirmation of the receipt of the samples: RECEIPT FORM

Surname of Participant	
First name of Participant	
Institute	
Address	
Country	

Content of the parcel

a) → An amber glass crimp vial containing about 15 g of lyophilized (freeze dried) mussels sample;
b) → An amber glass crimp vial containing about 30 g of frozen mussels;
c) → One brown glass ampoule with 1 ml standard solution of 4EU markers PAHs in solvent (acetonitrile or toluene) (concentrations known)
d) → A specification sheet for the item b) content (standard solution)
e) → Material safety data sheets for acetonitrile / toluene
f) → One outline of the study and reporting instructions
g) → One paper sheet with the Laboratory Code (assigned for anonymous evaluation of data and for the PT report to be kept for all further communication) and the Password key (for accessing the webpage for reporting data)
h) → One inter-laboratory comparison sample receipt form (= this form)

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Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.
E-mail: jrc-irmm-crl-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 materials	
All items have been received undamaged	YES ...../ NO...
If NO, please list damaged items according to the letters associated at each item in the list above (in case of samples, please specify the numeric code too)	
Please write one item per row	
Items are missing	YES ...../ NO...
If YES, please list missing items according to the letters associated at each item in the list above	
Please write one item per row	
Serial number of the frozen mussel sample you received	
Serial number of the freeze dried mussel sample you received	
Serial number of the standard solution(s) with known concentrations you received	

Signature.....

Store the frozen mussel sample in a freezer below -10°C and the freeze dried mussels sample refrigerated below 10°C

ATTENTION

Please, submit the filled in form by mail to the following address:

jrc-irmm-eurl-pah@ec.europa.eu

or print it and send the printout by fax at the attention of Stefanka Bratinova at the following number:

+32 – 14 – 571783

2

GUIDANCE FOR REPORTING

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European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

ILC-1060

Twelfth Inter-laboratory comparison study organised by the EU-RL PAHs

Analysis of the four EU marker PAHs in bivalve molluscs

Confirmation of the receipt of the samples: RECEIPT FORM

Surname of Participant	
First name of Participant	
Institute	
Address	
Country	

Content of the parcel

a) → An amber glass crimp vial containing about 15 g of lyophilized (freeze dried) mussels sample;
b) → An amber glass crimp vial containing about 30 g of frozen mussels;
c) → One brown glass ampoule with 1 ml standard solution of 4EU markers PAHs in solvent (acetonitrile or toluene) (concentrations known)
d) → A specification sheet for the item b) content (standard solution)
e) → Material safety data sheets for acetonitrile / toluene
f) → One outline of the study and reporting instructions
g) → One paper sheet with the Laboratory Code (assigned for anonymous evaluation of data and for the PT report to be kept for all further communication) and the Password key (for accessing the webpage for reporting data)
h) → One inter-laboratory comparison sample receipt form (= this form)

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Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.
E-mail: jrc-irmm-crl-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 materials	
All items have been received undamaged	YES ...../ NO...
If NO, please list damaged items according to the letters associated at each item in the list above (in case of samples, please specify the numeric code too)	
Please write one item per row	
Items are missing	YES ...../ NO...
If YES, please list missing items according to the letters associated at each item in the list above	
Please write one item per row	
Serial number of the frozen mussel sample you received	
Serial number of the freeze dried mussel sample you received	
Serial number of the standard solution(s) with known concentrations you received	

Signature.....

Store the frozen mussel sample in a freezer below -10°C and the freeze dried mussels sample refrigerated below 10°C

ATTENTION

Please, submit the filled in form by mail to the following address:

jrc-irmm-eurl-pah@ec.europa.eu

or print it and send the printout by fax at the attention of Stefanka Bratinova at the following number:

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2

PARTICIPANT CODES

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

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 03/07/2013

«Title» «Firstname» «Surname»
«Organisation», «Department»
«Address»
«Zip» «Town»
«Country»

Dear Madame/Sir,

Please find below your participation key for

ILC 1060 4 EU markers PAH in bivalve molluscs 2013.

You need this unique key for the reporting of results via the web portal: http://irmm.jrc.ec.europa.eu/Pages/ilcReporting.aspx

Participation/password key:

«Part_key»

Your laboratory code is:

«LCode»

Results have to be reported before 09 September 2013!

With kind regards,

Stefanka Bratinova

(on behalf of the Operating Manager of the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons)

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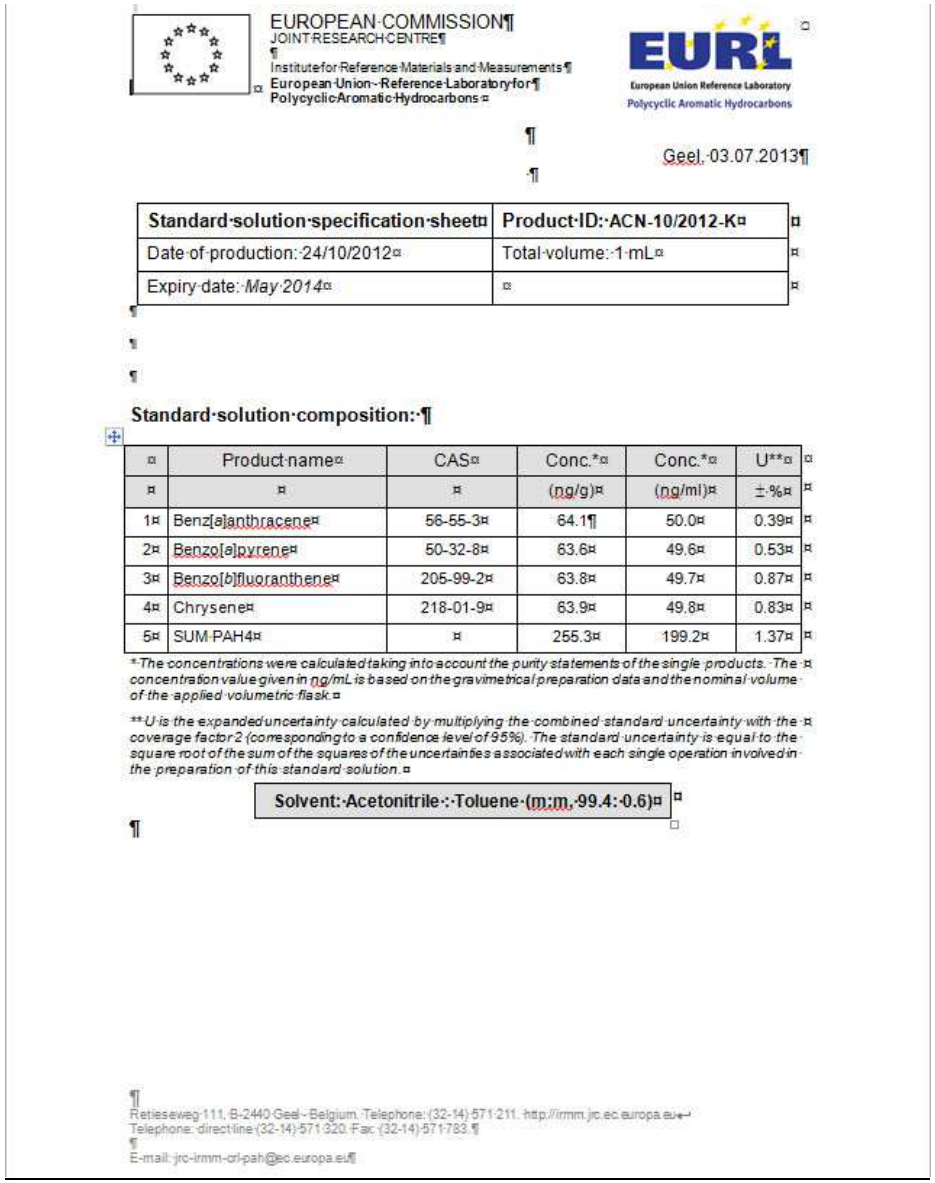
ANNEX 5: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION



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Geel, 03.07.2013

Standard solution specification sheet	Product ID: ACN-10/2012-K
Date of production: 24/10/2012	Total volume: 1 mL
Expiry date: *May 2014*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/ml)	U** ±%
1	Benz[a]anthracene	56-55-3	64.1	50.0	0.39
2	Benzo[a]pyrene	50-32-8	63.6	49.6	0.53
3	Benzo[b]fluoranthene	205-99-2	63.8	49.7	0.87
4	Chrysene	218-01-9	63.9	49.8	0.83
5	SUM PAH4		255.3	199.2	1.37

*The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the nominal volume of the applied volumetric flask.

**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)

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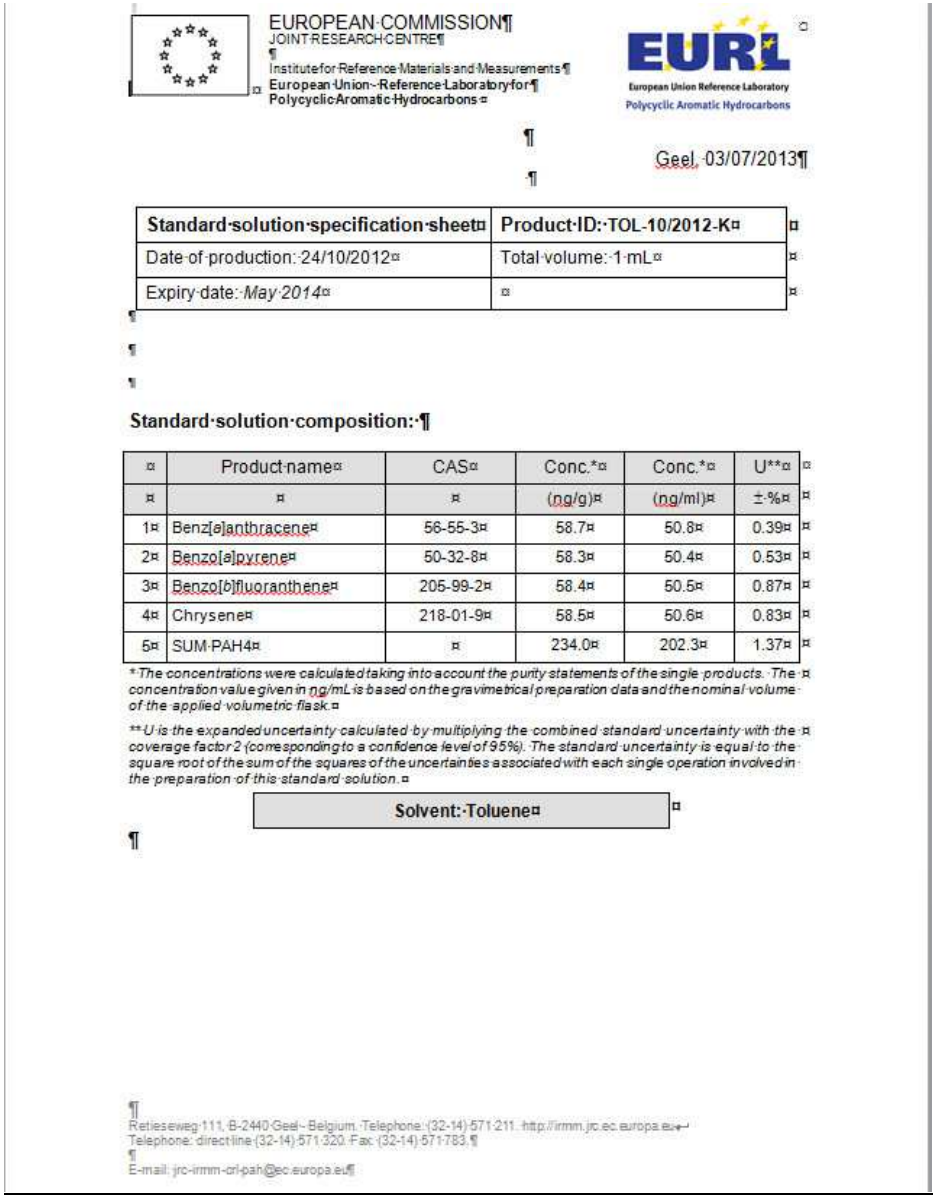
TOLUENE SOLUTION



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European Union Reference Laboratory for
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Polycyclic Aromatic Hydrocarbons

Geel, 03/07/2013

Standard solution specification sheet	Product ID: TOL-10/2012-K
Date of production: 24/10/2012	Total volume: 1 mL
Expiry date: *May 2014*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/ml)	U** ±%
1	Benz[a]anthracene	56-55-3	58.7	50.8	0.39
2	Benzo[a]pyrene	50-32-8	58.3	50.4	0.53
3	Benzo[b]fluoranthene	205-99-2	58.4	50.5	0.87
4	Chrysene	218-01-9	58.5	50.6	0.83
5	SUM PAH4		234.0	202.3	1.37

*The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the nominal volume of the applied volumetric flask.

**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

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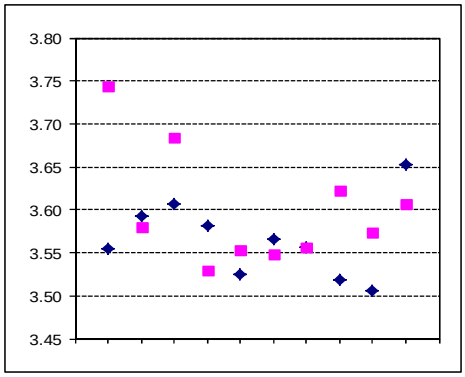
ANNEX 6: Homogeneity of the frozen mussels test material

Analyte: **BAA**

	n =	10		
	mean =	3.5830	22%	= **σ-trg(%)**
0.001845408	s_x =	0.0430	0.7883	= **σ-trg**
√MSW =	s_w =	0.0561		
	s_s =	0.0166	0.2365	= **0,3*s**

ISO-13528	passed		
F =	1.1745167	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	0.0003	0.1083	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 10	3.55	3.74	-0.19	7.30	3.65
Ampoule 15	3.59	3.58	0.01	7.17	3.59
Ampoule 27	3.61	3.68	-0.08	7.29	3.65
Ampoule 35	3.58	3.53	0.05	7.11	3.56
Ampoule 46	3.53	3.55	-0.03	7.08	3.54
Ampoule 49	3.57	3.55	0.02	7.11	3.56
Ampoule 56	3.56	3.56	0.00	7.11	3.56
Ampoule 69	3.52	3.62	-0.10	7.14	3.57
Ampoule 78	3.51	3.57	-0.07	7.08	3.54
Ampoule 86	3.65	3.61	0.05	7.26	3.63



∑(diff)^2 = 0.06284825

var(sum)/2 = 0.00369 =MSB

Stability Study for : BAA			
Data for T= -20°C, Treference = - 80°C			
==========		==========	
DATASET PROPERTIES		Shelf Life / Uncertainty Estimation	
----------		----------	
# of Determinations =	18	CALCULATION OF Ults for given Xshelf	
Average of Dataset =	3.56	Given Xshelf = 12 Weeks	
R.S.D. of Average(%) =	3.57	U_b =0.01	
R.S.E. of Average(%) =	0.84		
StDev of Average =	0.13	Ults = 0.07	
S.E. of Average =	0.03	Ults[%] = 2%	
==========		==========	
REGRESSION LINE PARAMETERS			

Slope =	0		
SE Slope =	0.01		
Intercept =	3.58		
SE Intercept =	0.05		
Correlation Coefficient =	0.03		
Slope of the linear regression significantly <> 0 (95%) :	No		
Slope of the linear regression significantly <> 0 (99%) :	No		

Analyte: **CHR**

	n =	10		
	mean =	5.2901	22%	= **σ-trg(%)**
0.002344388	s_x =	0.0484	1.1638	= **σ-trg**
√MSW =	s_w =	0.0888		
	s_s =	0.0399	0.3491	= **0,3*s**

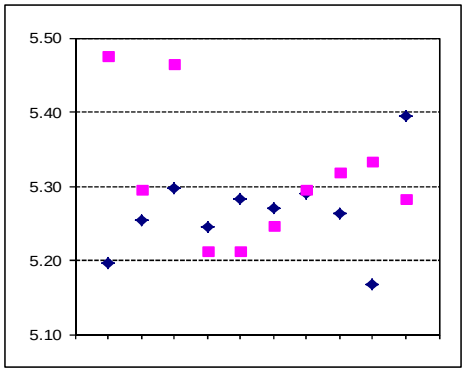
ISO-13528	passed		
F =	0.59517655	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0016	0.2371	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 10	5.20	5.48	-0.28	10.67	5.34
Ampoule 15	5.25	5.30	-0.04	10.55	5.27
Ampoule 27	5.30	5.46	-0.17	10.76	5.38
Ampoule 35	5.25	5.21	0.03	10.46	5.23
Ampoule 46	5.28	5.21	0.07	10.50	5.25
Ampoule 49	5.27	5.25	0.02	10.52	5.26
Ampoule 56	5.29	5.30	-0.01	10.59	5.29
Ampoule 69	5.26	5.32	-0.06	10.58	5.29
Ampoule 78	5.17	5.33	-0.17	10.50	5.25
Ampoule 86	5.40	5.28	0.11	10.68	5.34

$\sum$**(diff)**^{2} = 0.15755915

var(sum)/2 = 0.00469 =MSB



Stability Study for : CHR						
Data for T= -20°C, Treference = - 80°C						
==========			==========			
DATASET PROPERTIES			Shelf Life / Uncertainty Estimation			
----------			----------			
# of Determinations =	18		CALCULATION OF Ults for given Xshelf			
Average of Dataset =	5.29		Given Xshelf = 12 Weeks			
R.S.D. of Average(%) =	3.39		U_b =0.01			
R.S.E. of Average(%) =	0.8					
StDev of Average =	0.18		Ults = 0.10			
S.E. of Average =	0.04		Ults[%] = 2%			
==========			==========			
REGRESSION LINE PARAMETERS						

Slope =	-0.01					
SE Slope =	0.01					
Intercept =	5.32					
SE Intercept =	0.07					
Correlation Coefficient =	0.03					
Slope of the linear regression significantly <> 0 (95%) :	No					
Slope of the linear regression significantly <> 0 (99%) :	No					

Analyte: **BBF**

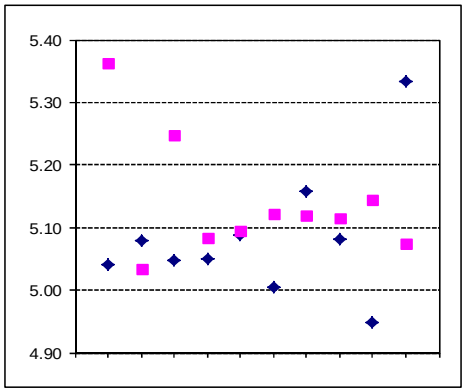
	n =	10		
	mean =	5.1115	22%	= **σ-trg(%)**
0.003451199	s_x =	0.0587	1.1245	= **σ-trg**
√MSW =	s_w =	0.1158		
	s_s =	0.0571	0.3374	= **0,3*s**

ISO-13528	passed		
F =	0.51463125	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	-0.0033	0.2275	= $F1*(0,3*s)^2+F2*MSW$
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 10	5.04	5.36	-0.32	10.40	5.20
Ampoule 15	5.08	5.03	0.04	10.11	5.06
Ampoule 27	5.05	5.25	-0.20	10.29	5.15
Ampoule 35	5.05	5.08	-0.03	10.13	5.07
Ampoule 46	5.09	5.10	-0.01	10.18	5.09
Ampoule 49	5.00	5.12	-0.12	10.13	5.06
Ampoule 56	5.16	5.12	0.04	10.28	5.14
Ampoule 69	5.08	5.12	-0.03	10.20	5.10
Ampoule 78	4.95	5.14	-0.19	10.09	5.05
Ampoule 86	5.33	5.08	0.26	10.41	5.20

$\sum(diff)^2$ = 0.26824639

var(sum)/2 = 0.00690 =MSB



Stability Study for : BBF

Data for T= -20°C, Treference = - 80°C

DATASET PROPERTIES		Shelf Life / Uncertainty Estimation
# of Determinations =	18	CALCULATION OF Ults for given Xshelf
Average of Dataset =	4.46	Given Xshelf = 12 Weeks
R.S.D. of Average(%) =	5.45	U_b =0.01
R.S.E. of Average(%) =	1.28	
StDev of Average =	0.24	Ults = 0.14
S.E. of Average =	0.06	Ults[%] = 3%

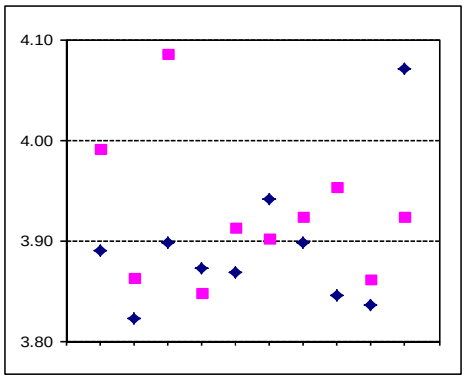
REGRESSION LINE PARAMETERS	
Slope =	0
SE Slope =	0.01
Intercept =	4.49
SE Intercept =	0.09
Correlation Coefficient =	0.01
Slope of the linear regression significantly <> 0 (95%) :	No
Slope of the linear regression significantly <> 0 (99%) :	No

Analyte: **BAP**

	n =	10		
	mean =	3.9104	22%	= **σ-trg(%)**
0.002957901	s_x =	0.0544	0.8603	= **σ-trg**
√MSW =	s_w =	0.0654		
	s_s =	0.0286	0.2581	= **0,3*s**

ISO-13528	passed		
F =	1.38230905	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	0.0008	0.1295	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 10	3.89	3.99	-0.10	7.88	3.94
Ampoule 15	3.82	3.86	-0.04	7.69	3.84
Ampoule 27	3.90	4.09	-0.19	7.98	3.99
Ampoule 35	3.87	3.85	0.02	7.72	3.86
Ampoule 46	3.87	3.91	-0.04	7.78	3.89
Ampoule 49	3.94	3.90	0.04	7.84	3.92
Ampoule 56	3.90	3.92	-0.02	7.82	3.91
Ampoule 69	3.85	3.95	-0.11	7.80	3.90
Ampoule 78	3.84	3.86	-0.03	7.70	3.85
Ampoule 86	4.07	3.92	0.15	7.99	4.00
		∑(**diff**)^2 =	0.08559303		
		var(sum)/2 =		0.00592 =MSB	



Stability Study for : BAP			
Data for T= -20°C, Treference = - 80°C			
==========		==========	
DATASET PROPERTIES		Shelf Life / Uncertainty Estimation	
----------		----------	
# of Determinations =	18	CALCULATION OF Ults for given Xshelf	
Average of Dataset =	3.92	Given Xshelf = 12 Weeks	
R.S.D. of Average(%) =	4.33	U_b =0.01	
R.S.E. of Average(%) =	1.02		
StDev of Average =	0.17	Ults = 0.10	
S.E. of Average =	0.04	Ults[%] = 2%	
==========		==========	
REGRESSION LINE PARAMETERS			

Slope =	0		
SE Slope =	0.01		
Intercept =	3.92		
SE Intercept =	0.07		
Correlation Coefficient =	0		
Slope of the linear regression significantly <> 0 (95%) :	No		
Slope of the linear regression significantly <> 0 (99%) :	No		

ANNEX 7:

International Atomic Energy Agency
Analytical Quality Control Services
Wagramer Strasse 5, P.O.Box 100, A-1400 Vienna, Austria

REFERENCE SHEET

REFERENCE MATERIAL

IAEA-432

ORGANOCHLORINE COMPOUNDS AND PETROLEUM HYDROCARBONS IN A MUSSEL HOMOGENATE

Date of issue: April 2004

PESTICIDES AND PCBs

Recommended Values
(Based on dry weight)

Analyte	Concentration ng/g	Standard deviation ng/g	N*
HCB	0.2	0.1	21
pp' DDE	2.1	1.0	39
pp' DDD	0.88	0.49	30
PCB No 49	0.29	0.08	6
PCB No 70	0.64	0.35	7
PCB No 101	1.2	0.49	24
PCB No 110	1.12	0.4	10
PCB No 118	1.09	0.42	24
PCB No 138	2.2	0.84	31
PCB No 149	1.4	0.41	10
PCB No 153	2.8	0.99	31
PCB No 180	0.2	0.11	16

* *Number of accepted laboratory results which were used to calculate the recommended value and its standard deviation about the mean value.*

PETROLEUM HYDROCARBONS

Recommended Values
(Based on dry weight)

Analyte	Concentration ng/g	Standard deviation ng/g	N*
Phenanthrene	27	21	32
1 Methyl Phenanthrene	4.2	2.8	8
2 Methyl Phenanthrene	9.4	4.9	5
Anthracene	1.5	1.1	11
Chrysene	5.5	3.8	23
Fluorene	4.1	2.2	8
Fluoranthene	12	6.5	27
Pyrene	13	6.0	25
Benzo (b) Fluoranthene	4.8	1.7	10
Benzo (k) Fluoranthene	1.9	1.1	12
Benz (a) Anthracene	3.8	3.1	24
Benzo (a) Pyrene	0.9	0.5	17
Benzo (e) Pyrene	4.5	1.7	11

* *Number of accepted laboratory results which were used to calculate the recommended value and its standard deviation about the mean value.*

PETROLEUM HYDROCARBONS

Information Values
(Based on dry weight)

Analyte	Concentration ng/g	Standard deviation ng/g	N*
UVF equivalent ROPME oil	11000	4900	3
Total Aliphatics	10000	9000	5
Resolved Aliphatics	18000	20000	9
Unresolved Aliphatics	38000	43000	5
Pristane	140	130	10
n - C 17	200	140	12
n - C 18	67	68	11
Phytane	41	44	9
Σ n-Alkanes (C 14 - C 34)	4500	4800	10
Total Aromatics	3000	3900	8
Resolved Aromatics	1500	1800	10
Naphthalene	15	18	15
1 Methyl Naphthalene	8.8	9.5	3
2 Methyl Naphthalene	14	13	3
Perylene	5.0	2.8	3

* *Number of accepted laboratory results which were used to calculate the information values and its standard deviation about the mean value.*

The values listed above were established on the basis of statistically valid results submitted by laboratories which had participated in an international intercomparison exercise conducted in 2003. The details concerning the criteria for qualification as a recommended or information value can be found in the report (IAEA/AL/146; IAEA/MEL/74), "World-wide and Regional Intercomparison for Determination of Organochlorine Compounds and Petroleum Hydrocarbons in Mussel Tissue IAEA-432" [1]. This report is available free of charge upon request.

Intended Use

This sample is intended to be used as a reference material for the determination of chlorinated compounds and petroleum hydrocarbons in biota samples. It can also be used as a quality control material for the assessment of a laboratory's analytical work, for the validation of analytical methods and for quality assurance within a laboratory.

Origin and preparation of the material

A large batch of mussels (*Mytilus edulis*) was collected from the North Sea to be used as an intercomparison material. This material was freeze-dried and ground. It was further sieved through a 250 µm stainless steel sieve.

The mussel powder fraction of particle size less than 250 µm was further homogenized by mixing in a rotating drum for two weeks. Then, aliquots of about 45 grams were packaged into glass bottles with aluminum screw caps and sealed with Teflon tape.

Homogeneity

The homogeneity of the material for organochlorine compounds and petroleum hydrocarbons was checked by determining the concentration of some compounds (chlorinated pesticides and petroleum hydrocarbons) in 10 replicate analyses taken randomly in the bulk of the powder. A one-way variance analysis indicated that the material could be considered homogeneous.

Dry weight determination

The moisture content of the lyophilized sample as determined by drying to a constant weight at 105°C, was found to be 2.5 %. Since the moisture content can change with the ambient humidity and temperature, it is recommended that the water content of this material always be determined in a separate sub-sample (not that taken for analysis) by drying to a constant weight (~24 hours) at 105°C. Results should always be reported on a dry weight basis.

Instructions for use

The recommended sample size for analysis is 2 g for petroleum hydrocarbons and 5 g for organochlorine pesticides and PCB's respectively. Analysts are reminded to take appropriate precautions in order to avoid contamination of the material during handling. The material should be stored in the dark and kept in a refrigerator.

Legal disclaimer

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.

References

[1] Villeneuve J. P., de Mora S. J. and Cattini C., World-wide and Regional Intercomparison for Determination of Organochlorine Compounds and Petroleum Hydrocarbons in Mussel Tissue IAEA-432.
IAEA/AL/146 (IAEA/MEL/74), IAEA, Monaco, 2004.

ANNEX 8. Questionnaire and method performance characteristics - BLANK TEMPLATE

Milc questionnaire

Comparison for ILC 1060 PAHs in bivalve molluscs

Please report the method performance parameters for the determination of PAHs in the olive oil material as indicated below. The unit for limit of detection (LOD), limit of quantitation (LOQ) and for the working range limits is µg/kg. The method recovery shall be reported as percentage (%) and has to be intended as the yield of the method. Please describe also the key elements of the applied analysis procedure. Thank you for your cooperation. The EU-RL Team

Submission Form

1. Is the applied analysis method accredited according to ISO 17025?

- ○ a) Yes
- ○ b) No

2. Are mussels within the scope of the accredited method?

- ○ a) Yes
- ○ b) No

3. How many mussels samples did you analyse so far for PAH content?

- ○ A) <10
- ○ B) 10-50
- ○ C) 50-100
- ○ D) 100-500
- ○ E) 500-1000
- ○ F) > 1000

4. Which analysis technique did you apply?

- ☐ A) GC-FID
- ☐ B) GC-MS
- ☐ C) GC-MS/MS
- ☐ D) GC-HRMS
- ☐ E) HPLC-FD
- ☐ F) HPLC-UV/FD
- ☐ G) LC-MS
- ☐ H) LC-MS/MS
- ☐ I) UHPLC-FD
- ☐ J) UHPLC-UV/FD

5. Which chromatographic column did you apply for the analyses?

6. Which sample amount did you take per analysis? (g)

(number)

7. Which of the following sample preparation procedures did you apply for the mussels sample? *

- ☐ 1) Extraction with organic solvent
- ☐ 2) Liquid/Liquid partitioning
- ☐ 3) Saponification
- ☐ 4) Chromatography/fractionation

7.1. If applicable: Which extraction technique was applied?

- ☐ A) Pressurised liquid extraction (PLE)
- ☐ B) Sonication
- ☐ C) Soxhlet extraction
- ☐ D) Other

7.2. If applicable: Which chromatography/fractionation technique was applied?

- [ ] A) Column chromatography on silica
- [ ] B) Gel permeation chromatography (GPC)
- [ ] C) Donor acceptor complex chromatography (DACC)
- [ ] D) Solid phase extraction (SPE)
- [ ] E) Other

7.2.1. If applicable: Please specify SPE cartridge(s).

8. **How did you calibrate your instrument?**

8.1. Did you apply external calibration? *

- ◯ a) Yes
- ◯ b) No

8.1.1. In case of external calibration: How did you calibrate? *

- [ ] A) with standards in an organic solvent
- [ ] B) with matrix matched standards

8.2. Did you apply internal standardisation? *

- ◯ a) Yes
- ◯ b) No

8.2.1. Which internal standards did you apply *

- [ ] A) Structural analogue(s) of the analyte(s)
- [ ] B) Stable isotope labelled analogue(s)

8.2.2. Please provide details on the applied internal standards *

8.3. Did you apply standard addition? *

- ◯ a) Yes
- ◯ b) No

9. **Did you experience any problems during sample preparation of the mussels sample?**

- ◯ a) Yes
- ◯ b) No

9.1. Please specify: *

10. **Did you experience chromatographic interferences?**

- ◯ a) Yes
- ◯ b) No

10.1. Please specify: *

11. **Please provide details of method performance parameters for the determination of PAHs in frosen mussels** *

See table **Table 1. Frozen mussels** at bottom

12. **Please provide details on method performance parameters for the determination of PAHs in lyophylized mussels (if different from frozen mussels)** *

See table **Table 2. Lyophylized mussels** at bottom

Table 1. Frozen mussels

Questions/Response table	*LOD [µg/kg]*	*LOQ [µg/kg]*	*Recovery [%]*
BaA			
BaP			
BbF			
CHR			

Table 2. Lyophylized mussels

Questions/Response table	*LOD [µg/kg]*	*LOQ [µg/kg]*	*Recovery [%]*
BaA			
BaP			
BbF			
CHR			

QUESTIONNAIRE:

1) Is the applied analysis method accredited according to ISO 17025?
2) Are mussels within the scope of the accredited method?
3) How many mussel samples did you analyse so far for PAH content?
4) Which analysis technique did you apply?
5) Which chromatographic column did you apply for the analyses?
6) Which sample amount did you take per analysis?

LCode	1	2	3	4	5	6
101	a) Yes	a) Yes	D) 100-500	B) GC-MS	Varian pah select	5
102	a) Yes	a) Yes	B) 10-50	B) GC-MS	DB-35ms	4
103	a) Yes	a) Yes	D) 100-500	E) HPLC-FD	PAH C18, 5µm, 4.6x250 mm	2
104	a) Yes	b) No	B) 10-50	B) GC-MS	SELECT PAH (30mx0.25mmx0.15um)	1.25
105	a) Yes	b) No	A) <10	E) HPLC-FD	PAH C18 5 um, 4,6x250mm, 5 um (Waters P/N 186001265)	1
106	a) Yes	a) Yes	A) <10	E) HPLC-FD	PAH specific (C18) 250 mm x 4,6 mm, particle size 5 um	2
107	a) Yes	a) Yes	A) <10	C) GC-MS/MS	Varian GC Capillary column, select PAH - 15mm ID DF=0.10mm	2
108	b) No	b) No	B) 10-50	D) GC-HRMS	varian select PAH, 30 m x 0.25 mm x 0.15 µm	2.5
110	b) No	b) No	A) <10	E) HPLC-FD	LiChroCART 250-4, LiChrosper PAH (5 µm)	15
111	a) Yes	b) No	A) <10	B) GC-MS	Select PAH (30m×0,25mm×0,15µm)	2
112	b) No	b) No	A) <10	B) GC-MS	Restek Rxi-PAH 30m 0.25 mm ID 0.10 um df	1
113	a) Yes	b) No	A) <10	B) GC-MS	5% Diphenyl polysiloxane	5
114	a) Yes	a) Yes	A) <10	C) GC-MS/MS	SelectPAH, 30 m × 0,25 mm × 0,15 µm	2
115	a) Yes	a) Yes	A) <10	E) HPLC-FD	Restek Pinnacle II PAH 150*4,6*4	1.8
116	a) Yes	a) Yes	C) 50-100	B) GC-MS, E) HPLC-FD	SELECT PAH 30m, 0.25 mm ID, 0.15 f.t. (GC-MS); VIADAC 201 TP 54, 250 x 4.6 mm, 5 um (HPLC)	5
117	a) Yes	b) No	B) 10-50	B) GC-MS	35% phenyl/65% methylpolysiloxane; 30m, 0.25 mm i.d., 0.25 µm film	3
118	a) Yes	a) Yes	D) 100-500	C) GC-MS/MS	PAH Select column	1
119	a) Yes	b) No	A) <10	C) GC-MS/MS	Agilent Select PAH	5
120	a) Yes	b) No	A) <10	B) GC-MS	ZB-35, 30m, 0.25 mm, 0.25 um	2
121	b) No	b) No	A) <10	H) LC-MS/MS	Zorbax Eclipse PAH 2.1x50 mm, 1.8µm	9
122	a) Yes	a) Yes	B) 10-50	B) GC-MS		5
123	a) Yes	b) No	A) <10	E) HPLC-FD	Waters PAH C18, 5 µm, 3x250mm	2
124	b) No	b) No	A) <10	F) HPLC-UV/FD	SUPELCOSIL LC-PAH, 25cm x 4.6mm, 5um	3
125	a) Yes	b) No	A) <10	E) HPLC-FD	Agilent Zorbaz Eclipse Plus C18 3.5µm 100x4.6mm	2
126	a) Yes	b) No	A) <10	F) HPLC-UV/FD	201 TP 54 GRACE 250 x 4,6 mm	2
501	a) Yes	a) Yes	B) 10-50	B) GC-MS	DB-EUPAH, 20m x 0.18mm ID x 0.14um	4
502	a) Yes	a) Yes	A) <10	C) GC-MS/MS	DB-5MS	2
503	b) No	b) No	A) <10	E) HPLC-FD		
506	a) Yes	b) No	A) <10	B) GC-MS	Varian Select PAH	5
508	b) No	b) No	true	E) HPLC-FD	Lichrospher PAH	3
510	a) Yes	a) Yes	A) <10	C) GC-MS/MS	Select PAH (30mx250µmx0,15µm)	2
511	a) Yes	a) Yes	D) 100-500	E) HPLC-FD	Supelcosil LC-PAH (150 * 3,0) mm * 5 um	3
512	a) Yes	a) Yes	C) 50-100	E) HPLC-FD	ENVIROSEP PP	2
513	a) Yes	a) Yes	B) 10-50	E) HPLC-FD	SUPELCOSIL"TM" LC-PAH 15 cm x 4.6 mm, 5um.	5
514	a) Yes	a) Yes	B) 10-50	C) GC-MS/MS	agilent technologies Select PAH	1
515	a) Yes	a) Yes	C) 50-100	C) GC-MS/MS	VF 17 MS	1
516	a) Yes	a) Yes	B) 10-50	C) GC-MS/MS	Select PAH 30m*0.25 mm * 0.25 µm	1
517	a) Yes	a) Yes	B) 10-50	C) GC-MS/MS	SELECT PAH	5

LCode	1	2	3	4	5	6
518	b) No	b) No	A) <10	E) HPLC-FD	CLHP VYDAC 201 TP 54 C18 reversed phase 5 µm (4,6 x 250 mm)	2
519	a) Yes	a) Yes	B) 10-50	C) GC-MS/MS	Select PAH , 30 m × 0,25 mm × 0,15 µm	1
520	a) Yes	a) Yes	A) <10	F) HPLC-UV/FD	Zorbax Eclipse PAH 150x4,6 mm 3,5µ	
521	a) Yes	a) Yes	B) 10-50	E) HPLC-FD	Monolithic C18 2x100x4.6 mm	5
522	a) Yes	a) Yes	B) 10-50	E) HPLC-FD	MN Nucleosil 18 PAH	5
523	a) Yes	b) No	A) <10	B) GC-MS	Agilent Select PAH 15 m x 0,15 mm x 0,10 µ	2.5

7) Which of the following sample preparation procedures did you apply for the mussels sample?
7.1) If applicable: Which extraction technique was applied?
7.2) If applicable: Which chromatography/fractionation technique was applied?
7.2.1) If applicable: Please specify SPE cartridge(s)

LCode	7	7.1.	7.2	7.2.1
101	1) Extraction with organic solvent, 3) Saponification	X	A) Column chromatography on silica	
102	3) Saponification	D) Other	D) Solid phase extraction (SPE)	Silica 5g (Strata) and PAH-HC 1g (Isolute)
103	1) Extraction with organic solvent	X	B) Gel permeation chromatography (GPC)	
104	4) Chromatography/fractionation	X	D) Solid phase extraction (SPE)	MSPD, PSA column
105	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC)	
106	1) Extraction with organic solvent, 4) Chromatography/fractionation	C) Soxhlet extraction	D) Solid phase extraction (SPE)	
107	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	Supelclean ENVI Chrom P Spe 6ml (0,50g) Supelco
108	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC)	
109				
110	1) Extraction with organic solvent, 2) Liquid/Liquid partitioning, 3) Saponification, 4) Chromatography/fractionation	X	A) Column chromatography on silica	
111	3) Saponification	D) Other	D) Solid phase extraction (SPE)	Strata SI-1 Silica (55µm, 70A) 500 mg/6mL
112	2) Liquid/Liquid partitioning	B) Sonication	D) Solid phase extraction (SPE)	SUPELCO SupelMIP PAHs 50mg/3ml
113	2) Liquid/Liquid partitioning, 3) Saponification, 4) Chromatography/fractionation	X	A) Column chromatography on silica	
114	1) Extraction with organic solvent	B) Sonication	A) Column chromatography on silica	
115	1) Extraction with organic solvent	B) Sonication	D) Solid phase extraction (SPE)	SupelMIP
116	3) Saponification	X	X	FLORISIL 500 mg 3 ml, C18 2g 12 ml
117	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC)	
118	1) Extraction with organic solvent, 4) Chromatography/fractionation	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	SPE Envi Chrom-P (styrene divinylbenzene stationnary phase)
119	1) Extraction with organic solvent, 4) Chromatography/fractionation	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	Supelco Envi-Chrom P
120	1) Extraction with organic solvent	B) Sonication	B) Gel permeation chromatography (GPC)	
121	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC), D) Solid phase extraction (SPE)	Isolute 500mg Si (3ml)
122	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC)	
123	1) Extraction with organic solvent	C) Soxhlet extraction	B) Gel permeation chromatography (GPC)	

LCode	7	7.1.	7.2	7.2.1
124	3) Saponification	D) Other	D) Solid phase extraction (SPE)	Strata C18-E 2g/12mL and Strata Florisil (FL-PR) 500mg/3mL
125	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	C) Donor acceptor complex chromatography (DACC)	
126	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC)	
501	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	B) Gel permeation chromatography (GPC), D) Solid phase extraction (SPE)	
502	1) Extraction with organic solvent	X	B) Gel permeation chromatography (GPC)	
503	1) Extraction with organic solvent	X	X	
506	1) Extraction with organic solvent	D) Other	A) Column chromatography on silica	
508	3) Saponification	B) Sonication	A) Column chromatography on silica	
510	2) Liquid/Liquid partitioning	C) Soxhlet extraction	B) Gel permeation chromatography (GPC)	
511	1) Extraction with organic solvent, 2) Liquid/Liquid partitioning, 4) Chromatography/fractionation	D) Other	E) Other	
512	1) Extraction with organic solvent, 3) Saponification	X	D) Solid phase extraction (SPE)	SILICA
513	1) Extraction with organic solvent	B) Sonication	D) Solid phase extraction (SPE)	SupelMIP"TM" PAHs SPE 50 mg/3ml
514	1) Extraction with organic solvent, 2) Liquid/Liquid partitioning	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	ENVI CHROM P
515	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	envi chrom
516	1) Extraction with organic solvent	C) Soxhlet extraction	D) Solid phase extraction (SPE)	Supelco Envi Chrom P
517	1) Extraction with organic solvent, 4) Chromatography/fractionation	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	ENVI CHROM P SUPELCO 0.5G 6 ML
518	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	Silica and SupelMIP PAH (Supelco)
519	1) Extraction with organic solvent	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	ENVI CHROM P
520	2) Liquid/Liquid partitioning, 3) Saponification, 4) Chromatography/fractionation	X	A) Column chromatography on silica	
521	3) Saponification	D) Other	A) Column chromatography on silica	
522	1) Extraction with organic solvent	C) Soxhlet extraction	D) Solid phase extraction (SPE)	MN Chromabond HR-P
523	1) Extraction with organic solvent, 4) Chromatography/fractionation	A) Pressurised liquid extraction (PLE)	D) Solid phase extraction (SPE)	MN HRX ; Silicagel

8) How did you calibrate your instrument?
8.1) Did you apply external calibration?
8.1.1) In case of external calibration: How did you calibrate?
8.2) Did you apply internal standardization?
8.2.1) Which internal standards did you apply?
8.2.2) Please provide details on internal standards
8.3) Did you apply standard addition?

LCode	8.1.	8.1.1.	8.2.	8.2.1.	8.2.2.	8.3
101	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	EPA16 PAH Cocktail	b) No
102	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	Mix of 9 deuterated PAH standards	b) No
103	a) Yes	A) with standards in an organic solvent	b) No	X		b) No
104	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)		a) Yes
105	a) Yes	A) with standards in an organic solvent	a) Yes	A) Structural analogue(s) of the analyte(s)	benzo(b)chrysene	b) No
106	a) Yes	A) with standards in an organic solvent	b) No	X		a) Yes
107	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	13C -maked	b) No

LCode	8.1.	8.1.1.	8.2.	8.2.1.	8.2.2.	8.3
108	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	deuterated PAHs	b) No
109						
110	b) No	X	a) Yes	A) Structural analogue(s) of the analyte(s)	Benzo(b)chrysene	b) No
111	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	Benzo(a)pyrene-D12; Benzo(b)fluoranthene-D12; Chrysene-D12; Benzo(a)anthracene-D12	a) Yes
112	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	Benzo [a] Anthracene D12 and Benzo[a]Pyrene D12	a) Yes
113	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	Ehrensdorf PAH mix 9 + D14 DIP + 13C6 DEP	b) No
114	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	Benzo(a)pyrene-D12, Chrysene-D12	b) No
115	a) Yes	A) with standards in an organic solvent	b) No	X		a) Yes
116	b) No	X	a) Yes	A) Structural analogue(s) of the analyte(s), B) Stable isotope labelled analogue(s)	D12chrysene (GC-MS), Benzo(b)chrysene (HPLC/FLD)	a) Yes
117	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	BaA, BaP, BbF, CHR	b) No
118	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	BaP 13C4, BaA 13C6, CHR 13C6 and BbF 13C6	b) No
119	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	B(a)P 13C4, CHR 13C6, B(a)A 13C6, B(b)F 13C6	b) No
120	a) Yes	B) with matrix matched standards	b) No	X		b) No
121	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	PAH mix-9 (eppendorfer)	b) No
122	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	B(a)A,D12 and B(a)pD12	b) No
123	a) Yes	A) with standards in an organic solvent	b) No	X		a) Yes
124	a) Yes	A) with standards in an organic solvent	b) No	X		b) No
125	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	DiP D14	b) No
126	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	D12-Benzo(a)anthracene	b) No
501	b) No	X	a) Yes	A) Structural analogue(s) of the analyte(s)	B(a)A D12, B(b)F D12, B(a)P D12	b) No
502	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)		a) Yes
503	b) No	X	b) No	X		b) No
506	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	Benzo(a)pyren - D12	b) No
508	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	13C6 Benzo(a)anthracene, 13C6 Chrysene, 13C6 Benzo[b]fluoranthene, , 13C4 Benzo[a]pyrene	b) No
510	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	Benzo(a)anthracene D12	b) No
511	a) Yes	A) with standards in an organic solvent	b) No	X		b) No
512	a) Yes	A) with standards in an organic solvent	b) No	X		b) No
513	a) Yes	A) with standards in an organic solvent	b) No	X		b) No
514	b) No	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	internal standards use for calculed the concentration	b) No
515	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	4 HAP	b) No
516	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	the internal standards are added to the geginning of sample handling	b) No
517	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	EACH ISOTOPE OF ANALYTE	a) Yes
518	a) Yes	A) with standards in an organic solvent	a) Yes	A) Structural analogue(s) of the analyte(s)	Benzo(b)chrysene	b) No
519	a) Yes	A) with standards in an organic solvent	a) Yes	B) Stable isotope labelled analogue(s)	SI 13C (HAP 27)	a) Yes

LCode	8.1.	8.1.1.	8.2.	8.2.1.	8.2.2.	8.3
520	a) Yes	A) with standards in an organic solvent	a) Yes	A) Structural analogue(s) of the analyte(s)	Benzo(b)chrysene	b) No
521	b) No	X	a) Yes	A) Structural analogue(s) of the analyte(s)	Benzo(c)chrysen	b) No
522	a) Yes	A) with standards in an organic solvent	a) Yes	A) Structural analogue(s) of the analyte(s)	Benuzo(b)chrysen	b) No
523	b) No	X	a) Yes	B) Stable isotope labelled analogue(s)	Deuterated BaA; Chry; BbF; BaP	b) No

9) Did you experience any problems during sample preparation of the chocolate/cocoa butter sample?
9.1) Please specify:
10) Did you experience any chromatographic interferences?
10.1) Please specify:

LCode	9	9.1.	10	10.1
101	b) No		b) No	
102	a) Yes	Sample has to be kept warm during the separation of phases. At room temperature it emulsifies too much.	b) No	
103	a) Yes	The Coefficients of variation for the 4 PAHs in lyophilized samples were 3 times higher than CV in frozen mussels. Those high CV´s are unusual in the analysis of mussels by our method (GPC + LC-FL). Given the type of matrix (lyophilised) and the sample size (2g), it may be indicative of an insufficient homogeneity in the sample.(see additional comments in our e-mail of 13-09-13)	a) Yes	A small "shoulder" next to BaP in lyophilized mussels. However, it did not caused any problem because the global peak represented < LOQ for BaP
104	a) Yes	in the preparation of the frozen mussel sample there was no problem. in the preparation of the freeze dried mussel sample I had a problem how to deal with the sample that is very dry (which solvent would be most appropriate).	a) Yes	in the frozen mussel sample were not present interferences, but in the freeze dried mussel sample were present interferences.
105	b) No		b) No	
106	b) No		a) Yes	mainly for chrysene, a little artificial signal interfers with benz(a)anthracene, deconvolution approach has been done in this cases
107	b) No		a) Yes	Chrysene and Triphenylene
108	b) No		b) No	
109				
110	a) Yes	Formation of slurry during separation of mussels extracts	b) No	
111	b) No		a) Yes	Background
112	b) No		a) Yes	for Benzo [b] Fluoranthene (BbF)
113	b) No		b) No	
114	b) No		b) No	
115	b) No		b) No	
116	b) No		a) Yes	In Benzo(a)anthracene peak
117	b) No		b) No	
118	b) No	no pb	b) No	no pb
119	b) No		b) No	
120	b) No		a) Yes	unspecified peaks around BaP retention time (in case of FREEZE DRIED sample)
121	b) No		b) No	
122	b) No		b) No	
123	b) No		a) Yes	interferences mainly with BaA
124	b) No		b) No	
125	b) No		a) Yes	interference on the BaA peak
126	b) No		b) No	
501	b) No		b) No	
502	b) No		b) No	
503	b) No		b) No	
506	b) No		b) No	

LCode	9	9.1.	10	10.1
508	b) No		a) Yes	Interferences on Chrysene
510	b) No		a) Yes	Benzo[a]pyrene interferences in the freeze dried mussels
511	a) Yes	The freeze dried mussels isn't a typical sample analyzed in our laboratory. We have tested 1 g of sample instead of three normally used.	b) No	
512	b) No		b) No	
513	b) No		b) No	
514	b) No		b) No	
515	b) No		b) No	
516	b) No		b) No	
517	a) Yes	BAD RECOVERY FOR ONE EXTRACTION	b) No	
518	a) Yes	Residues after extraction that where not fatty and not very soluble in small heptane quantities.	a) Yes	For freeze dried sample, co-elution for BaA, BaP and IS.
519	b) No		b) No	
520	b) No		b) No	
521	b) No		b) No	
522	b) No		a) Yes	background in freeze dried mussels sample mainly with chrysene and benzo(a)anthracene
523	b) No		b) No	

METHOD PERFORMANCE PARAMETERS

With reference to Commission Regulation (EC) No 333/2007 as amended by Commission Regulation (EU) No 836/2011, non-compliant method performance characteristics are marked in the tables in bold red font. Threshold values for the evaluation were LOD≤ 0.30 µg/kg, LOQ ≤ 0.90 µg/kg. Despite it was requested to express recovery as a yield of the assay, many participants seemed to have reported apparent recovery values. Due to this inconsistency in reporting, recovery values were not rated.

Method performance data reported by participants for the determination of BAA

		Frozen mussels			Lyophilized mussels (if different)		
LabCode	Measurand	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]
101	BaA	0.01	0.01	72			
102	BaA	0.1	0.3	72			
103	BaA	0.014	0.89	113.6	0.014	0.89	110.7
104	BaA	**1**	**2**	115			
105	BaA	0.12	0.36	96.6	0.12	0.36	96.6
106	BaA	0.11	0.21	88			
107	BaA	0.01	0.3	n.r.	0.01	0.3	
108	BaA	0.002	0.004	63	0.004	0.007	66
109	BaA	n.r.	n.r.	n.r.			
110	BaA	0.06	0.2	100.9	0.06	0.2	100.9
111	BaA	0,07	0,22	89	0,20	0,67	114
112	BaA	0.2	0.6	86	0.3	0.7	80
113	BaA	0.3	0.9	80	0.3	0.9	80
114	BaA	0.03	0.1	99.7	0.03	0.1	93.7
115	BaA	0.1	0.5	90	0.1	0.5	90
116	BaA	0.2	0.6	111	0.2	0.6	109
117	BaA	0.2	0.6	110	0.2	0.6	110
118	BaA	0.01	0.03	50	0.03	0.09	50
119	BaA	0.3	0.6	96	0.3	0.6	96
120	BaA	0.5	0.9	86	0.5	0.9	86
121	BaA	0.2	0.6	73			
122	BaA	0.1	0.2	102			
123	BaA	0.025	0.05	81	0.025	0.05	100
124	BaA	0.08	0.28	91.3			
125	BaA	0.2	0.4	87	0.2	0.4	87
126	BaA	0.06	0.2	95			
501	BaA	0.1	0.3	83	0.3	1	83
502	BaA	**<2.5**	**<5**	80-120			
503	BaA	n.r.	n.r.	n.r.			
506	BaA	0.1	0.3	n.r.	0.1	0.3	
508	BaA	0.07	0.2	90	0.05	0.1	85
510	BaA	**0.5**	**1**	100	0.5	1	100
511	BaA	0.3	0.9	88	0.3	0.9	88
512	BaA	0.1	0.5	73			
513	BaA	0.2	0.5	63			
514	BaA	0.02	0.02	67	0.08	0.08	66
515	BaA	0.2	0.5	100	0.2	0.5	100
516	BaA	0.02	0.05	79	0.1	0.2	80
517	BaA	0.03	0.1	77	0.03	0.1	86
518	BaA	0.1	0.3	86	0.1	0.3	85
519	BaA	0.1	0.2	101			
520	BaA	0.03	0.15	71.7			
521	BaA	0.1	0.3	n.r.			
522	BaA	0.3	0.9	85			
523	BaA	0.2	0.5	91			

n.r.: not reported

Method performance data reported by participants for the determination of BAP

		Frozen mussels			Lyophilized mussels (if different)		
LabCode	Measurand	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]
101	BaP	0.08	0.08	60			
102	BaP	0.1	0.3	79			
103	BaP	0.006	0.89	114.2	0.006	0.89	112.7
104	BaP	1	2	108			
105	BaP	0.08	0.24	101.8	0.08	0.24	101.8
106	BaP	0.09	0.18	79.8			101.4
107	BaP	0.01	0.3	n.r.	0.01	0.3	
108	BaP	0.002	0.004	48	0.003	0.006	53
109	BaP	n.r.	n.r.	n.r.			
110	BaP	0.06	0.2	84.5	0.06	0.2	84.5
111	BaP	0,15	0,51	98	0,25	0,83	88
112	BaP	0.2	0.7	95	0.3	0.8	91
113	BaP	0.3	0.9	80	0.3	0.9	80
114	BaP	0.05	0.2	97.3	0.1	0.3	78
115	BaP	0.04	0.2	90	0.04	0.2	90
116	BaP	0.1	0.3	114	0.1	0.3	93
117	BaP	0.2	0.6	105	0.2	0.6	105
118	BaP	0.01	0.03	70	0.03	0.09	70
119	BaP	0.3	0.6	102	0.3	0.6	102
120	BaP	0.5	0.9	93	0.5	0.9	93
121	BaP	0.2	0.6	73			
122	BaP	0.1	0.3	102			
123	BaP	0.025	0.05	88	0.025	0.05	90
124	BaP	0.01	0.04	89.2			
125	BaP	0.2	0.4	94	0.2	0.4	94
126	BaP	0.06	0.2	105			
501	BaP	0.1	0.3	100	0.3	1	100
502	BaP	<0.5	<1	80-120			
503	BaP	n.r.	n.r.	n.r.			
506	BaP	0.1	0.3	n.r.	0.1	0.3	
508	BaP	0.05	0.1	85	0.06	0.1	79
510	BaP	0.2	0.4	100	0.2	0.4	100
511	BaP	0.3	0.9	76	0.3	0.9	76
512	BaP	0.1	0.5	69			
513	BaP	0.07	0.2	78			
514	BaP	0.02	0.02	88	0.09	0.09	83
515	BaP	0.2	0.5	105	0.2	0.5	105
516	BaP	0.02	0.05	80	0.1	0.2	73
517	BaP	0.03	0.1	91	0.03	0.1	74
518	BaP	0.03	0.1	86	0.03	0.1	85
519	BaP	0.1	0.2	101			
520	BaP	0.05	0.25	72.8			
521	BaP	0.1	0.3	89			
522	BaP	0.3	0.9	85			
523	BaP	0.2	0.5	103			

n.r.: not reported

Method performance data reported by participants for the determination of BBF

		Frozen mussels			Lyophilized mussels (if different)		
LabCode	Measurand	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]
101	BbF	0.06	0.06	62			
102	BbF	0.1	0.3	97			
103	BbF	0.028	0.9	112.2	0.028	0.9	107.6
104	BbF	1	2	104			
105	BbF	0.11	0.33	100.8	0.11	0.33	100.8
106	BbF	0.21	0.41	95.2			
107	BbF	0.01	0.3	n.r.	0.01	0.3	
108	BbF	0.001	0.002	54	0.002	0.004	51
109	BbF	n.r.	n.r.	n.r.			
110	BbF	0.06	0.2	86	0.06	0.2	86
111	BbF	0,11	0,35	107	0,11	0,37	85
112	BbF	0.1	0.4	102	0.2	0.5	90
113	BbF	0.3	0.9	80	0.3	0.9	80
114	BbF	0.05	0.2	94.6	0.03	0.1	67.5
115	BbF	0.04	0.2	90	0.04	0.2	90
116	BbF	0.3	0.9	115	0.3	0.9	117
117	BbF	0.2	0.6	98	0.2	0.6	98
118	BbF	0.01	0.03	60	0.03	0.09	60
119	BbF	0.3	0.6	93	0.3	0.6	93
120	BbF	0.5	0.9	92	0.5	0.9	92
121	BbF	0.2	0.6	104			
122	BbF	0.1	0.3	105			
123	BbF	0.05	0.1	85	0.05	0.1	90
124	BbF	0.1	0.33	91.4			
125	BbF	0.2	0.4	97	0.2	0.4	97
126	BbF	0.1	0.3	92			
501	BbF	0.1	0.3	87	0.3	1	87
502	BbF	<2.5	<5	80-120			
503	BbF	n.r.	n.r.	n.r.			
506	BbF	0.1	0.3	n.r.	0.1	0.3	
508	BbF	0.08	0.2	90	0.08	0.2	93
510	BbF	0.2	0.4	100	0.2	0.4	100
511	BbF	0.3	0.9	83	0.3	0.9	83
512	BbF	0.1	0.5	67			
513	BbF	0.2	0.5	81			
514	BbF	0.03	0.03	75	0.1	0.1	71
515	BbF	0.2	0.5	110	0.2	0.5	110
516	BbF	0.02	0.05	78	0.1	0.2	76
517	BbF	0.03	0.1	99	0.03	0.1	86
518	BbF	0.1	0.3	86	0.1	0.3	85
519	BbF	0.1	0.2	96			
520	BbF	0.02	0.1	86.8			
521	BbF	0.4	1.2	n.r.			
522	BbF	0.3	0.9	85			
523	BbF	0.2	0.5	96			

n.r.: not reported

Method performance data reported by participants for the determination CHR.

		Frozen mussels			Lyophilized mussels (if different)		
LabCode	Measurand	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]
101	CHR	0.04	0.04	65			
102	CHR	0.1	0.3	72			
103	CHR	0.014	0.89	114.2	0.014	0.89	105.8
104	CHR	1	2	101			
105	CHR	0.03	0.09	99.6	0.03	0.09	99.6
106	CHR	0.11	0.22	96.3			
107	CHR	0.01	0.3	n.r.	0.01	0.3	
108	CHR	0.003	0.006	60	0.004	0.009	61
109	CHR	n.r.	n.r.	n.r.			
110	CHR	0.2	0.5	100.7	0.2	0.5	100.7
111	CHR	0,05	0,17	98	0,16	0,54	96
112	CHR	0.4	1.1	93	0.6	1.3	87
113	CHR	0.3	0.9	80	0.3	0.9	80
114	CHR	0.1	0.3	95.1	0.05	0.2	104.3
115	CHR	0.1	0.5	90	0.1	0.5	90
116	CHR	0.3	0.9	100	0.3	0.9	100
117	CHR	0.2	0.6	102	0.2	0.6	102
118	CHR	0.01	0.03	55	0.03	0.09	55
119	CHR	0.3	0.6	100	0.3	0.6	100
120	CHR	0.5	0.9	90	0.5	0.9	90
121	CHR	0.2	0.6	90			
122	CHR	0.1	0.3	102			
123	CHR	0.025	0.05	82	0.025	0.05	98
124	CHR	0.18	0.58	91.1			
125	CHR	0.2	0.4	120	0.2	0.4	120
126	CHR	0.03	0.1	97			
501	CHR	0.1	0.3	83	0.3	1	83
502	CHR	<2.5	<5	80-120			
503	CHR	n.r.	n.r.	n.r.			
506	CHR	0.1	0.3	n.r.	0.1	0.3	
508	CHR	0.08	0.2	92	0.1	0.2	89
510	CHR	1	2	100	1	2	100
511	CHR	0.3	0.9	92	0.3	0.9	92
512	CHR	0.1	0.5	79			
513	CHR	0.1	0.5	77			
514	CHR	0.04	0.04	75	0.16	0.16	68
515	CHR	0.2	0.5	105	0.2	0.5	105
516	CHR	0.02	0.05	73	0.1	0.2	76
517	CHR	0.03	0.1	73	0.03	0.1	86
518	CHR	0.2	0.6	86	0.2	0.6	85
519	CHR	0.1	0.2	104			
520	CHR	0.04	0.22	78.2			
521	CHR	0.2	0.6	n.r.			
522	CHR	0.3	0.9	85			
523	CHR	0.2	0.5	93			

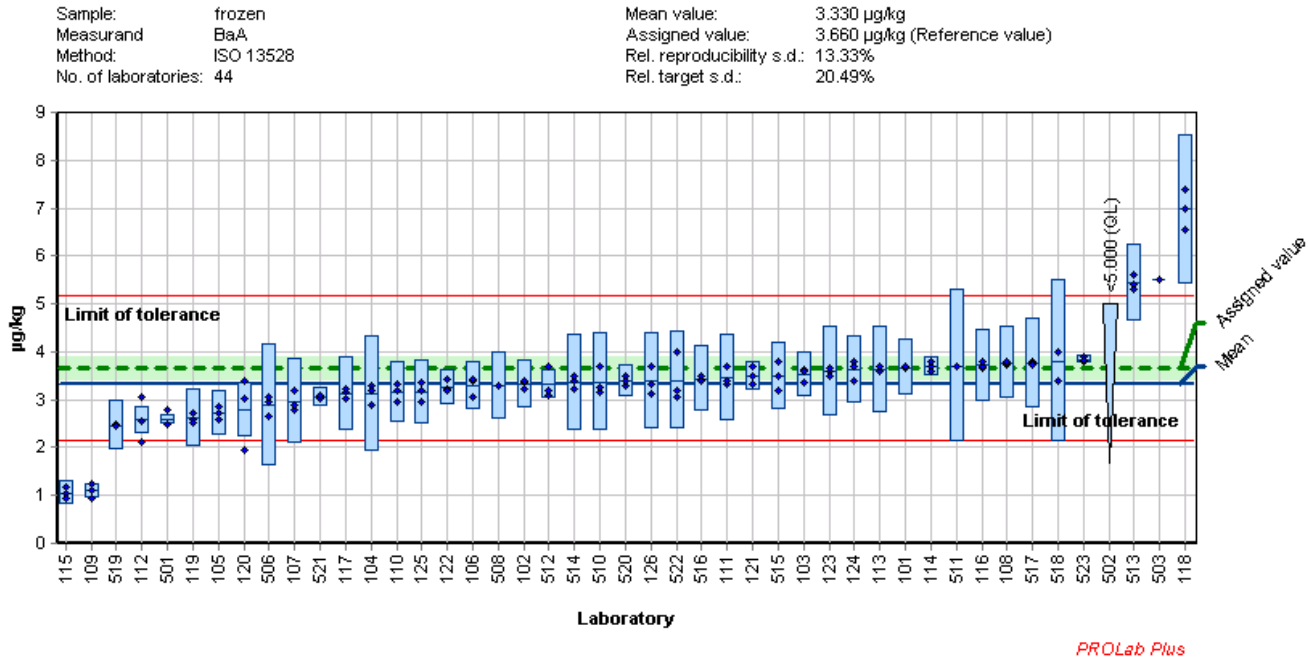
n.r.: not reported

ANNEX 9: Data reported by participants

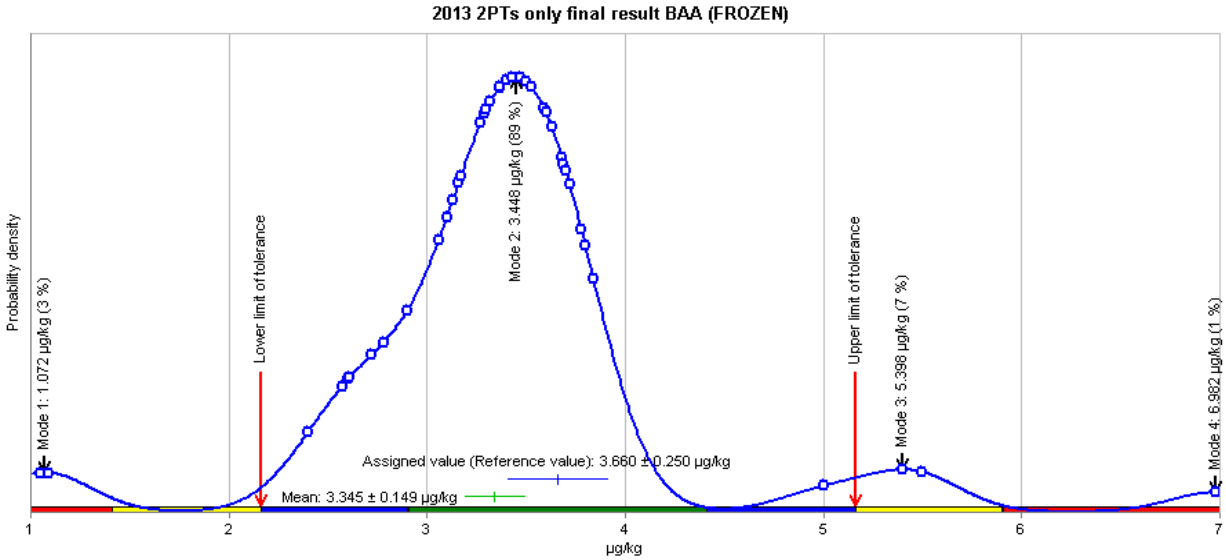
The data reported by the participants are compiled in the following tables. Uncertainty values that do not comply with the U_f thresholds (individual PAHs), respectively that are not equal to the propagated uncertainties of the individual analytes (SUM4PAH parameter) are marked by bold red font. The 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 in frozen mussels 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; green band: confidence interval of the assigned value



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



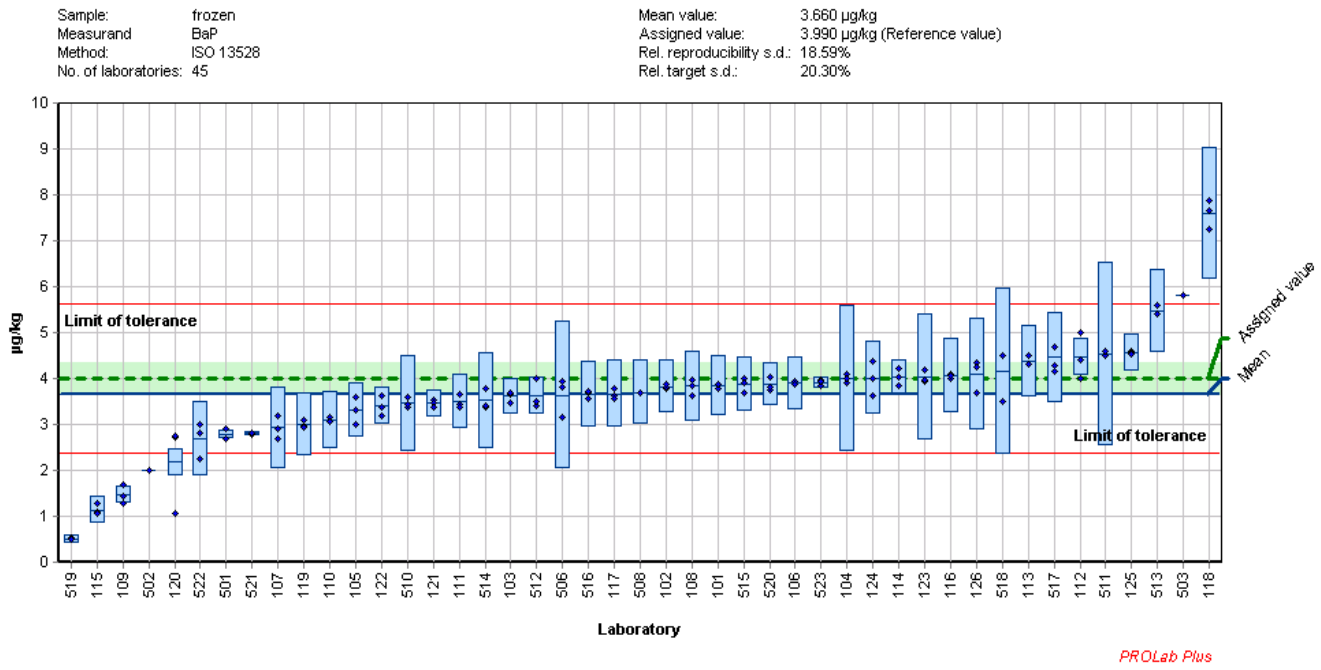
Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA) in frozen mussels.
Assigned value is 3.66 µg/kg**.** The uncertainty refers to the value for proficiency assessment.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BaA	3.68	3.66	3.68	3.68	0.58	B) GC-MS
102	BaA	3.24	3.35	3.38	3.32	0.50	B) GC-MS
103	BaA	3.35	3.63	3.61	3.53	0.48	E) HPLC-FD
104	BaA	3.3	2.9	3.2	3.1	1.2	B) GC-MS
105	BaA	2.58	2.84	2.73	2.72	0.46	E) HPLC-FD
106	BaA	3.39	3.06	3.41	3.29	0.50	E) HPLC-FD
107	BaA	2.8	3.2	2.9	2.9	0.88	C) GC-MS/MS
108	BaA	3.73	3.77	3.79	3.78	0.76	D) GC-HRMS
109	BaA	0.93	1.25	1.095	1.09	0.16	
110	BaA	3.31	3.19	2.97	3.16	0.63	E) HPLC-FD
111	BaA	3.33	3.38	3.69	3.47	0.90	B) GC-MS
112	BaA	2.11	2.54	3.06	2.57	0.3	B) GC-MS
113	BaA	3.6	3.6	3.7	3.6	0.9	B) GC-MS
114	BaA	3.69	3.59	3.80	3.69	0.2	C) GC-MS/MS
115	BaA	1.05	1.16	0.943	1.05	0.26	E) HPLC-FD
116	BaA	3.67	3.70	3.79	3.72	0.75	B) GC-MS, E) HPLC-FD
117	BaA	3.14	3.03	3.22	3.13	0.78	B) GC-MS
118	BaA	7.39	6.55	6.98	6.98	1.56	C) GC-MS/MS
119	BaA	2.58	2.73	2.53	2.61	0.6	C) GC-MS/MS
120	BaA	1.94	3.01	3.40	2.78	0.56	B) GC-MS
121	BaA	3.48	3.33	3.68	3.50	0.3	H) LC-MS/MS
122	BaA	3.41	3.21	3.18	3.27	0.37	B) GC-MS
123	BaA	3.61	3.49	3.67	3.59	0.93	E) HPLC-FD
124	BaA	3.38	3.81	3.69	3.63	0.69	F) HPLC-UV/FD
125	BaA	2.96	3.207	3.349	3.172	0.673	E) HPLC-FD
126	BaA	3.71	3.34	3.12	3.4	1.02	F) HPLC-UV/FD
501	BaA	2.8	2.5	2.5	2.6	0.1	B) GC-MS
502	BaA	<5	<5	<5	<5	n.r.	C) GC-MS/MS
503	BaA	5.5	5.5	5.5	5.5	n.r.	E) HPLC-FD
506	BaA	2.65	2.97	3.07	2.90	1.27	B) GC-MS
510	BaA	3.17	3.26	3.69	3.37	1.01	E) HPLC-FD
508	BaA	3.3	3.3	3.3	3.3	0.7	C) GC-MS/MS
511	BaA	3.7	3.7	3.7	3.7	1.6	E) HPLC-FD
512	BaA	3.1	3.7	3.2	3.3	0.3	E) HPLC-FD
513	BaA	5.6	5.4	5.3	5.4	0.8	E) HPLC-FD
514	BaA	3.225	3.396	3.477	3.366	1.010	C) GC-MS/MS
515	BaA	3.5	3.2	3.8	3.5	0.7	C) GC-MS/MS
516	BaA	3.42	3.50	3.38	3.43	0.69	C) GC-MS/MS
517	BaA	3.81	3.77	3.72	3.72	0.93	C) GC-MS/MS
518	BaA	3.4	4.0	4.0	3.8	1.7	E) HPLC-FD
519	BaA	2.46	2.47	2.46	2.40	0.5	C) GC-MS/MS
520	BaA	3.49	3.29	3.38	3.43	0.33	F) HPLC-UV/FD
521	BaA	3.06	3.02	3.10	3.06	0.20	E) HPLC-FD
522	BaA	3.99	3.04	3.18	3.40	1.02	E) HPLC-FD
523	BaA	3.80	3.89	3.84	3.84	0.09	B) GC-MS

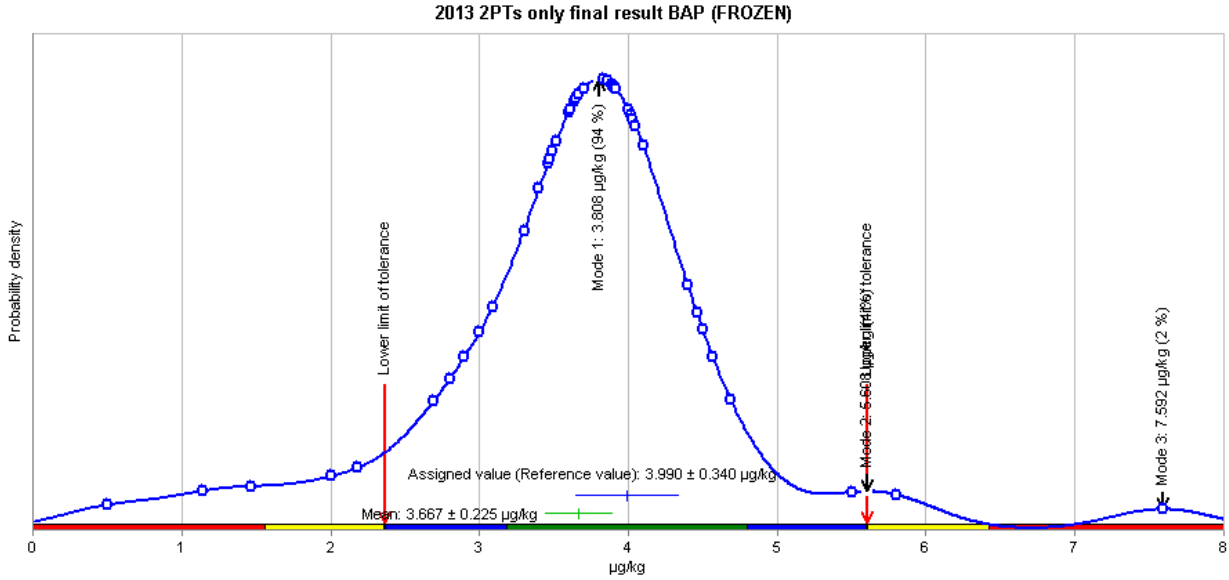
n.r.: not reported

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



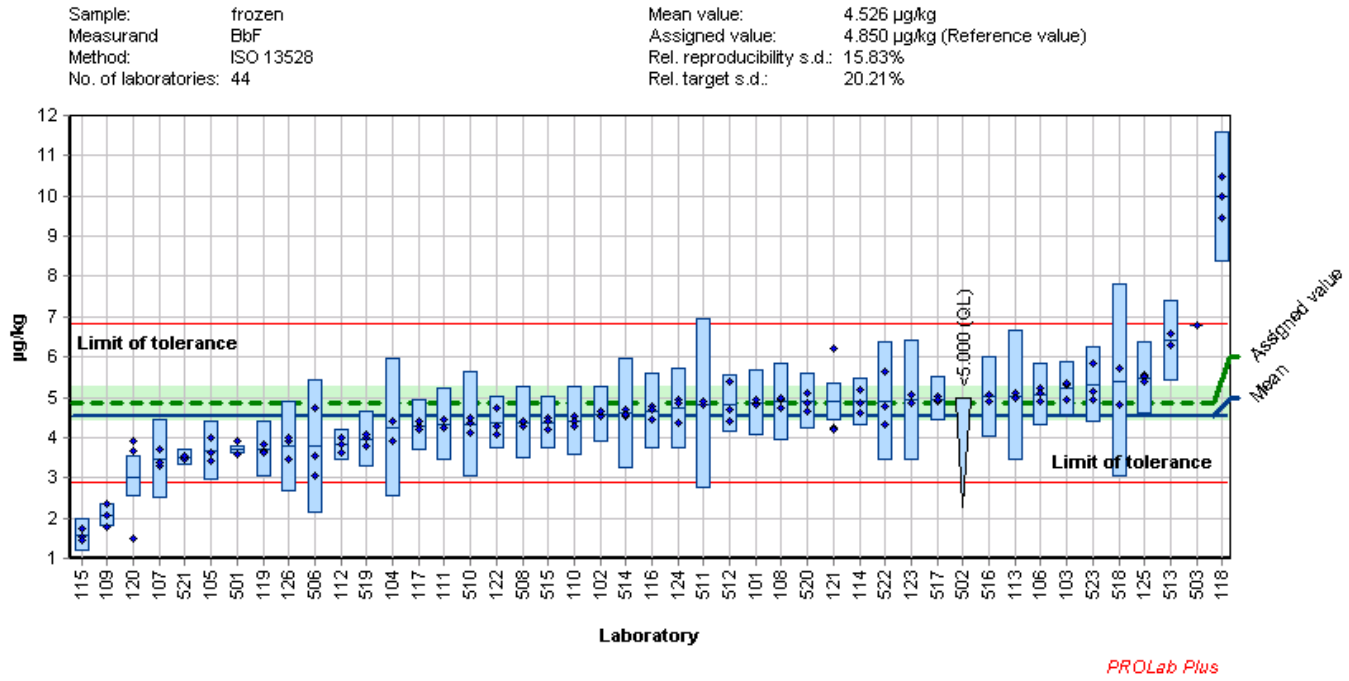
Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP) in frozen mussels test material.
Assigned value is 3,99 µg/kg**.** The uncertainty refers to the final value.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BaP	3.86	3.78	3.88	3.86	0.67	B) GC-MS
102	BaP	3.78	3.82	3.88	3.83	0.57	B) GC-MS
103	BaP	3.47	3.66	3.70	3.61	0.38	E) HPLC-FD
104	BaP	4.1	3.9	4.0	4.0	1.6	B) GC-MS
105	BaP	3.59	2.99	3.32	3.30	0.59	E) HPLC-FD
106	BaP	3.93	3.87	3.88	3.89	0.59	E) HPLC-FD
107	BaP	2.7	3.2	2.9	2.9	0.88	C) GC-MS/MS
108	BaP	3.64	3.84	3.97	3.90	0.78	D) GC-HRMS
109	BaP	1.27	1.68	1.45	1.47	0.20	
110	BaP	3.16	3.05	3.07	3.09	0.62	E) HPLC-FD
111	BaP	3.45	3.38	3.65	3.49	0.59	B) GC-MS
112	BaP	3.99	4.41	4.99	4.46	0.4	B) GC-MS
113	BaP	4.3	4.5	4.3	4.4	0.8	B) GC-MS
114	BaP	4.02	3.85	4.22	4.03	0.37	C) GC-MS/MS
115	BaP	1.08	1.29	1.05	1.14	0.29	E) HPLC-FD
116	BaP	3.99	4.10	4.07	4.05	0.81	B) GC-MS, E) HPLC-FD
117	BaP	3.64	3.57	3.79	3.67	0.73	B) GC-MS
118	BaP	7.89	7.24	7.66	7.59	1.43	C) GC-MS/MS
119	BaP	3.08	2.98	2.95	3.00	0.7	C) GC-MS/MS
120	BaP	1.07	2.72	2.75	2.18	0.29	B) GC-MS
121	BaP	3.53	3.48	3.38	3.47	0.3	H) LC-MS/MS
122	BaP	3.62	3.20	3.38	3.40	0.40	B) GC-MS
123	BaP	3.94	3.96	4.19	4.03	1.37	E) HPLC-FD
124	BaP	3.64	4.39	4.01	4.02	0.80	F) HPLC-UV/FD
125	BaP	4.606	4.561	4.536	4.568	0.412	E) HPLC-FD
126	BaP	4.33	4.25	3.69	4.1	1.23	F) HPLC-UV/FD
501	BaP	2.9	2.7	2.7	2.8	0.1	B) GC-MS
502	BaP	2	2	2	2	n.r.	C) GC-MS/MS
503	BaP	5.8	5.8	5.8	5.8	n.r.	E) HPLC-FD
506	BaP	3.16	3.81	3.95	3.64	1.60	B) GC-MS
510	BaP	3.37	3.43	3.59	3.46	1.04	E) HPLC-FD
508	BaP	3.7	3.7	3.7	3.7	0.7	C) GC-MS/MS
511	BaP	4.5	4.5	4.6	4.5	2.0	E) HPLC-FD
512	BaP	3.4	4.0	3.5	3.6	0.4	E) HPLC-FD
513	BaP	5.4	5.6	5.4	5.5	0.9	E) HPLC-FD
514	BaP	3.378	3.401	3.773	3.517	1.055	C) GC-MS/MS
515	BaP	4.0	3.7	3.9	3.9	0.6	C) GC-MS/MS
516	BaP	3.68	3.73	3.55	3.65	0.73	C) GC-MS/MS
517	BaP	4.17	4.27	4.69	4.69	1.03	C) GC-MS/MS
518	BaP	3.5	4.5	4.5	4.1	1.8	E) HPLC-FD
519	BaP	0.52	0.50	0.49	0.50	0.1	C) GC-MS/MS
520	BaP	4.03	3.76	3.81	3.92	0.47	F) HPLC-UV/FD
521	BaP	2.79	2.80	2.81	2.80	0.05	E) HPLC-FD
522	BaP	2.24	2.82	3.00	2.69	0.81	E) HPLC-FD
523	BaP	3.84	3.96	3.93	3.91	0.12	B) GC-MS

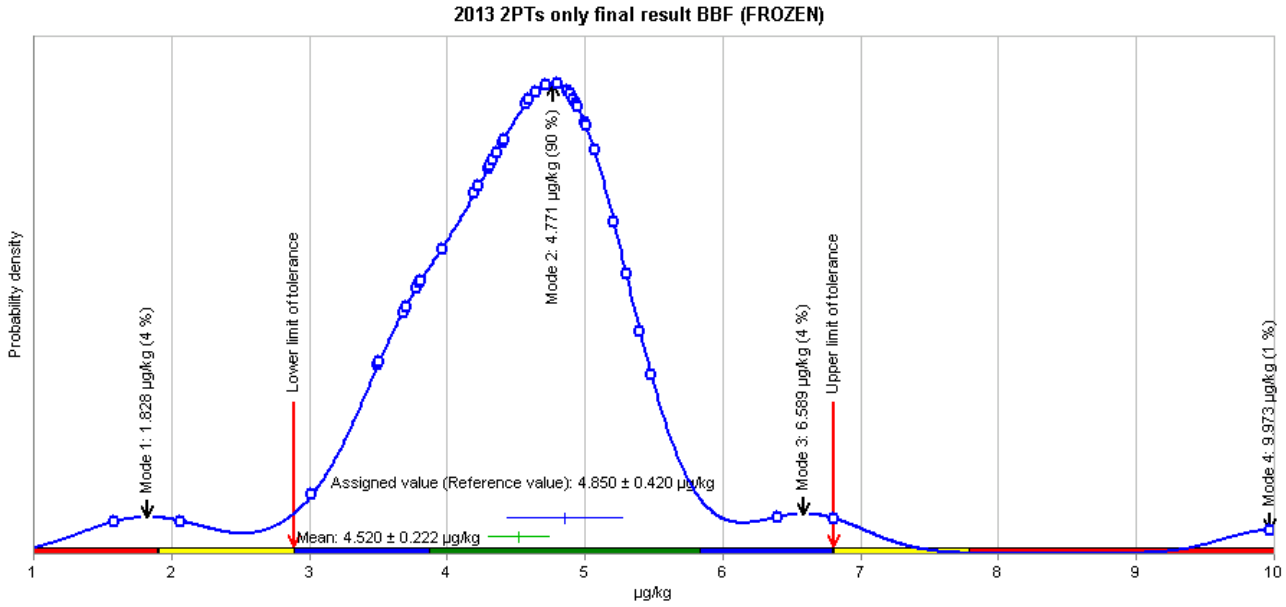
n.r.: not reported

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



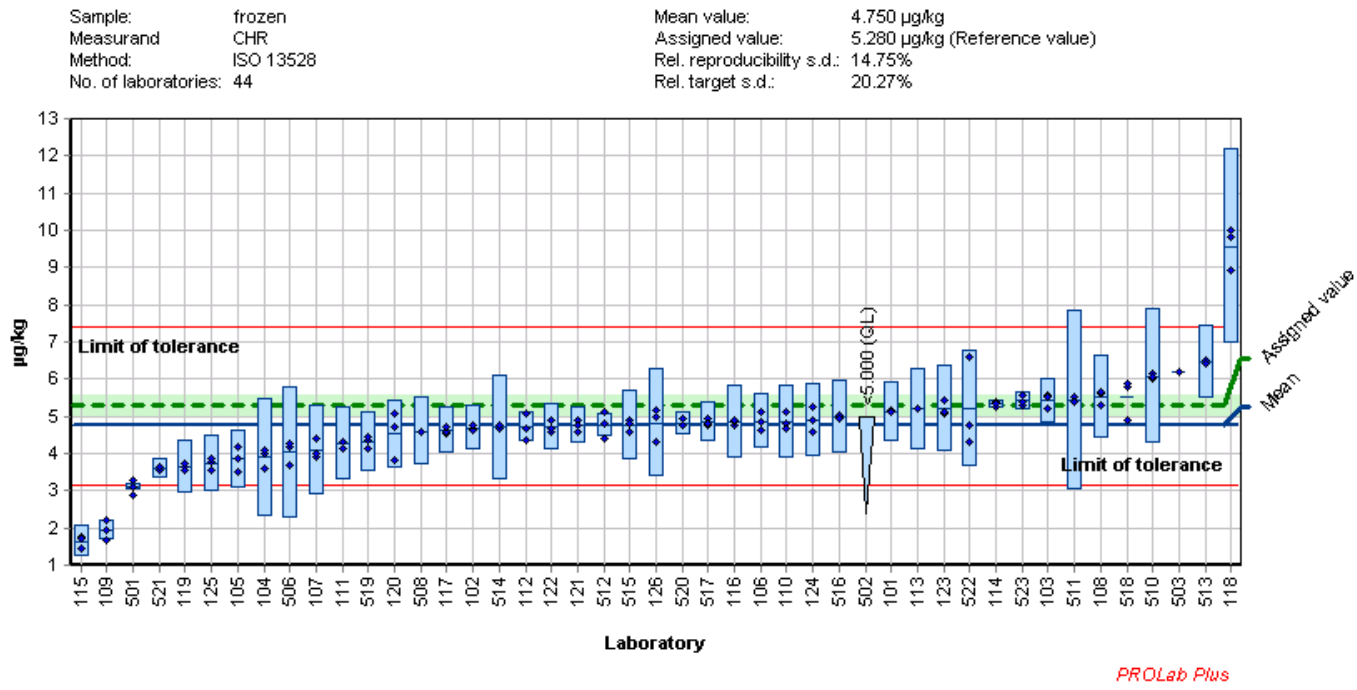
Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF) in frozen mussels test material.
Assigned value is 4,85 µg/kg. The uncertainty refers to the final value.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BbF	4.87	4.81	4.92	4.87	0.83	B) GC-MS
102	BbF	4.52	4.54	4.65	4.57	0.69	B) GC-MS
103	BbF	4.96	5.31	5.37	5.21	0.68	E) HPLC-FD
104	BbF	4.4	3.9	4.4	4.2	1.7	B) GC-MS
105	BbF	3.41	4.01	3.63	3.68	0.74	E) HPLC-FD
106	BbF	5.22	4.89	5.11	5.07	0.77	E) HPLC-FD
107	BbF	3.3	3.7	3.4	3.5	1.0	C) GC-MS/MS
108	BbF	4.74	4.94	4.97	4.95	0.99	D) GC-HRMS
109	BbF	1.79	2.35	2.05	2.07	0.28	
110	BbF	4.54	4.40	4.28	4.41	0.88	E) HPLC-FD
111	BbF	4.26	4.43	4.25	4.31	0.91	B) GC-MS
112	BbF	3.61	3.84	3.99	3.81	0.4	B) GC-MS
113	BbF	5.0	5.1	5.0	5.0	1.6	B) GC-MS
114	BbF	4.61	5.2	4.86	4.89	0.59	C) GC-MS/MS
115	BbF	1.53	1.75	1.47	1.58	0.40	E) HPLC-FD
116	BbF	4.77	4.69	4.45	4.64	0.94	B) GC-MS, E) HPLC-FD
117	BbF	4.28	4.20	4.42	4.30	0.63	B) GC-MS
118	BbF	10.47	9.44	10.00	9.97	1.64	C) GC-MS/MS
119	BbF	3.65	3.84	3.62	3.70	0.7	C) GC-MS/MS
120	BbF	1.48	3.93	3.65	3.02	0.51	B) GC-MS
121	BbF	4.24	4.22	6.21	4.23	0.4	H) LC-MS/MS
122	BbF	4.74	4.08	4.28	4.36	0.66	B) GC-MS
123	BbF	4.85	4.86	5.05	4.92	1.48	E) HPLC-FD
124	BbF	4.38	4.94	4.85	4.72	1.00	F) HPLC-UV/FD
125	BbF	5.566	5.5	5.379	5.482	0.910	E) HPLC-FD
126	BbF	3.90	3.99	3.46	3.80	1.14	F) HPLC-UV/FD
501	BbF	3.9	3.6	3.6	3.7	0.1	B) GC-MS
502	BbF	<5	<5	<5	<5	n.r.	C) GC-MS/MS
503	BbF	6.8	6.8	6.8	6.8	n.r.	E) HPLC-FD
506	BbF	3.56	4.74	3.05	3.78	1.66	B) GC-MS
510	BbF	4.13	4.37	4.49	4.33	1.3	E) HPLC-FD
508	BbF	4.4	4.3	4.4	4.4	0.9	C) GC-MS/MS
511	BbF	4.8	4.8	4.9	4.8	2.1	E) HPLC-FD
512	BbF	4.4	5.4	4.7	4.8	0.7	E) HPLC-FD
513	BbF	6.3	6.6	6.3	6.4	1.0	E) HPLC-FD
514	BbF	4.697	4.528	4.555	4.593	1.378	C) GC-MS/MS
515	BbF	4.2	4.5	4.4	4.3	0.6	C) GC-MS/MS
516	BbF	4.89	5.08	5.07	5.01	1.00	C) GC-MS/MS
517	BbF	4.9	5.04	4.92	4.92	0.54	C) GC-MS/MS
518	BbF	4.8	5.7	5.7	5.4	2.4	E) HPLC-FD
519	BbF	3.80	4.01	4.07	3.96	0.7	C) GC-MS/MS
520	BbF	5.12	4.67	4.87	4.94	0.71	F) HPLC-UV/FD
521	BbF	3.49	3.48	3.55	3.51	0.19	E) HPLC-FD
522	BbF	5.65	4.31	4.79	4.92	1.48	E) HPLC-FD
523	BbF	4.94	5.13	5.84	5.30	0.95	B) GC-MS

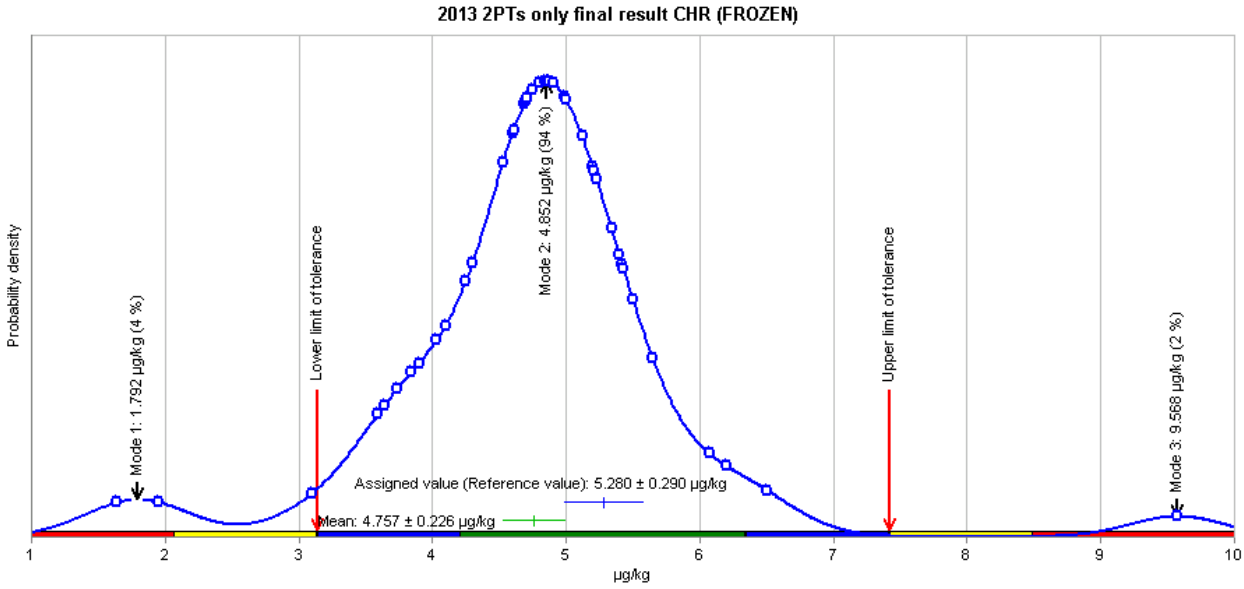
n.r.: not reported

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



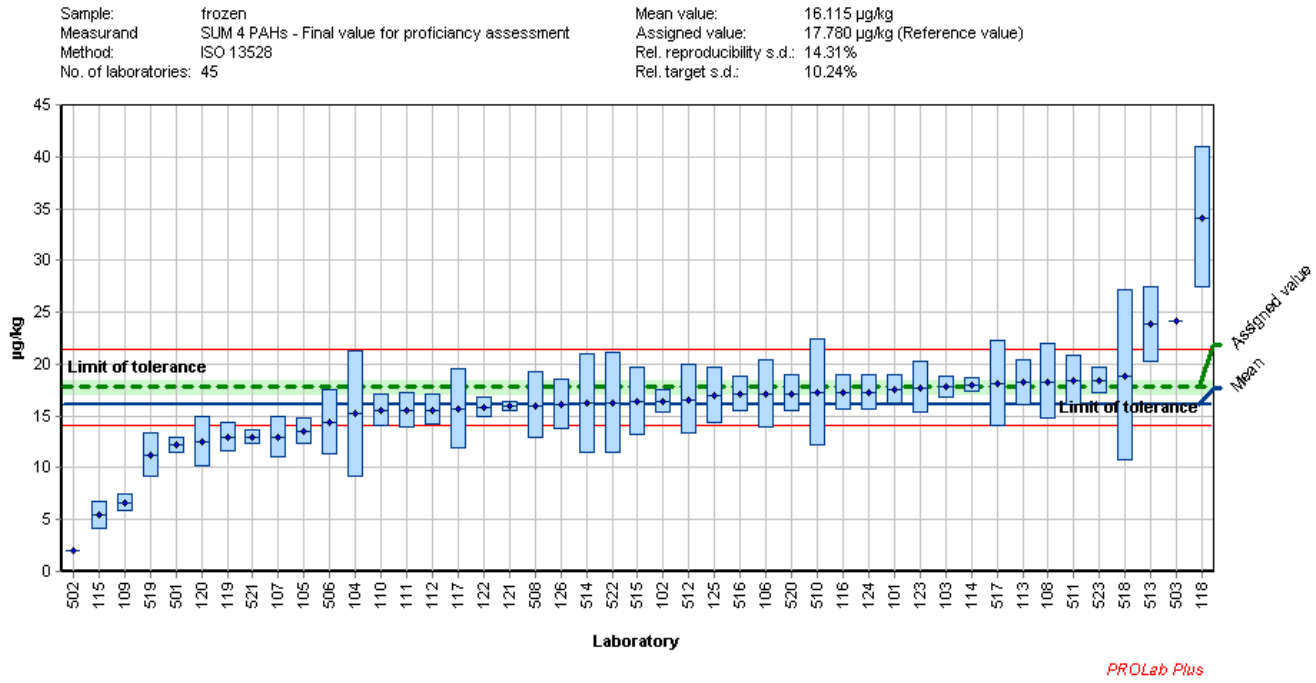
Results, as reported by the participants, for the content of chrysene (CHR) in frozen mussels test material.
Assigned value is 5.28 µg/kg. The uncertainty refers to the final value.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	CHR	5.12	5.16	5.11	5.12	0.81	B) GC-MS
102	CHR	4.66	4.63	4.78	4.69	0.59	B) GC-MS
103	CHR	5.20	5.55	5.53	5.43	0.61	E) HPLC-FD
104	CHR	4.0	3.6	4.1	3.9	1.6	B) GC-MS
105	CHR	3.49	3.88	4.16	3.84	0.77	E) HPLC-FD
106	CHR	5.11	4.62	4.84	4.86	0.74	E) HPLC-FD
107	CHR	3.9	4.4	4.0	4.1	1.2	C) GC-MS/MS
108	CHR	5.29	5.63	5.67	5.65	1.13	D) GC-HRMS
109	CHR	1.69	2.22	1.95	1.95	0.26	
110	CHR	5.11	4.80	4.68	4.86	0.98	E) HPLC-FD
111	CHR	4.32	4.31	4.13	4.25	0.98	B) GC-MS
112	CHR	4.38	4.67	5.08	4.71	0.4	B) GC-MS
113	CHR	5.2	5.2	5.2	5.2	1.1	B) GC-MS
114	CHR	5.27	5.38	5.36	5.34	0.12	C) GC-MS/MS
115	CHR	1.76	1.72	1.45	1.64	0.41	E) HPLC-FD
116	CHR	4.76	4.86	4.90	4.84	0.98	B) GC-MS, E) HPLC-FD
117	CHR	4.53	4.57	4.73	4.61	0.63	B) GC-MS
118	CHR	9.98	8.91	9.81	9.57	2.62	C) GC-MS/MS
119	CHR	3.62	3.74	3.56	3.64	0.7	C) GC-MS/MS
120	CHR	5.06	4.72	3.80	4.53	0.91	B) GC-MS
121	CHR	4.6	4.90	4.74	4.75	0.5	H) LC-MS/MS
122	CHR	4.88	4.60	4.65	4.71	0.62	B) GC-MS
123	CHR	5.08	5.12	5.43	5.21	1.15	E) HPLC-FD
124	CHR	4.56	5.24	4.88	4.90	1.00	F) HPLC-UV/FD
125	CHR	3.563	3.793	3.861	3.739	0.772	E) HPLC-FD
126	CHR	5.15	5.00	4.31	4.8	1.45	F) HPLC-UV/FD
501	CHR	3.3	2.9	3.1	3.1	0.1	B) GC-MS
502	CHR	<5	<5	<5	<5	n.r.	C) GC-MS/MS
503	CHR	6.2	6.2	6.2	6.2	n.r.	E) HPLC-FD
506	CHR	3.68	4.16	4.25	4.03	1.77	B) GC-MS
510	CHR	6.16	6.01	6.04	6.07	1.82	E) HPLC-FD
508	CHR	4.6	4.6	4.6	4.6	0.9	C) GC-MS/MS
511	CHR	5.4	5.5	5.4	5.4	2.4	E) HPLC-FD
512	CHR	4.4	5.1	4.8	4.8	0.3	E) HPLC-FD
513	CHR	6.5	6.5	6.4	6.5	1.0	E) HPLC-FD
514	CHR	4.668	4.693	4.747	4.703	1.411	C) GC-MS/MS
515	CHR	4.6	4.9	4.8	4.7	0.9	C) GC-MS/MS
516	CHR	5.00	5.01	4.95	4.99	1.00	C) GC-MS/MS
517	CHR	4.95	4.76	4.8	4.8	0.53	C) GC-MS/MS
518	CHR	4.9	5.8	5.9	5.5	n.r.	E) HPLC-FD
519	CHR	4.14	4.34	4.43	4.30	0.8	C) GC-MS/MS
520	CHR	4.96	4.74	4.77	4.87	0.31	F) HPLC-UV/FD
521	CHR	3.62	3.53	3.63	3.59	0.27	E) HPLC-FD
522	CHR	6.60	4.30	4.78	5.23	1.57	E) HPLC-FD
523	CHR	5.30	5.40	5.55	5.42	0.25	B) GC-MS

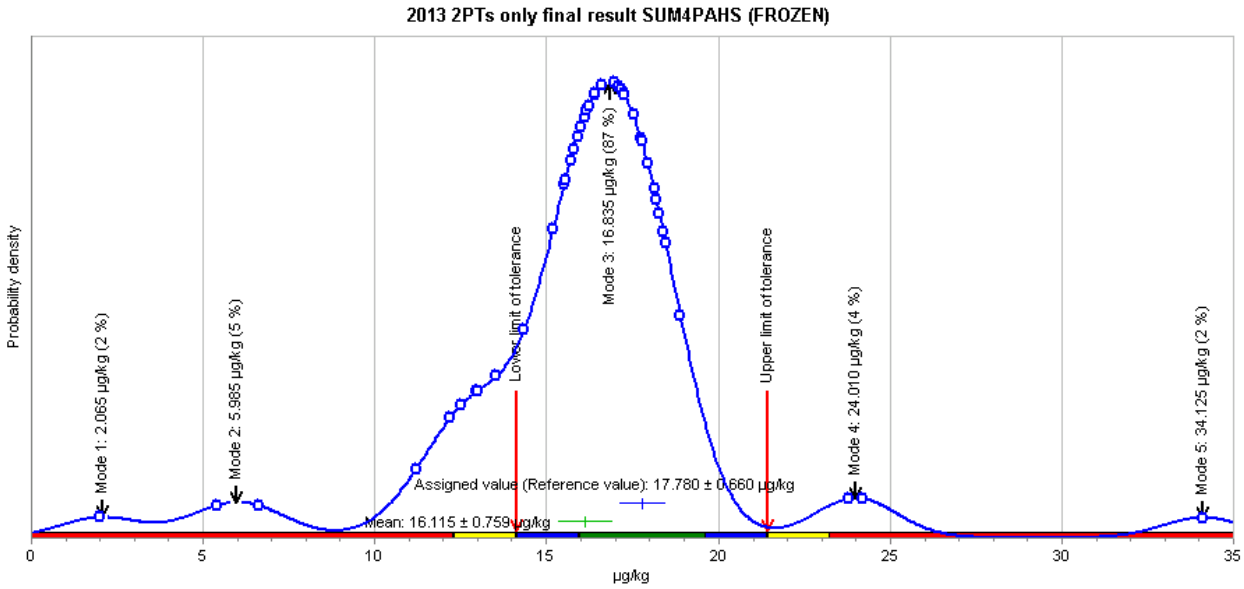
n.r.: not reported

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content of frozen mussels 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 SUM of 4 PAH content of frozen mussels test sample.



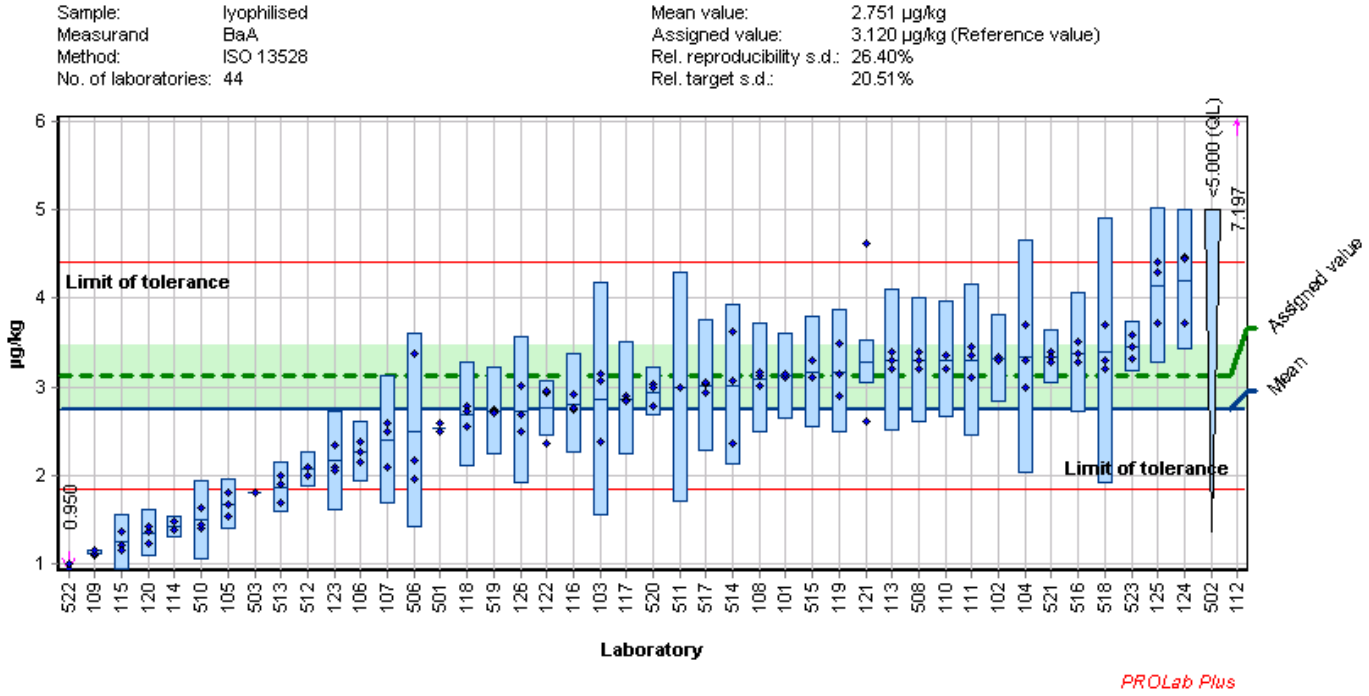
Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH) in frozen mussels test material. Assigned value is 17,78 µg/kg.

LCode	Measurant	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	SUM 4PAH	17.53	1.47	B) GC-MS
102	SUM 4PAH	16.41	1.18	B) GC-MS
103	SUM 4PAH	17.78	1.10	E) HPLC-FD
104	SUM 4PAH	15.2	6.1	B) GC-MS
05	SUM 4PAH	13.54	1.30	E) HPLC-FD
106	SUM 4PAH	17.11	3.34	E) HPLC-FD
107	SUM 4PAH	13	2.0	C) GC-MS/MS
108	SUM 4PAH	18.29	3.66	D) GC-HRMS
109	SUM 4PAH	6.60	0.90	
110	SUM 4PAH	15.52	1.59	E) HPLC-FD
111	SUM 4PAH	15.52	1.71	B) GC-MS
112	SUM 4PAH	15.55	1.5	B) GC-MS
113	SUM 4PAH	18.2	2.2	B) GC-MS
114	SUM 4PAH	17.95	0.7	C) GC-MS/MS
115	SUM 4PAH	5.41	1.35	E) HPLC-FD
116	SUM 4PAH	17.25	1.75	B) GC-MS, E) HPLC-FD
117	SUM 4PAH	15.70	3.9	B) GC-MS
118	SUM 4PAH	34.11	6.86	C) GC-MS/MS
119	SUM 4PAH	12.96	1.4	C) GC-MS/MS
120	SUM 4PAH	12.51	2.50	B) GC-MS
121	SUM 4PAH	15.9	0.5	H) LC-MS/MS
122	SUM 4PAH	15.8	1.06	B) GC-MS
123	SUM 4PAH	17.75	2.50	E) HPLC-FD
124	SUM 4PAH	17.26	1.77	F) HPLC-UV/FD
125	SUM 4PAH	16.961	2.768	E) HPLC-FD
126	SUM 4PAH	16.1	2.44	F) HPLC-UV/FD
501	SUM 4PAH	12.2	0.8	B) GC-MS
502	SUM 4PAH	2.0	n.r.	C) GC-MS/MS
503	SUM 4PAH	24.2	n.r.	E) HPLC-FD
506	SUM 4PAH	14.35	3.17	B) GC-MS
510	SUM 4PAH	17.24	5.2	E) HPLC-FD
508	SUM 4PAH	16	3.2	C) GC-MS/MS
511	SUM 4PAH	18.4	2.4	E) HPLC-FD
512	SUM 4PAH	16.6	3.4	E) HPLC-FD
513	SUM 4PAH	23.8	3.7	E) HPLC-FD
514	SUM 4PAH	16.179	4.854	C) GC-MS/MS
515	SUM 4PAH	16.4	3.3	C) GC-MS/MS
516	SUM 4PAH	17.08	1.73	C) GC-MS/MS
517	SUM 4PAH	18.13	4.17	C) GC-MS/MS
518	SUM 4PAH	18.9	8.3	E) HPLC-FD
519	SUM 4PAH	11.20	2.2	C) GC-MS/MS
520	SUM 4PAH	17.16	1.79	F) HPLC-UV/FD
521	SUM 4PAH	12.96	0.71	E) HPLC-FD
522	SUM 4PAH	16.23	4.87	E) HPLC-FD
523	SUM 4PAH	18.47	1.29	B) GC-MS

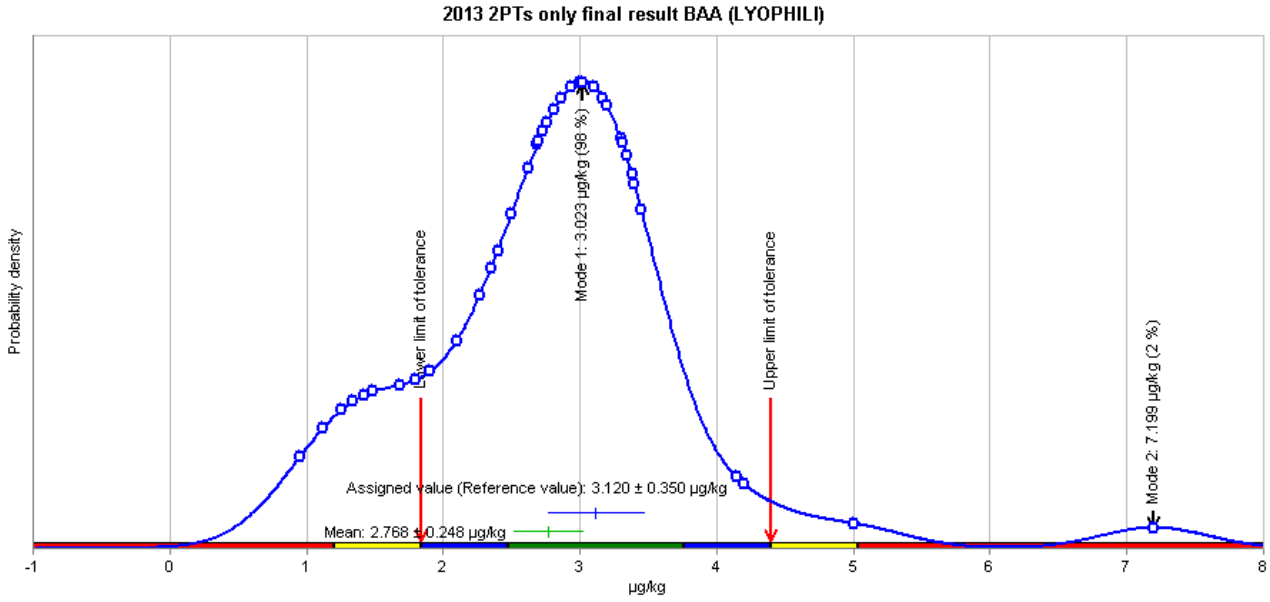
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the freeze dried (lyophilized) mussels 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) anthracene (BAA) content of freeze dried (lyophilized) mussels test sample



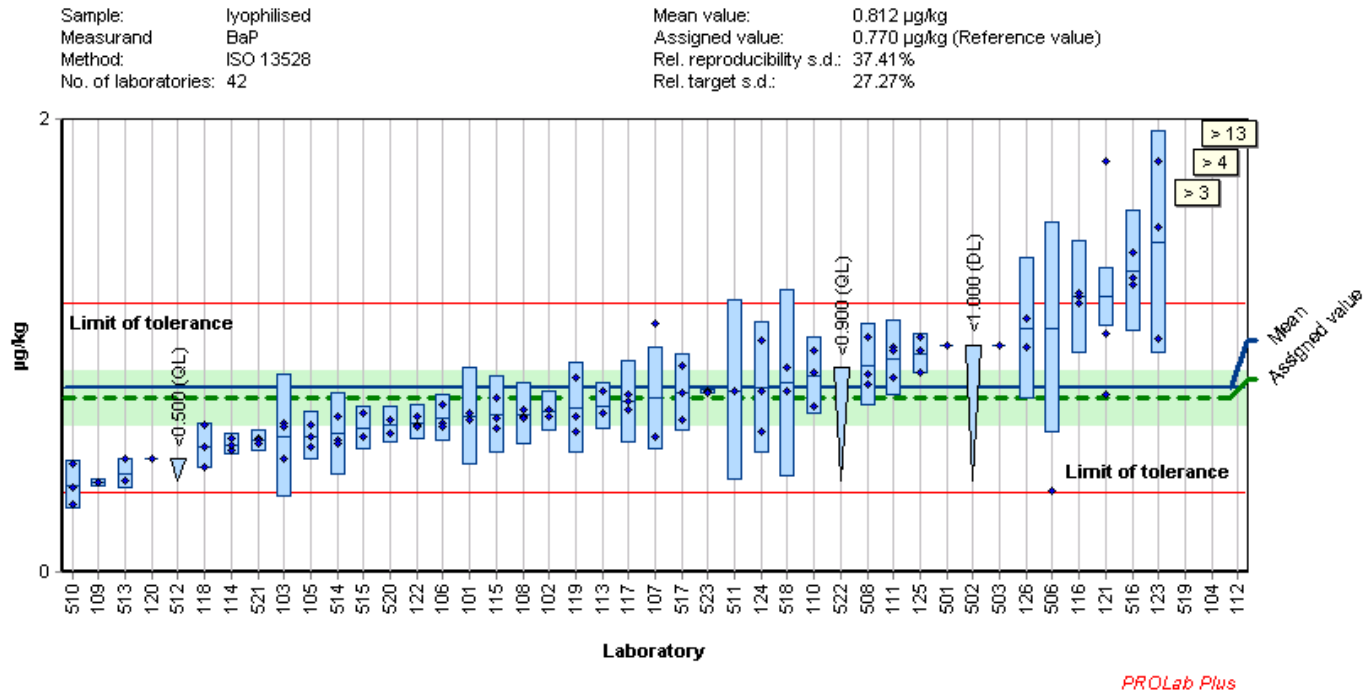
Results, as reported by participants, for the content of benz[*a*]anthracene (BAA) in the freeze dried (lyophilized) mussels test material.
Assigned value is 3,12 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BaA	3.10	3.14	n.r.	3.10	0.49	B) GC-MS
102	BaA	3.34	3.30	3.30	3.31	0.50	B) GC-MS
103	BaA	3.07	2.38	3.14	2.86	1.32	E) HPLC-FD
104	BaA	3.3	3.7	3.0	3.3	1.3	B) GC-MS
105	BaA	1.54	1.80	1.68	1.68	0.28	E) HPLC-FD
106	BaA	2.15	2.39	2.26	2.27	0.34	E) HPLC-FD
107	BaA	2.1	2.6	2.5	2.4	0.73	C) GC-MS/MS
108	BaA	3.12	3.01	3.16	3.10	0.62	D) GC-HRMS
109	BaA	1.10	1.12	1.15	1.12	0.03	
110	BaA	3.35	3.20	3.36	3.30	0.66	E) HPLC-FD
111	BaA	3.45	3.36	3.10	3.30	0.86	B) GC-MS
112	BaA	6.88	7.64	7.07	7.20	0.7	B) GC-MS
113	BaA	3.2	3.4	3.3	3.3	0.8	B) GC-MS
114	BaA	1.38	1.49	1.38	1.42	0.12	C) GC-MS/MS
115	BaA	1.22	1.16	1.36	1.25	0.31	E) HPLC-FD
116	BaA	2.75	2.91	2.77	2.81	0.57	B) GC-MS, E) HPLC-FD
117	BaA	2.89	2.86	2.84	2.86	0.64	B) GC-MS
118	BaA	2.55	2.79	2.72	2.69	0.60	C) GC-MS/MS
119	BaA	2.90	3.14	3.48	3.17	0.7	C) GC-MS/MS
120	BaA	1.36	1.24	1.43	1.34	0.27	B) GC-MS
121	BaA	2.61	4.61	2.62	2.62	0.2	H) LC-MS/MS
122	BaA	2.37	2.94	2.96	2.76	0.31	B) GC-MS
123	BaA	2.35	2.09	2.05	2.35	0.61	E) HPLC-FD
124	BaA	4.46	3.71	4.44	4.20	0.80	F) HPLC-UV/FD
125	BaA	4.412	3.721	4.298	4.143	0.879	E) HPLC-FD
126	BaA	3.02	2.69	2.49	2.7	0.82	F) HPLC-UV/FD
501	BaA	2.6	2.5	2.5	2.5	1.0	B) GC-MS
502	BaA	<5	<5	<5	<5	n.r.	C) GC-MS/MS
503	BaA	1.8	1.8	1.8	1.8	n.r.	E) HPLC-FD
506	BaA	3.38	1.96	2.17	2.50	1.10	B) GC-MS
508	BaA	3.3	3.2	3.4	3.3	0.7	C) GC-MS/MS
510	BaA	1.64	1.40	1.44	1.49	0.45	E) HPLC-FD
511	BaA	3.0	3.0	3.0	3.0	1.3	E) HPLC-FD
512	BaA	2.1	2.1	2.0	2.1	0.2	E) HPLC-FD
513	BaA	2.0	1.7	1.9	1.9	0.3	E) HPLC-FD
514	BaA	3.623	2.362	3.078	3.021	0.906	C) GC-MS/MS
515	BaA	3.1	3.3	3.1	3.2	0.6	C) GC-MS/MS
516	BaA	3.50	3.28	3.37	3.38	0.68	C) GC-MS/MS
517	BaA	2.94	3.03	3.05	2.94	0.73	C) GC-MS/MS
518	BaA	3.7	3.2	3.3	3.4	1.5	E) HPLC-FD
519	BaA	2.75	2.73	2.71	2.73	0.5	C) GC-MS/MS
520	BaA	3.04	2.79	3.00	2.94	0.28	F) HPLC-UV/FD
521	BaA	3.40	3.33	3.28	3.34	0.30	E) HPLC-FD
522	BaA	0.94	1.00	0.91	0.95	0.29	E) HPLC-FD
523	BaA	3.31	3.59	3.46	3.45	0.28	B) GC-MS

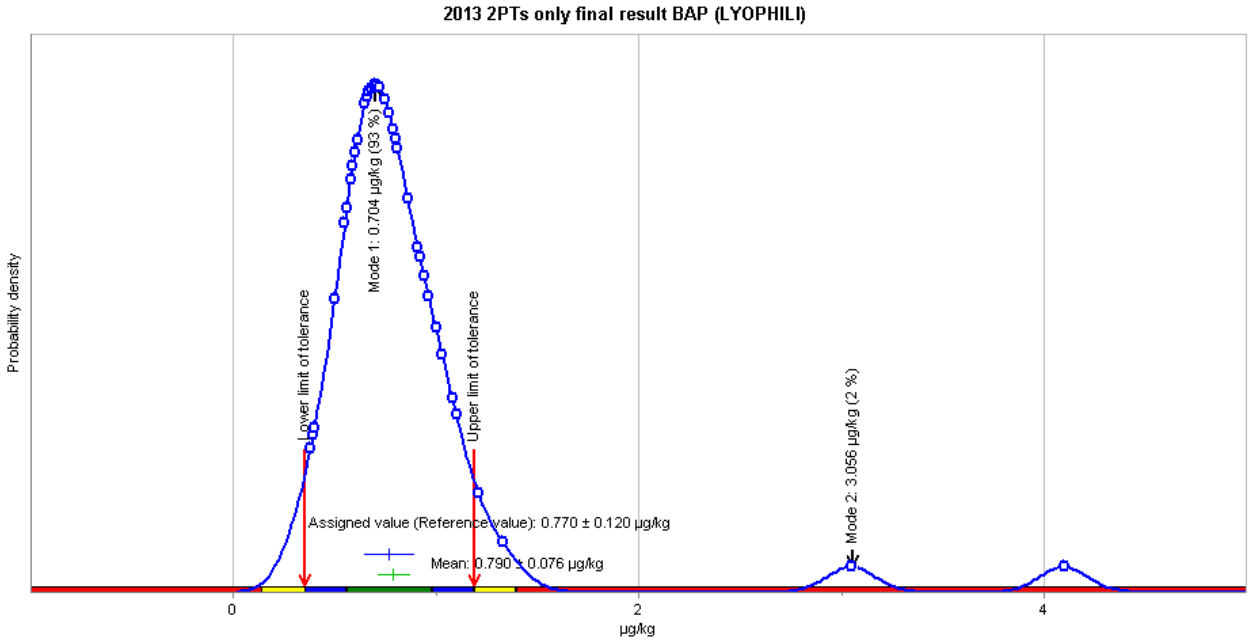
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benzo[*a*]pyrene (BAP) content of the freeze dried (lyophilized) mussels 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 freeze dried (lyophilized) mussels test sample



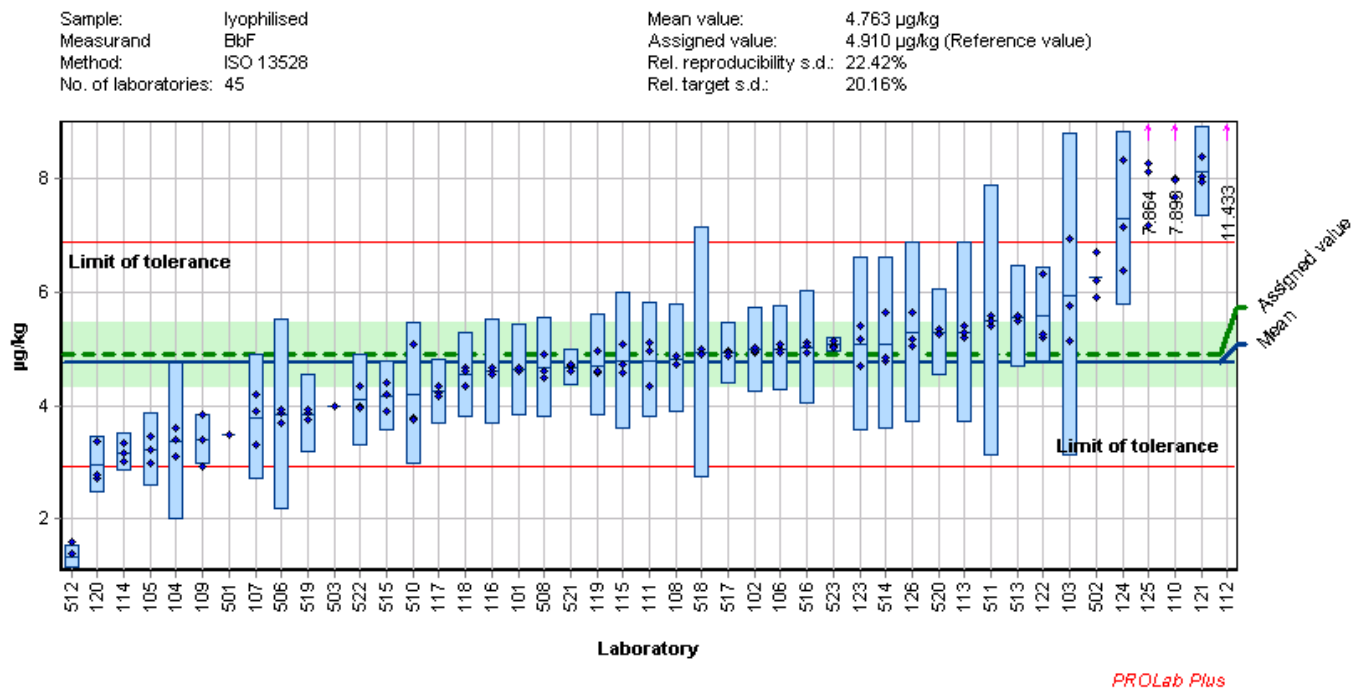
Results, as reported by participants, for the content of benzo[*a*]pyrene (BAP) in the freeze dried (lyophilized) mussels test material.
Assigned value is 0.77 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Ref 1	Ref 2	Ref 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BaP	0.67	0.70	n.r.	0.67	0.21	B) GC-MS
102	BaP	0.69	0.72	0.72	0.71	0.09	B) GC-MS
103	BaP	0.66	0.5	0.64	0.59	0.27	E) HPLC-FD
104	BaP	4.2	4.2	4.0	4.1	1.6	B) GC-MS
105	BaP	0.55	0.60	0.65	0.6	0.11	E) HPLC-FD
106	BaP	0.66	0.74	0.64	0.68	0.10	E) HPLC-FD
107	BaP	0.6	1.1	0.6	0.77	0.23	C) GC-MS/MS
108	BaP	0.72	0.69	0.68	0.70	0.14	D) GC-HRMS
109	BaP	0.392	0.395	0.395	0.394	0.02	
110	BaP	0.73	0.98	0.88	0.86	0.17	E) HPLC-FD
111	BaP	0.99	0.98	0.86	0.94	0.17	B) GC-MS
112	BaP	13.30	14.27	15.09	14.22	1.5	B) GC-MS
113	BaP	0.8	0.7	0.7	0.7	0.1	B) GC-MS
114	BaP	0.59	0.54	0.56	0.56	0.05	C) GC-MS/MS
115	BaP	0.682	0.632	0.766	0.693	0.173	E) HPLC-FD
116	BaP	1.22	1.19	1.23	1.21	0.25	B) GC-MS, E) HPLC-FD
117	BaP	0.75	0.78	0.72	0.75	0.18	B) GC-MS
118	BaP	0.46	0.55	0.65	0.55	0.10	C) GC-MS/MS
119	BaP	0.86	0.69	0.62	0.72	0.2	C) GC-MS/MS
120	BaP	0.5	0.5	0.5	0.5	0.09	B) GC-MS
121	BaP	0.78	1.05	1.81	0.92	0.1	H) LC-MS/MS
122	BaP	0.65	0.64	0.69	0.66	0.08	B) GC-MS
123	BaP	1.03	1.52	1.81	1.03	0.35	E) HPLC-FD
124	BaP	1.02	0.62	0.80	0.81	0.29	F) HPLC-UV/FD
125	BaP	1.035	0.877	0.976	0.963	0.087	E) HPLC-FD
126	BaP	1.12	0.99	1.12	1.1	0.32	F) HPLC-UV/FD
501	BaP	1.0	1.0	1.0	1.0	0.4	B) GC-MS
502	BaP	<1	<1	<1	<1	n.r.	C) GC-MS/MS
503	BaP	1.0	1.0	1.0	1.0	n.r.	E) HPLC-FD
506	BaP	2.51	0.36	0.36	1.08	0.47	B) GC-MS
508	BaP	0.87	0.83	1.04	0.91	0.18	C) GC-MS/MS
510	BaP	0.48	0.37	0.30	0.38	0.11	E) HPLC-FD
511	BaP	0.8	0.8	0.8	0.8	0.4	E) HPLC-FD
512	BaP	<0.5	<0.5	<0.5	<0.5	n.r.	E) HPLC-FD
513	BaP	0.5	0.4	0.4	0.4	0.06	E) HPLC-FD
514	BaP	0.689	0.579	0.565	0.611	0.183	C) GC-MS/MS
515	BaP	0.6	0.6	0.7	0.6	0.1	C) GC-MS/MS
516	BaP	1.30	1.41	1.27	1.33	0.27	C) GC-MS/MS
517	BaP	0.79	0.91	0.67	0.79	0.17	C) GC-MS/MS
518	BaP	0.8	0.9	0.8	0.8	0.4	E) HPLC-FD
519	BaP	3.04	3.10	3.02	3.05	0.6	C) GC-MS/MS
520	BaP	0.67	0.61	0.67	0.65	0.08	F) HPLC-UV/FD
521	BaP	0.59	0.58	0.57	0.58	0.05	E) HPLC-FD
522	BaP	<0.9	<0.9	<0.9	<0.9	n.r.	E) HPLC-FD
523	BaP	0.79	0.80	0.79	0.79	0.01	B) GC-MS

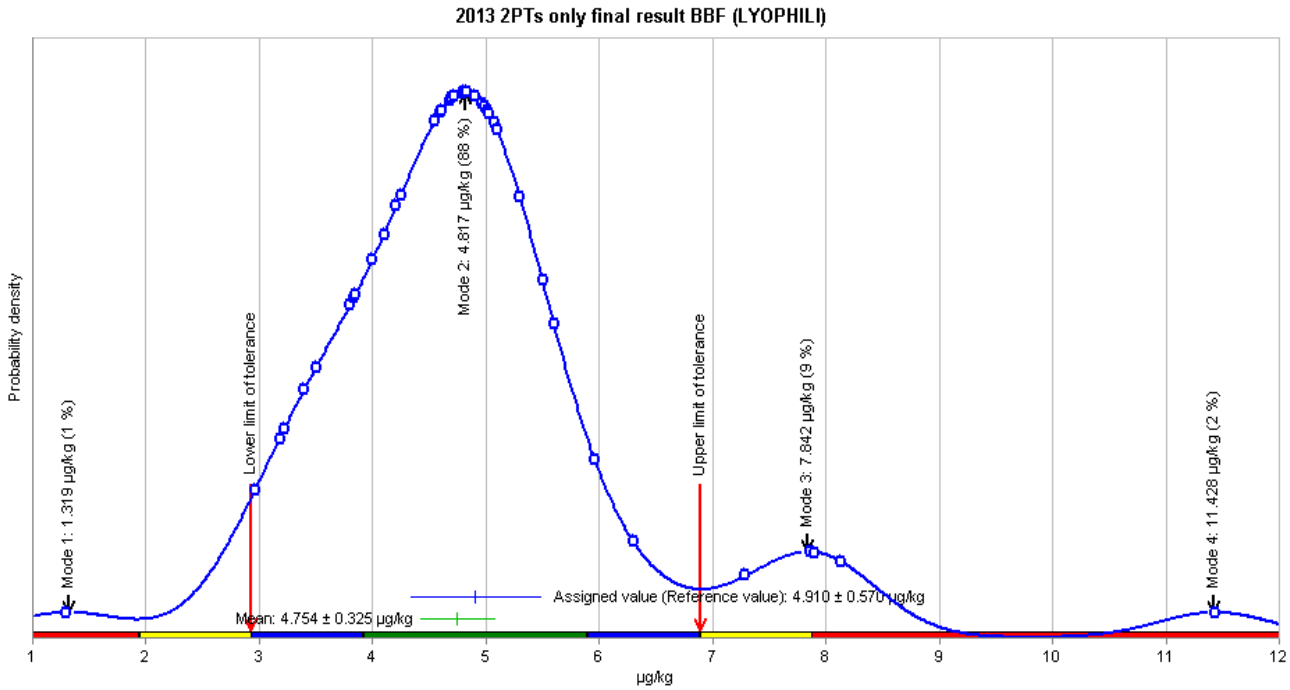
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content of the freeze dried (lyophilized) mussels 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 freeze dried (lyophilized) mussels test sample



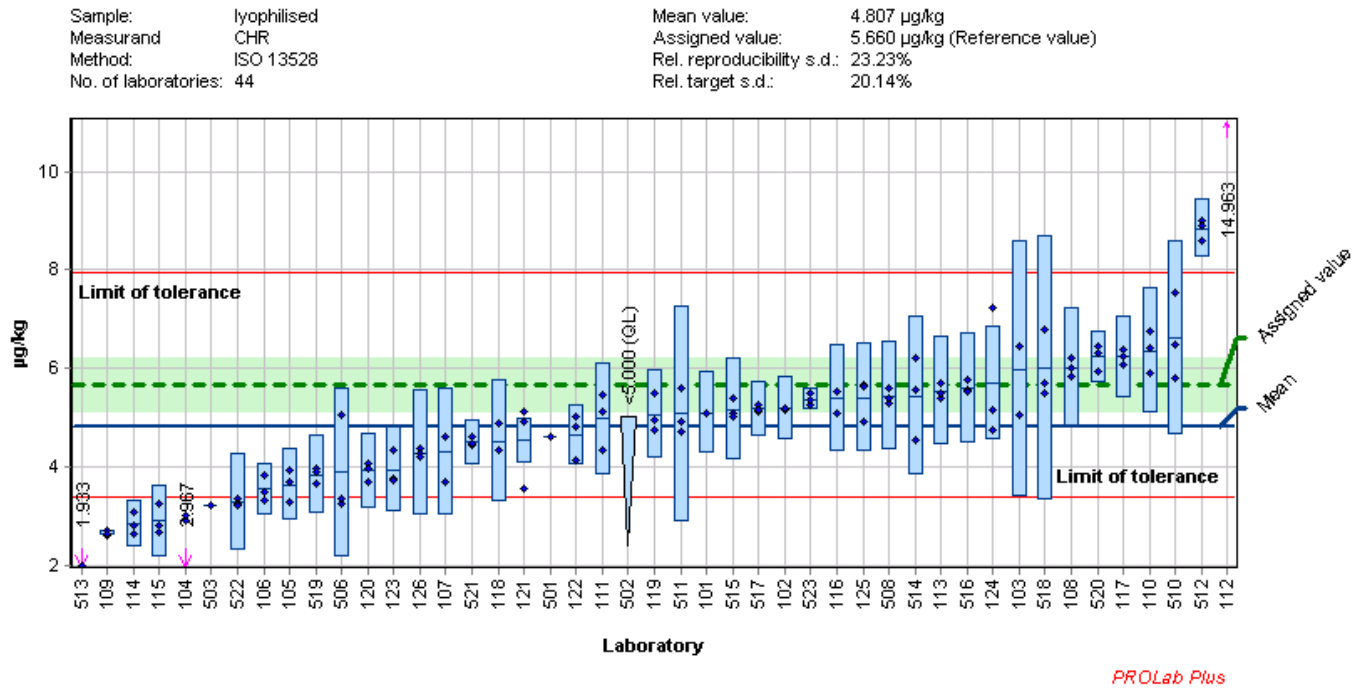
Results, as reported by participants, for the content of benzo[*b*]fluoranthene (BBF) in the freeze dried (lyophilized) mussels test material.
Assigned value is 4.91 µg/kg**.** The uncertainty refers to the final value.

LCode	Measurand	Ref 1	Ref 2	Ref 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	BbF	4.60	4.66	n.r.	4.60	0.80	B) GC-MS
102	BbF	4.94	4.98	5.04	4.99	0.75	B) GC-MS
103	BbF	6.95	5.16	5.76	5.96	2.86	E) HPLC-FD
104	BbF	3.1	3.6	3.4	3.4	1.4	B) GC-MS
105	BbF	2.98	3.22	3.47	3.22	0.64	E) HPLC-FD
106	BbF	5.00	5.10	4.93	5.01	0.76	E) HPLC-FD
107	BbF	3.3	4.2	3.9	3.8	1.1	C) GC-MS/MS
108	BbF	4.88	4.74	4.88	4.83	0.97	D) GC-HRMS
109	BbF	3.85	2.94	3.40	3.40	0.45	
110	BbF	7.69	8.00	7.99	7.90	1.58	E) HPLC-FD
111	BbF	4.96	5.11	4.34	4.80	1.01	B) GC-MS
112	BbF	10.73	11.46	12.11	11.43	1.0	B) GC-MS
113	BbF	5.2	5.4	5.3	5.3	1.6	B) GC-MS
114	BbF	3.17	3.35	3.02	3.18	0.33	C) GC-MS/MS
115	BbF	5.08	4.73	4.57	4.79	1.20	E) HPLC-FD
116	BbF	4.6	4.66	4.56	4.61	0.93	B) GC-MS, E) HPLC-FD
117	BbF	4.23	4.36	4.17	4.25	0.58	B) GC-MS
118	BbF	4.36	4.67	4.62	4.55	0.75	C) GC-MS/MS
119	BbF	4.58	4.61	4.96	4.72	0.9	C) GC-MS/MS
120	BbF	3.38	2.71	2.78	2.96	0.50	B) GC-MS
121	BbF	8.04	8.40	7.94	8.13	0.8	H) LC-MS/MS
122	BbF	6.34	5.21	5.25	5.60	0.85	B) GC-MS
123	BbF	4.70	5.17	5.40	4.70	1.41	E) HPLC-FD
124	BbF	8.33	6.38	7.16	7.29	1.54	F) HPLC-UV/FD
125	BbF	8.137	7.179	8.277	7.864	1.305	E) HPLC-FD
126	BbF	5.64	5.18	5.06	5.3	1.59	F) HPLC-UV/FD
501	BbF	3.5	3.5	3.5	3.5	1.2	B) GC-MS
502	BbF	6.7	5.9	6.2	6.3	n.r.	C) GC-MS/MS
503	BbF	4.0	4.0	4.0	4.0	n.r.	E) HPLC-FD
506	BbF	3.69	3.88	3.94	3.84	1.69	B) GC-MS
508	BbF	4.5	4.6	4.9	4.7	0.9	C) GC-MS/MS
510	BbF	5.1	3.78	3.76	4.21	1.26	E) HPLC-FD
511	BbF	5.4	5.6	5.5	5.5	2.4	E) HPLC-FD
512	BbF	1.6	1.4	1.0	1.3	0.2	E) HPLC-FD
513	BbF	5.6	5.5	5.6	5.6	0.9	E) HPLC-FD
514	BbF	5.638	4.805	4.844	5.096	1.529	C) GC-MS/MS
515	BbF	3.9	4.4	4.2	4.1	0.6	C) GC-MS/MS
516	BbF	5.11	4.93	5.05	5.03	1.00	C) GC-MS/MS
517	BbF	4.97	4.95	4.89	4.97	0.55	C) GC-MS/MS
518	BbF	5.0	4.9	4.9	4.9	2.2	E) HPLC-FD
519	BbF	3.88	3.92	3.77	3.85	0.7	C) GC-MS/MS
520	BbF	5.36	5.25	5.27	5.30	0.76	F) HPLC-UV/FD
521	BbF	4.71	4.72	4.60	4.68	0.33	E) HPLC-FD
522	BbF	4.34	3.99	3.96	4.10	0.82	E) HPLC-FD
523	BbF	5.05	5.14	5.03	5.07	0.12	B) GC-MS

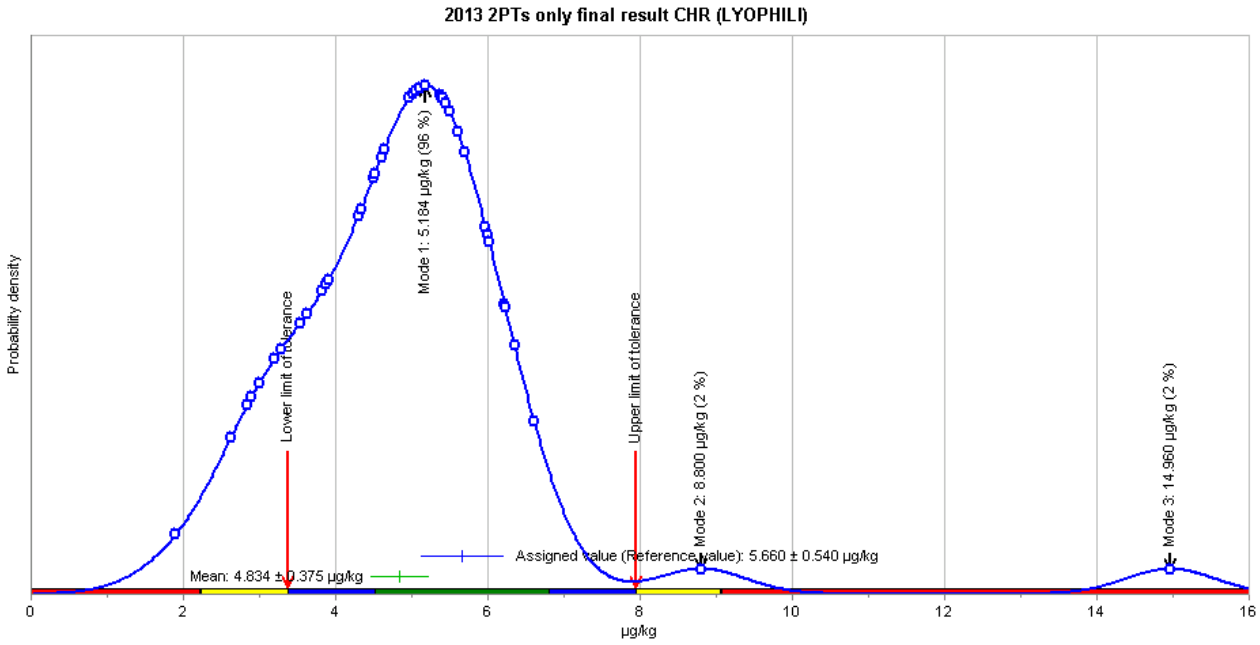
n.r.: not reported

Distribution of individual results of replicate determinations reported for the chrysene (CHR) content of the freeze dried (lyophilized) mussels 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 freeze dried (lyophilized) mussels test sample



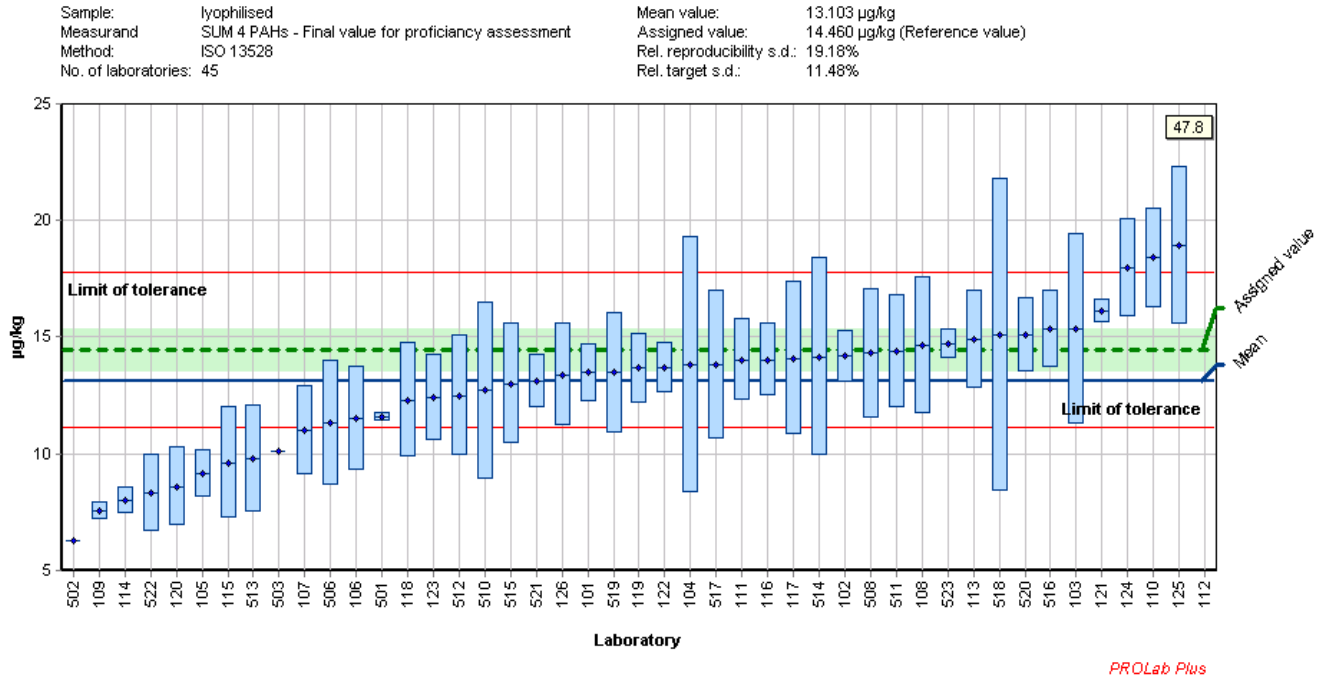
Results, as reported by participants, for the content of chrysene (CHR) in the freeze dried (lyophilized) mussels test material.
Assigned value is 5,66 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Ref 1	Ref 2	Ref 3	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	CHR	5.10	5.10	0	5.10	0.83	B) GC-MS
102	CHR	5.16	5.17	5.20	5.18	0.65	B) GC-MS
103	CHR	6.44	5.06	6.43	5.97	2.60	E) HPLC-FD
104	CHR	3.0	2.9	3.0	3.0	1.2	B) GC-MS
105	CHR	3.27	3.94	3.68	3.63	0.73	E) HPLC-FD
106	CHR	3.30	3.81	3.50	3.54	0.54	E) HPLC-FD
107	CHR	3.7	4.6	4.6	4.3	1.3	C) GC-MS/MS
108	CHR	6.01	5.82	6.22	6.02	1.20	D) GC-HRMS
109	CHR	2.59	2.70	2.62	2.63	0.05	
110	CHR	6.76	5.90	6.40	6.35	1.27	E) HPLC-FD
111	CHR	5.12	5.46	4.32	4.97	1.14	B) GC-MS
112	CHR	14.32	15.11	15.46	14.96	1.5	B) GC-MS
113	CHR	5.4	5.7	5.5	5.5	1.1	B) GC-MS
114	CHR	3.09	2.81	2.62	2.84	0.48	C) GC-MS/MS
115	CHR	3.24	2.81	2.66	2.90	0.73	E) HPLC-FD
116	CHR	5.52	5.52	5.10	5.38	1.09	B) GC-MS, E) HPLC-FD
117	CHR	6.25	6.36	6.08	6.23	0.83	B) GC-MS
118	CHR	4.34	4.87	4.35	4.52	1.24	C) GC-MS/MS
119	CHR	4.96	4.73	5.50	5.06	0.9	C) GC-MS/MS
120	CHR	4.07	3.69	3.97	3.91	0.78	B) GC-MS
121	CHR	4.91	5.12	3.55	5.02	0.5	H) LC-MS/MS
122	CHR	4.12	5.01	4.8	4.64	0.61	B) GC-MS
123	CHR	4.34	3.74	3.72	4.34	0.96	E) HPLC-FD
124	CHR	7.23	5.14	4.74	5.70	1.16	F) HPLC-UV/FD
125	CHR	5.665	4.922	5.628	5.405	1.117	E) HPLC-FD
126	CHR	4.36	4.28	4.20	4.3	1.28	F) HPLC-UV/FD
501	CHR	4.6	4.6	4.6	4.6	1.9	B) GC-MS
502	CHR	<5	<5	<5	<5	n.r.	C) GC-MS/MS
503	CHR	3.2	3.2	3.2	3.2	n.r.	E) HPLC-FD
506	CHR	5.05	3.25	3.35	3.88	1.71	B) GC-MS
508	CHR	5.3	5.4	5.6	5.4	1.1	C) GC-MS/MS
510	CHR	6.49	5.8	7.53	6.61	1.98	E) HPLC-FD
511	CHR	5.6	4.7	4.9	5.1	2.2	E) HPLC-FD
512	CHR	9.0	8.6	8.9	8.8	0.6	E) HPLC-FD
513	CHR	1.8	2.0	2.0	1.9	0.3	E) HPLC-FD
514	CHR	6.205	4.545	5.571	5.440	1.632	C) GC-MS/MS
515	CHR	5.1	5.4	5.0	5.1	1.0	C) GC-MS/MS
516	CHR	5.76	5.55	5.51	5.61	1.12	C) GC-MS/MS
517	CHR	5.11	5.25	5.15	5.11	0.56	C) GC-MS/MS
518	CHR	6.8	5.5	5.7	6.0	2.7	E) HPLC-FD
519	CHR	3.95	3.89	3.66	3.83	0.8	C) GC-MS/MS
520	CHR	6.44	5.93	6.30	6.22	0.53	F) HPLC-UV/FD
521	CHR	4.61	4.44	4.46	4.50	0.46	E) HPLC-FD
522	CHR	3.36	3.26	3.22	3.28	0.98	E) HPLC-FD
523	CHR	5.26	5.48	5.37	5.37	0.22	B) GC-MS

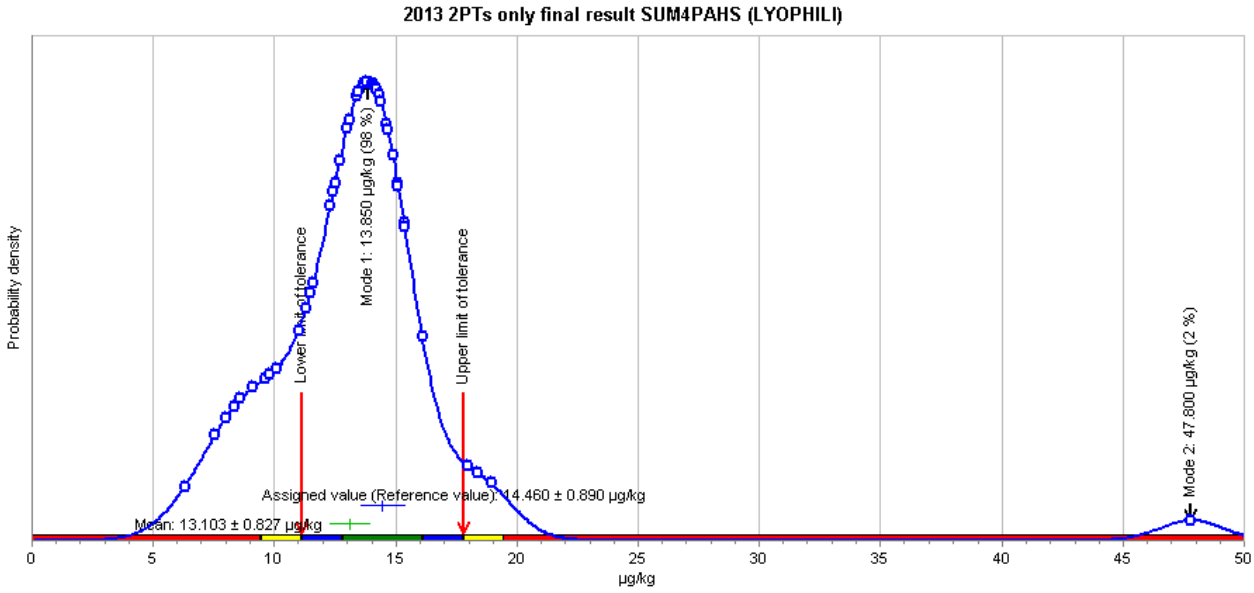
n.r.: not reported

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content of the freeze dried (lyophilized) mussels 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 freeze dried (lyophilized) mussels test sample



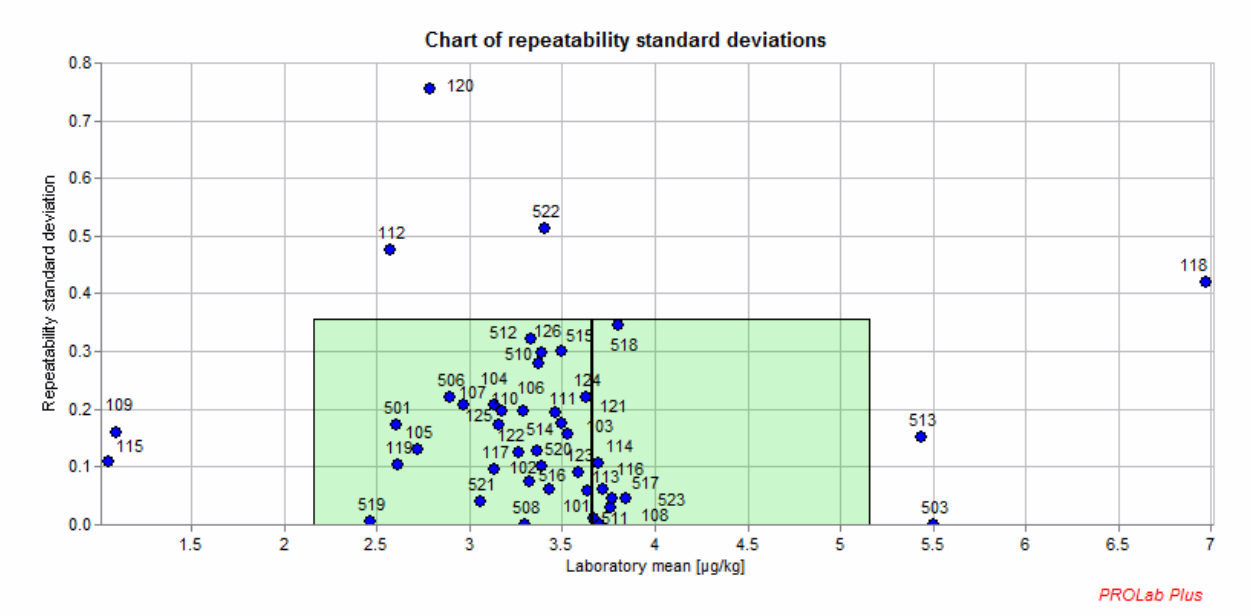
Results, as reported by participants, for the sum of the four markers PAHs (SUM4PAH) in the freeze dried (lyophilized) mussels test material.
Assigned value is 14,46 µg/kg. The uncertainty refers to the final value.

LCode	Measurand	Final value, µg/kg	Uncertainty, µg/kg	Analytical technique
101	SUM 4 PAHs	13.47	1.27	B) GC-MS
102	SUM 4 PAHs	14.19	1.12	B) GC-MS
103	SUM 4 PAHs	15.38	4.09	E) HPLC-FD
104	SUM 4 PAHs	13.8	5.5	B) GC-MS
105	SUM 4 PAHs	9.13	1.02	E) HPLC-FD
106	SUM 4 PAHs	11.49	2.24	E) HPLC-FD
107	SUM 4 PAHs	11	1.9	C) GC-MS/MS
108	SUM 4 PAHs	14.64	2.93	D) GC-HRMS
109	SUM 4 PAHs	7.56	0.39	
110	SUM 4 PAHs	18.41	2.14	E) HPLC-FD
111	SUM 4 PAHs	14.02	1.76	B) GC-MS
112	SUM 4 PAHs	47.81	4.0	B) GC-MS
113	SUM 4 PAHs	14.9	2.1	B) GC-MS
114	SUM 4 PAHs	8.00	0.6	C) GC-MS/MS
115	SUM 4 PAHs	9.63	2.41	E) HPLC-FD
116	SUM 4 PAHs	14.02	1.56	B) GC-MS, E) HPLC-FD
117	SUM 4 PAHs	14.09	3.3	B) GC-MS
118	SUM 4 PAHs	12.31	2.47	C) GC-MS/MS
119	SUM 4 PAHs	13.68	1.5	C) GC-MS/MS
120	SUM 4 PAHs	8.61	1.72	B) GC-MS
121	SUM 4 PAHs	16.1	0.5	H) LC-MS/MS
122	SUM 4 PAHs	13.7	1.10	B) GC-MS
123	SUM 4 PAHs	12.43	1.84	E) HPLC-FD
124	SUM 4 PAHs	18.00	2.11	F) HPLC-UV/FD
125	SUM 4 PAHs	18.950	3.388	E) HPLC-FD
126	SUM 4 PAHs	13.4	2.22	F) HPLC-UV/FD
501	SUM 4 PAHs	11.6	0.2	B) GC-MS
502	SUM 4 PAHs	6.3	n.r.	C) GC-MS/MS
503	SUM 4 PAHs	10.1	n.r.	E) HPLC-FD
506	SUM 4 PAHs	11.30	2.69	B) GC-MS
508	SUM 4 PAHs	14.3	2.8	C) GC-MS/MS
510	SUM 4 PAHs	12.7	3.8	E) HPLC-FD
511	SUM 4 PAHs	14.4	2.4	E) HPLC-FD
512	SUM 4 PAHs	12.5	2.6	E) HPLC-FD
513	SUM 4 PAHs	9.8	2.3	E) HPLC-FD
514	SUM 4 PAHs	14.168	4.250	C) GC-MS/MS
515	SUM 4 PAHs	13	2.6	C) GC-MS/MS
516	SUM 4 PAHs	15.35	1.67	C) GC-MS/MS
517	SUM 4 PAHs	13.81	3.18	C) GC-MS/MS
518	SUM 4 PAHs	15.1	6.7	E) HPLC-FD
519	SUM 4 PAHs	13.47	2.6	C) GC-MS/MS
520	SUM 4 PAHs	15.11	1.58	F) HPLC-UV/FD
521	SUM 4 PAHs	13.10	1.14	E) HPLC-FD
522	SUM 4 PAHs	8.33	1.67	E) HPLC-FD
523	SUM 4 PAHs	14.69	0.64	B) GC-MS

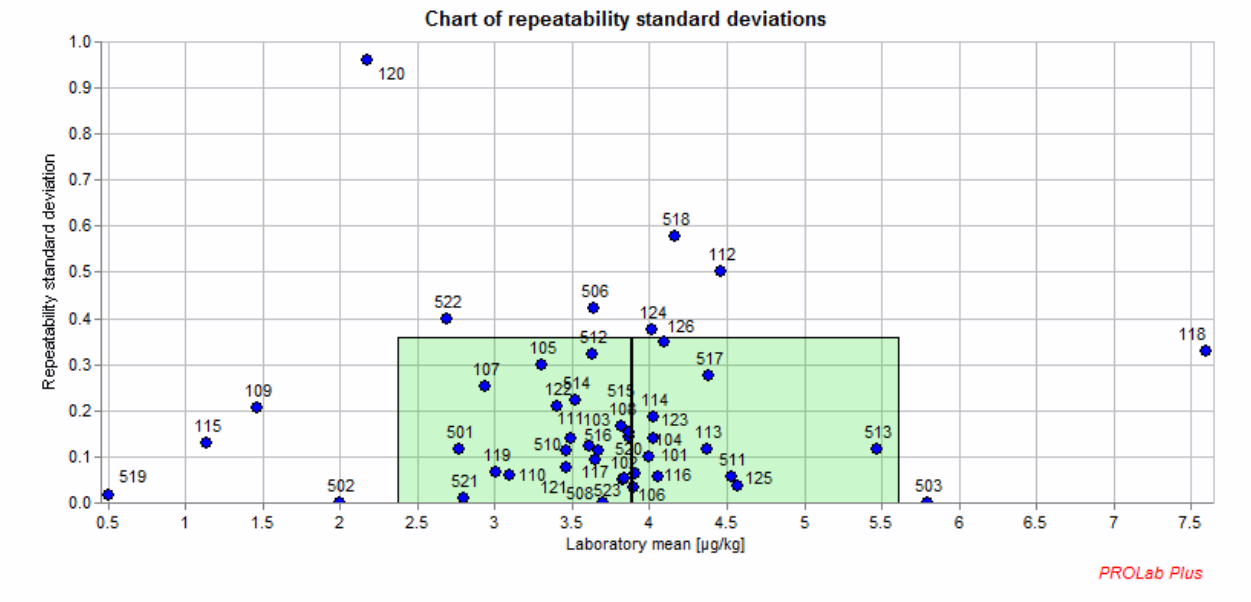
n.r: not reported

ANNEX 10: Laboratory means and repeatability standard deviation

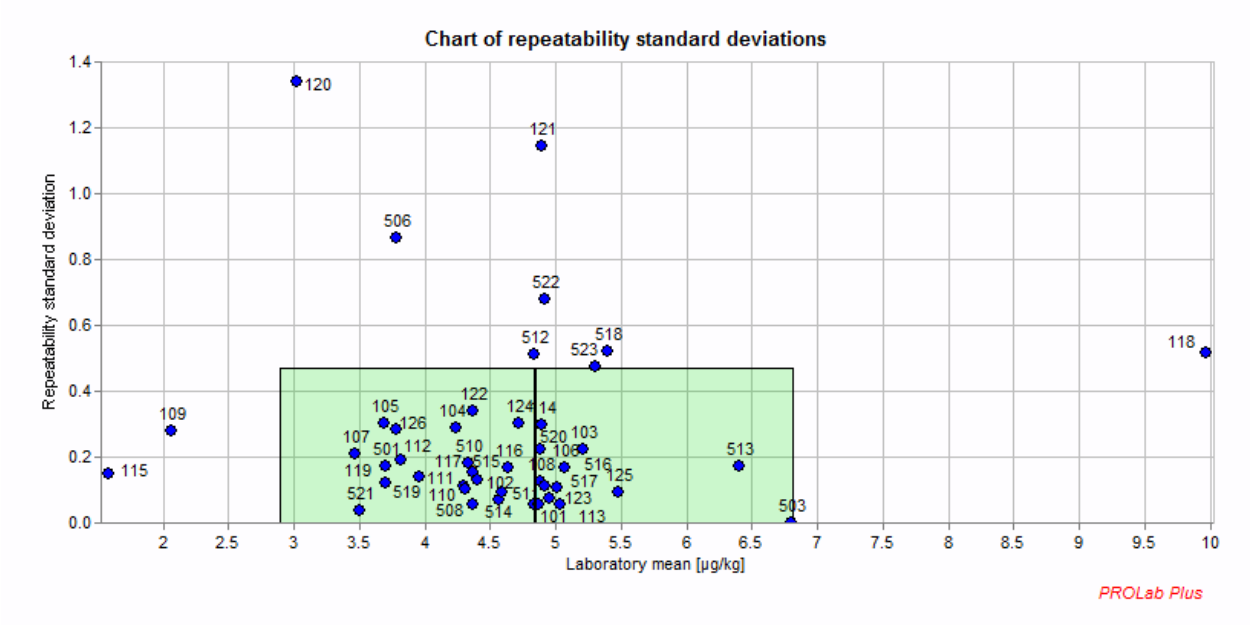
Lab means and repeatability standard deviation for the determination of BAA in the frozen mussels test material



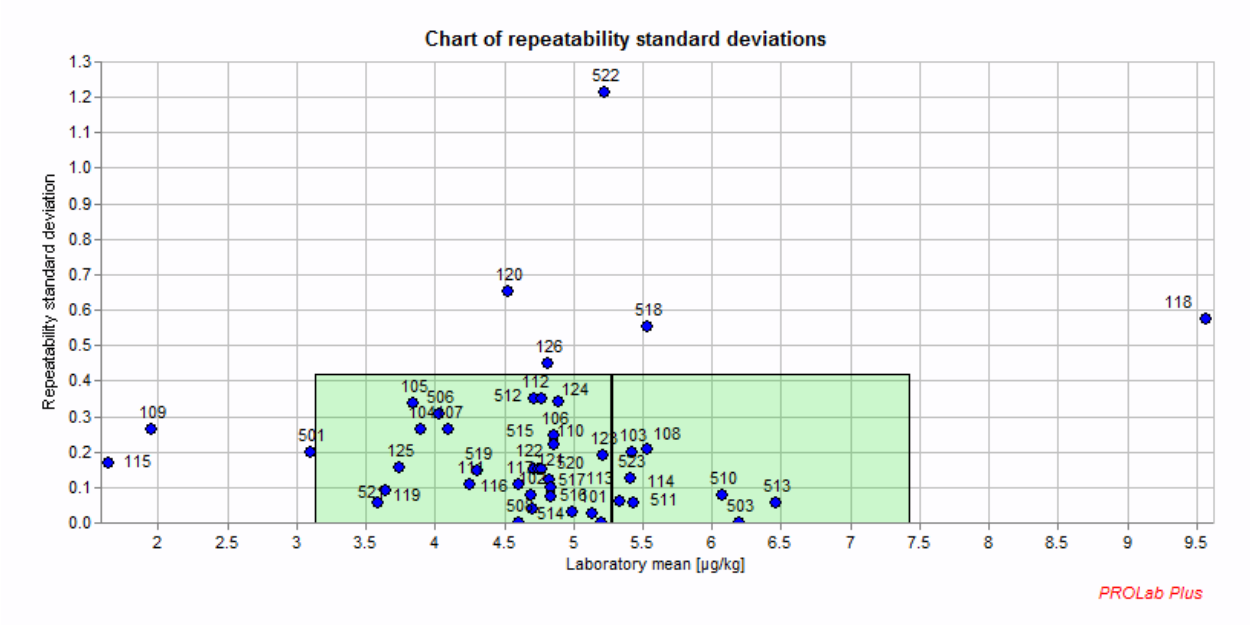
Lab means and repeatability standard deviation for the determination of BAP in the frozen mussels test material



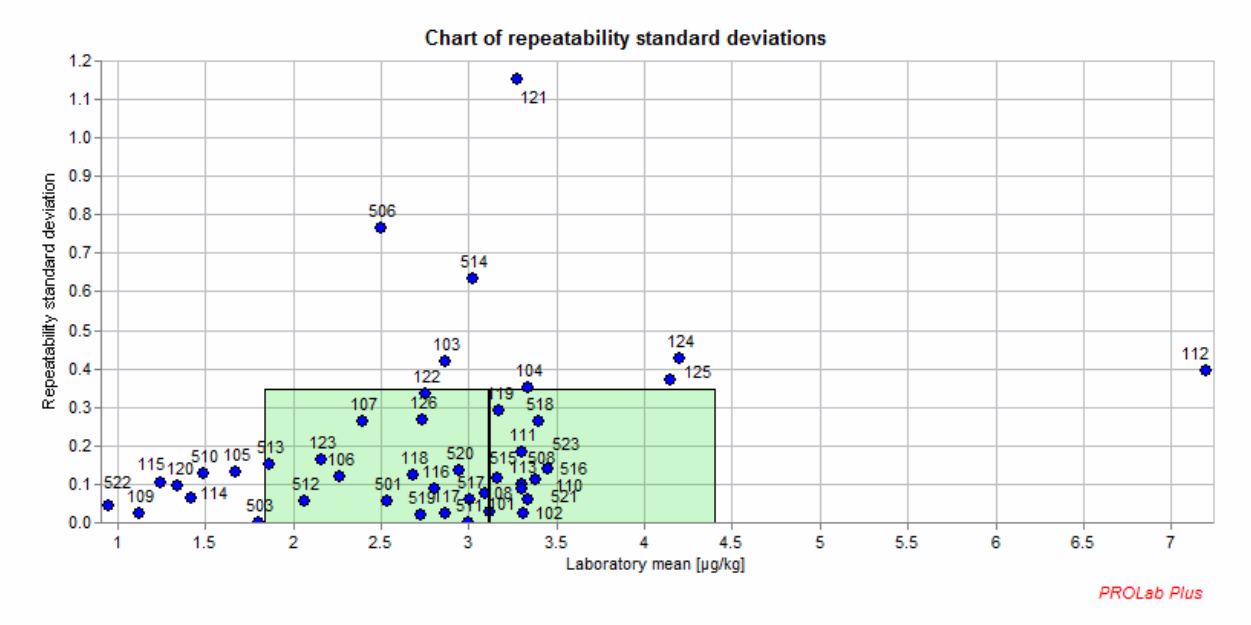
Lab means and repeatability standard deviation for the determination of BBF in the frozen mussels test material



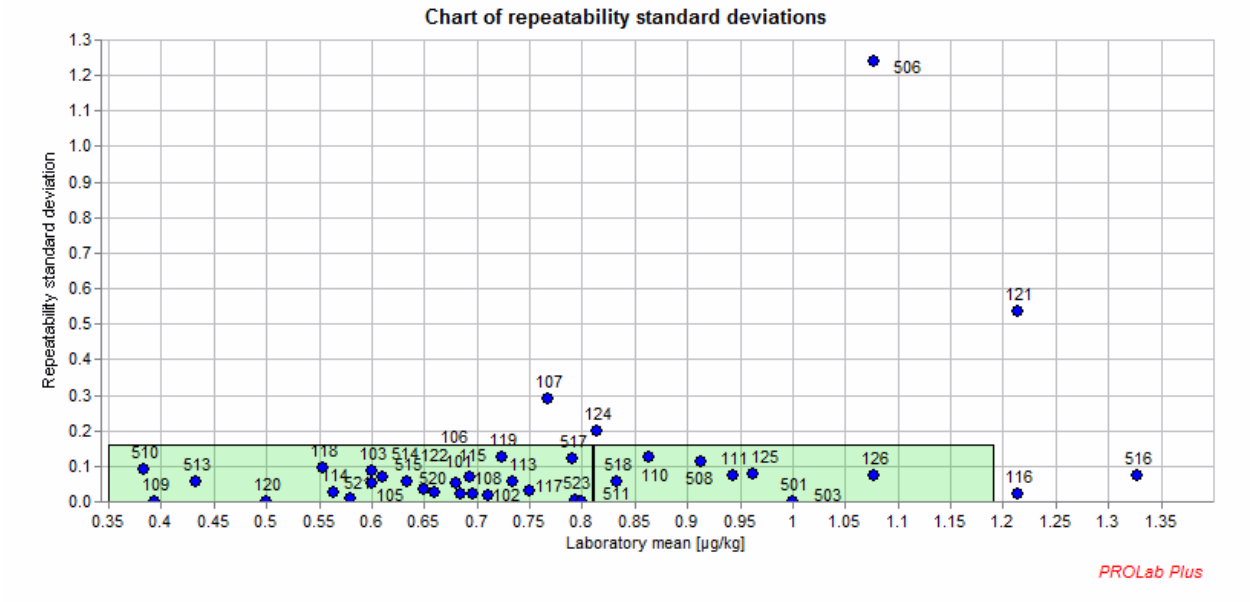
Lab means and repeatability standard deviation for the determination of CHR in the frozen mussels test material



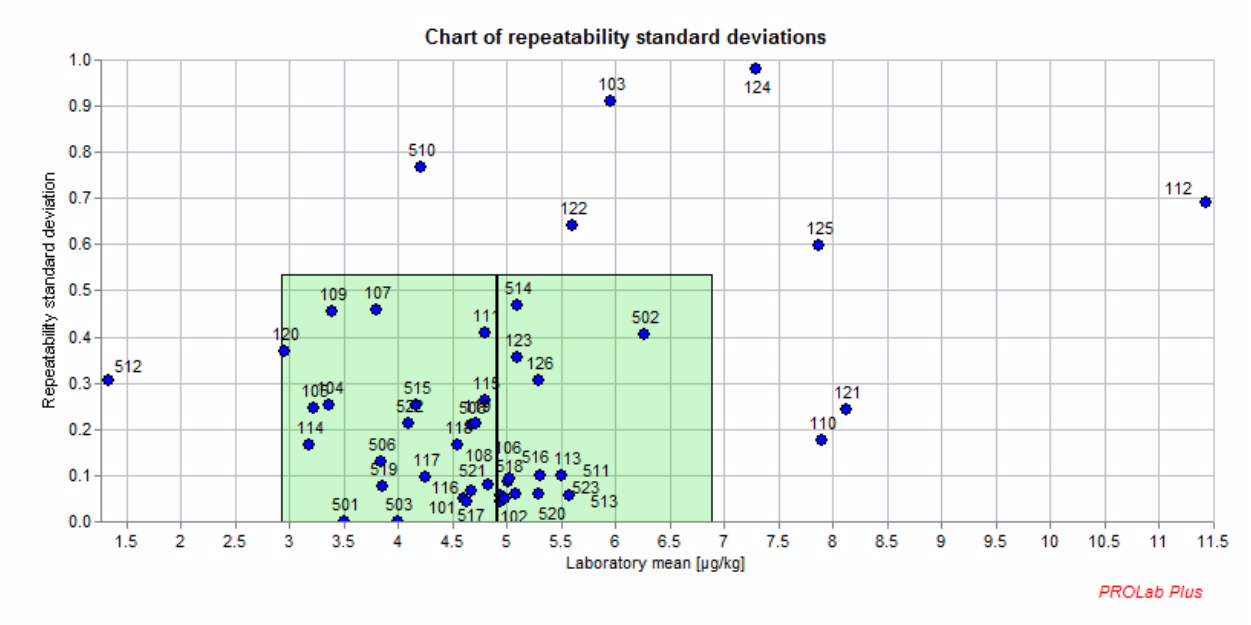
Lab means and repeatability standard deviation for the determination of BAA in the freeze dried (lyophilised) mussels test material



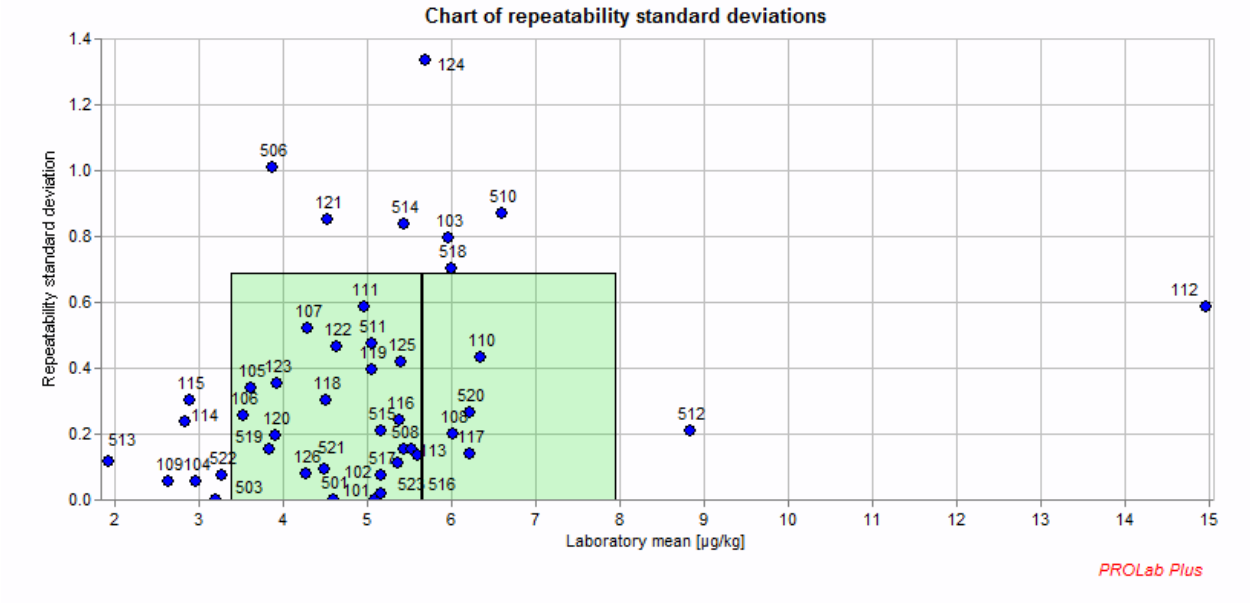
Lab means and repeatability standard deviation for the determination of BAP in the freeze dried (lyophilised) mussels test material



Lab means and repeatability standard deviation for the determination of BBF in the freeze dried (lyophilised) mussels test material



Lab means and repeatability standard deviation for the determination of CHR in the freeze dried (lyophilised) mussels test material



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Title: Report on the 12th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons. Four marker PAHs in bivalve molluscs

Authors: Stefanka Bratinova, Zuzana Zelinkova, Lubomir Karasek and Thomas Wenzl

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Abstract

This report presents the results of the twelfth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAHs) 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 bivalve moluscs, particularly in frozen and freeze dried (lyophilized) mussels. It was conducted under ISO Standard 17043 accreditation. In agreement with National Reference Laboratories, the test material used in this exercise were commercial products spiked with 4 markers PAHs and reference material provided by IAEA. 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 officially nominated 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 frozen and freeze dried mussels was expressed by z-scores. Satisfactory performance with regard to z-scores was assigned to about 82 % of the reported results.

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