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Report on the 16th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in smoked fish

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Foreword / Executive summary

This report presents the results of the sixteenth 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 smoked fish.

The test material used in this exercise was commercial smoked herring from a local supermarket. The fish was additionally hot smoked at the EURL PAH in order to increase the PAH content. Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with known 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 participated. Twenty-nine NRLs and 18 OCLs subscribed for participation.

The test material was characterised at the EURL PAH. The assigned values and their uncertainties were determined from independent replicate measurements on two different days.

Participants were free to choose the method of analysis. The performance of the participating laboratories in the determination of the target PAHs in the test materials was expressed by z scores and zeta-scores. Additionally, the compliance of reported method performance characteristics was checked against specifications given in legislation.

This PT demonstrated the competence of the participating laboratories in the analysis of regulated PAHs in smoked fish. Eighty three % of the reported test results were graded with z-scores that were below an absolute value of 2, indicating acceptable agreement with the assigned values of the test material.

Additionally, the EURL PAH asked participants to assess the compliance of the sample according to the legislative limits. Eighty eight % of the participants, who replied to the questionnaire, assessed the compliance of the test sample with EU legislation correctly.

JRC-IRMM is an ISO/IEC 17043 accredited PT provider and the respective rules were applied during all phases of this PT.

Acknowledgements

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Abstract

This report presents the results of the sixteenth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAH) on the determination of the four EU marker PAHs, benz[a]anthracene (BAA), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF) and chrysene (CHR) in smoked fish. Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States participated.

In agreement with National Reference Laboratories, the test material used in this exercise was smoked herring. Participants also received a solution of PAHs in solvent of their choice (either toluene or acetonitrile) with known content for the verification of their instrument calibration.

The participants were free to choose the method of analysis. Reference values were used to benchmark the results reported by participants. The performance of the participating laboratories in the determination of the target PAHs in smoked fish was expressed by z-scores. Satisfactory performance with regard to z-scores was assigned to about 83 % of the reported results.

JRC-IRMM is an ISO/IEC 17043 accredited provider of proficiency testing schemes and the respective rules were applied during all phases of this PT.

1. 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].

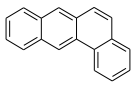
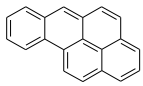
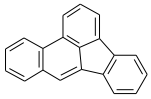
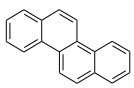
Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic compounds and can be found in the environment. In food, PAHs may be formed during industrial food processing and domestic food preparation, such as smoking, drying, roasting, baking, frying, or grilling [3,4].

Of the many hundreds of different PAHs, benzo[a]pyrene is, the most studied which is often used as a marker for PAHs in ambient air and food [5]. The European Commission revised in 2011 legislation on PAHs taking thereby into consideration the conclusions drawn by the European Food Safety Authority (EFSA) on "Polycylic Aromatic Hydrocarbons in Food" [6]. New maximum levels (MLs) for the sum of four substances (PAH4) - benzo[a]pyrene (BAP), benz[a]anthracene (BAA), benzo[b]fluoranthene (BBF) and chrysene (CHR), (Table 1) were introduced whilst a separate maximum level for benzo[a]pyrene was maintained [7, 8].

According to Commission Regulation(EU) No 835/2011 [7], lowered MLs for the contents of PAHs in smoked fish came into force as from 1 September 2014. However, EU Member States (MS) reported difficulties in complying with these new MLs especially for some traditionally smoked products. Therefore, it was appropriate to provide for certain Member States, for a transitional period of three years, derogating from the application of the lowered MLs for PAHs in smoked fish, under the condition that products that do not comply with the new MLs may not be traded across borders [9]. The Member States concerned should continue to monitor the presence of PAHs in those products and to establish programmes to implement good smoking practices where possible.

In support to the implementation of the lowered MLs and Commission Regulation (EU) No 1327/2014 [9] granting some EU MS derogation thereof, the EU RL PAH agreed with NRLs to focus in the 2015 EU-RL PAH proficiency test (PT) exercise on the determination of PAHs in smoked fish.

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)**	

2. 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 PTs.

This PT aimed to evaluate the comparability of results reported by NRLs and EU official food control laboratories (OCLs) for the four EU marker PAHs in smoked fish. 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 PT was designed and evaluated under the umbrella of IRMM's accreditation according to ISO/IEC Standard 17043:2010 [10].

3. Setup of the exercise

3.1 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 -	GREECE
Central Agricultural Office, Food & Feed Safety Directorate, Food Residues Toxicological Dept.	HUNGARY
Central Agricultural Office, Food and Feed Safety Directorate, Feed	HUNGARY
The Public Analyst's Laboratory Dublin	IRELAND
Istituto Superiore di Sanità	ITALY
BIOR - Institute of Food Safety, Animal Health and Environment	LATVIA
National Veterinary Laboratory (National Food and Veterinary Risk Assessment Institute)	LITHUANIA
National Health Laboratory of Luxembourg	LUXEMBOURG
RIKILT- Institute of Food Safety	The NETHERLANDS
NIFES - National Institute of Nutrition and Seafood Research	NORWAY
National Veterinary Research Institute	POLAND
National Institute of Public Health - National Institute of Hygiene	POLAND
Departamento de Riscos Alimentares e Laboratorios	PORTUGAL
Sanitary Veterinary and Food Safety Direction, Brasov	ROMANIA

SVUPUDK - State Veterinary and Food Institute Dolný Kubín	SLOVAKIA
Zavod za zdravstveno varstvo Maribor	SLOVENIA
AESAN - Centro Nacional de Alimentaciòn (Spanish Food Safety and Nutrition Agency)	SPAIN
SLV - Livsmedelsverket	SWEDEN
FERA - The Food and Environment Research Agency	UNITED KINGDOM

From the 29 NRLs registered for participation, 3 NRLs did not report results.

Table 3: List of participating Official Food Control Laboratories

Institute	*Country*
Hrvatski veterinarski institut,Veterinarski zavod Split	CROATIA
Sample Control d.o.o.	CROATIA
Institut Dr. Wagner Lebensmittel Analytik GmbH	AUSTRIA
Institut für Umwelt und Lebensmittelsicherheit	AUSTRIA
MA 38 - Lebensmitteluntersuchungsanstalt der Stadt Wien	AUSTRIA
Laboratorium ECCA NV	BELGIUM
LARECO	BELGIUM
Federal Laboratory for the Safety of the Food Chain	BELGIUM
Laboratory of SGS Bulgaria Ltd	BULGARIA
CVUA-Münsterland-Emscher-Lippe	GERMANY
LABOCEA (site de Ploufragan)	FRANCE
inovalys 44 (Idac)	FRANCE
Laboratoire Départemental d'Analyses du Morbihan	FRANCE
Laboratoire de l'Environnement et de l'Alimentation de Vendée	FRANCE
Service Commun des Laboratoires (SCL)	FRANCE
Nofalab	NETHERLANDS
Staffordshire Scientific Services	UNITED KINGDOM
Public Analyst Scientific Services Limited	UNITED KINGDOM

From the 18 registered OCLs, 3 OCLs did not report results.

3.2 Time frame

The PT was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on 17 April 2015 (see ANNEX 2) with deadline for registration via EUSurvey webpage (see ANNEX 3) until 04 May 2015. Test samples were dispatched (see ANNEX 4) on 26 May 2015 and the deadline for reporting of results was set to 1st July 2015. The documents sent to the participants are presented in ANNEX 5.

3.3 Confidentiality

The laboratory 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 codes of the respective laboratories will be also disclosed to the enrolling third party. In all other cases codes will only be disclosed on a request and upon the written consent of the participant.

3.4 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 "final 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; the "final value" had also to be accompanied by the respective expanded measurement uncertainty and the coverage factor. Only final values were used for performance assessment.

Participants were asked to report besides analysis results also details of the performance of the applied analytical method (see ANNEX 9). Additionally, the EURL asked participants (NRLs and official control laboratories) to assess the compliance of the sample according to the CURRENT legislative limits.

Each participant received at least one ampoule of a solution of the target PAHs in the chosen solvent (2 ml), with known content, and one amber glass vial containing the smoked fish test material.

4. Test materials

4.1 Preparation

The test item of this PT was smoked fish. Participants also received a solution of the 4 EU markers PAHs either in acetonitrile or in toluene (according to their choice, see ANNEX 5) with known concentrations, which allowed them to check their instrument calibration against an independent reference. Participants received the technical specifications (see ANNEX 6) of the chosen solution together with the test material.

The smoked fish test item was prepared at the EURL PAH starting from three kilos of smoked herring, acquired at a local supermarket. As the contents of all four marker PAHs were lower than 0.3 µg/kg, the herring filets were additionally hot-smoked using a commercial charcoal smoker. Afterwards the material was ground and homogenized, giving a fish paste. Aliquots of about 20 g were packed in amber glass screw cap vials and stored at –18 °C.

The standard solutions were prepared from neat certified reference materials (BCR®), (purchased from the Institute for Reference Materials and Measurements, Geel, Belgium,). Single standard stock solutions of each analyte were produced by substitution weighing of neat substances on a microbalance and dissolution in toluene. Mixed standards were prepared gravimetrically from the single standard stock solutions in the respective solvents and further diluted to the concentrations specified in ANNEX 6. The standard solutions were ampouled under inert atmosphere and flame sealed in 2 ml amber glass ampoules.

4.2 Homogeneity and stability

The smoked fish paste 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 13528:2005 [11]. Homogeneity experiments consisted of sample extraction by pressurized liquid extraction, size-exclusion chromatography followed by solid phase extraction clean-up and gas-chromatography with mass-spectrometric detection. The method precision complied with the requirements laid down in ISO 13528:2005 [11].

Homogeneity experiments included duplicate analysis of 10 samples randomly selected among the amber glass vials prepared for dispatch along the filling sequence. The duplicate analyses 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 7.

The stability of the test material was evaluated by applying an isochronous experimental design. Six randomly selected samples were stored at two different conditions over the period from the dispatch of the material to the end of the submission of the results.

The first set of 3 samples was stored in a freezer at recommended conditions (~ -18 °C). The second set of 3 samples was stored for the whole period of the study in a deep freezer at the reference conditions - (~ -80 °C). After the deadline for reporting of results had expired, all 6 samples were analysed in duplicate under repeatability conditions.

No significant difference of the analyte contents among the test samples was found. Hence stability of the samples over the whole period can be assumed under the recommended conditions (ANNEX 8)

4.3 Assigned value and standard deviation for proficiency assessment

The assigned values and their associated uncertainties were determined at the EURL PAH on basis of the analyses of homogeneity test samples. Data of the replicate analyses of ten test samples could be pooled as no significant difference between the analyte contents in the different test samples was found. The standard solutions used for instrument calibration were cross-checked against a certified reference material provided by NIST (SRM 2260a) in order to exclude bias stemming from instrument calibration. The stability of the analytical process was controlled via the analysis of well characterised quality control materials. The applied analytical method (WI-D-0607) [12] was fully validated by collaborative trial and is accredited according to ISO/IEC 17025. This method became recently a European standard.

The arithmetic mean values of twenty independent analyses of the test material were applied as assigned values. The assigned values and respective uncertainties together with the target standard deviations of the target PAHs are listed in Table 4. Uncertainty contributions resulting from (i) the characterisation of the material (method precision and uncertainty, purity of labelled standards, preparation of calibration solutions and the calibration function), (ii) potential inhomogeneity and (iii) potential instability of the test items were considered for the estimation of the uncertainty of the assigned values.

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

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	18.39	1.20	3.68	20.0%
Chysene	CHR	16.52	1.45	3.31	20.0%
Benzo[*b*]fluoranthene	BBF	9.09	0.60	1.82	20.1%
Benzo[*a*]pyrene	BAP	5.38	0.40	1.09	20.2%
Sum of the four marker PAHs	SUM4PAH	49.38	2.01	5.38	10.9%

σ_p standard deviation for proficiency assessment.

U expanded uncertainty of the assigned value (k=2).

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 error propagation considering covariances.

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 1 [8]. 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 1 $$U_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2}$$ [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 [8].

5. Evaluation of laboratories

5.1 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 10. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed.

5.2 Evaluation criteria

z-Scores

z-Scores were calculated based on the final values. Equation 2 presents the formula for calculation of z-scores.The compliance with legislation of the performance characteristics of the method used to determine the 4 marker PAHs was evaluated as well.

Equation 2 $$z = \frac{\left(x_{lab} - X_{assigned}\right)}{\sigma_P}$$ [9]

where z refers to the z-score, xlab to the reported "final value", Xassigned to the assigned value, and σP 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 3.

Equation 3 $$zeta = \frac{x_{lab} - X_{assigned}}{\sqrt{u_{lab}^2 + u_{assigned}^2}}$$ [9]

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, it was set to 0, which is most unfavourable for zeta score calculation.

Unsatisfactorily large zeta-scores might be caused by underestimated measurement uncertainties, large bias, or a combination of both. Therefore, reported uncertainties were checked against the uncertainties of the reference values. Only the green highlighted values indicate correct estimation of the uncertainty of the sum parameter. It should be mentioned that some laboratories might have reported absolute uncertainty instead of the requested relative measurement uncertainty, resulting in very low, unrealistic values for that parameter.

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 threshold values provided by the "fitness-for-

purpose" function (Equation 1). 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. Reported uncertainties that were non-compliant are highlighted in yellow in Table 6.

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [10]. 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

5.3 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 17 results; therefore the expected number of results of the 46 participants was 782. Six participants did not report results and other two participants reported only 1 result per analyte. In total 680 results were received, which equals to 87 %. The results, reported by participants are presented in ANNEX 10.

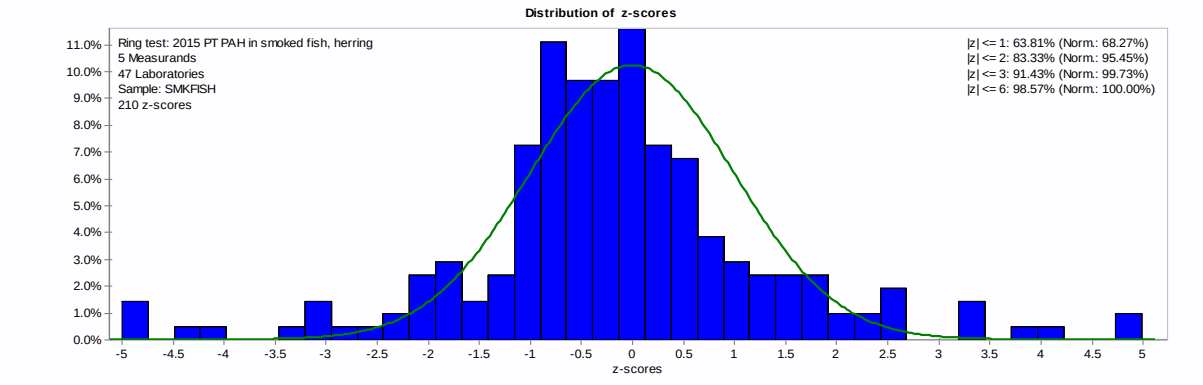
Statistical evaluation of the results was performed using PROLab software [13]. Robust mean values and robust standard deviations were calculated according to Algorithm A+S of ISO 13528:2005 [11].

It should be noted that the confidence intervals of the robust means calculated from the participants' results (ANNEX 10) overlap for most of the analytes with the confidence intervals of the assigned values. Robust standard deviations of the results of participants reported for the target PAHs in smoked fish test material are lower than the target standard deviations.

83.3% of the results reported by the participants obtained satisfactory z-scores ≤ +/-2.

9.6% of the results (18 result) fall into the unsatisfactory performance range with z-scores > |3| (Figure 1).

Figure 1: Histogram of z-scores for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH



Twenty-nine participants obtained more than 80 % satisfactory z-scores. However, satisfactory performance was attributed to less than 50% of reported results of five participants, while 6 participants did not report at all results. It should be mentioned that the smoked fish test material was highly contaminated with PAHs, which could have caused issues with the working range of methods applied by some participants. Moreover several participants reported chromatographic problems linked to interferences

stemming from the matrix or non-target PAHs. In general the overall performance of the participants could be summarised as satisfactory.

Figure 2 and Figure 3 provide overviews of the individual z-scores assigned to the results for smoked fish test material for NRLs and OCLs respectively. The larger the triangles, the larger were the differences to the assigned values. Yellow triangles represent z-scores in the questionable and red triangle in the non-satisfactory performance range. The corresponding scores are presented next to the triangles.

The numerical values of the calculated z-scores are compiled in Table 5. All z-scores in the questionable performance range are given in orange on a yellow background, while z-scores indicating unsatisfactory performance are presented in red colour on light red background. This mode of presentation allows easy distinction between the two performance ranges even on black-and-white prints.

The graphical representations of the distribution of results for the individual analytes are given in ANNEX 10 together with respective Kernel density plot.

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

Table 6 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. Only 64% of the zeta-scores assigned to the results of 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 z-scores, but still seem to have difficulties in estimating realistic measurement uncertainty values, although improvement is noticed compared to previous PTs.

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

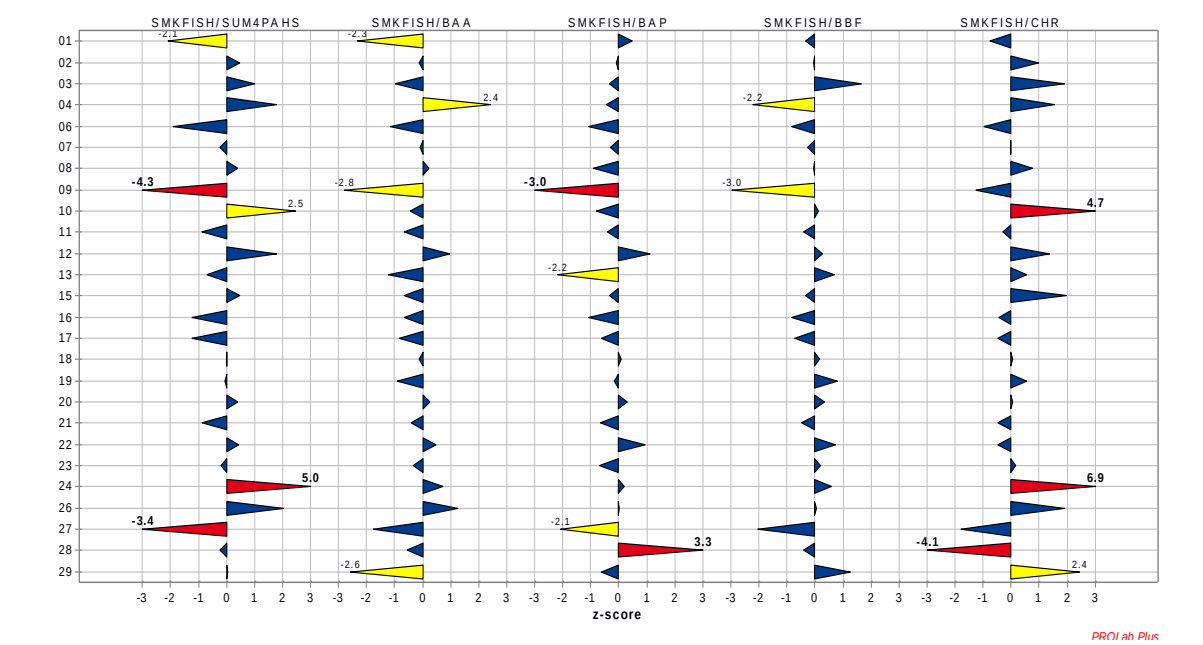


Figure 3: Graphical presentation of z-scores corresponding to the "final values for proficiency assessment" reported by the OCLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the smoked fish test material.

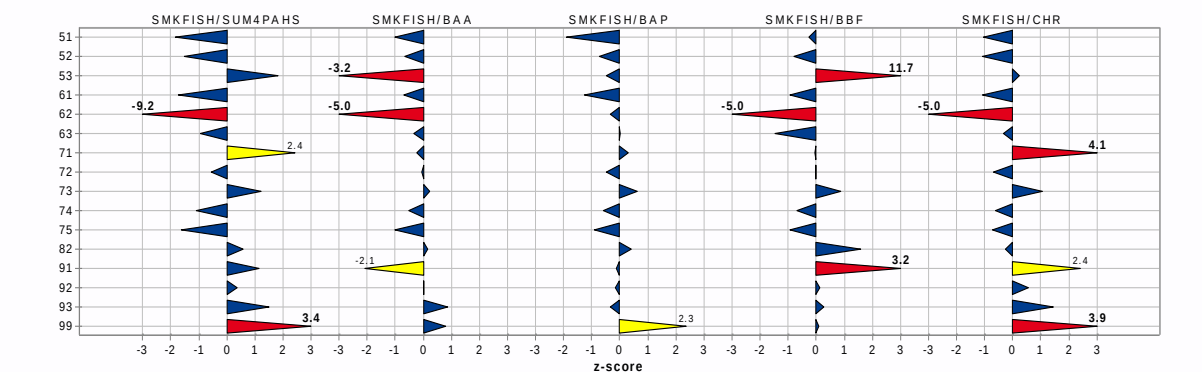


Table 5: Compilation of z-scores calculated from the "final values" reported by the participants for test material:

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

SMOKED FISH	Sample/Measurand				
Lab Code	BAA	BAP	BBF	CHR	SUM4PAH
	NATIONAL CONTROL LABORATORIES (NRLs)				
1	-2.3	0.5	-0.3	-0.8	-2.1
2	-0.1	-0.1	0.0	1.0	0.5
3	-1.0	-0.3	1.6	1.9	1.0
4	2.4	-0.4	-2.2	1.5	1.8
6	-1.1	-1.1	-0.8	-1.0	-1.9
7	-0.1	-0.3	-0.3	0.0	-0.2
8	0.2	-0.9	0.0	0.8	0.4
9	-2.8	-3.0	-3.0	-1.2	-4.3
10	-0.5	-0.8	0.1	4.7	2.5
11	-0.7	-0.4	-0.4	-0.3	-0.9
12	1.0	1.1	0.3	1.4	1.8
13	-1.2	-2.2	0.7	0.6	-0.7
15	-0.7	-0.3	-0.3	2.0	0.5
16	-0.7	-1.1	-0.8	-0.5	-1.2
17	-0.8	-0.6	-0.7	-0.5	-1.2
18	-0.1	0.1	0.2	0.1	0.0
19	-0.9	-0.2	0.8	0.6	0.0
20	0.3	0.3	0.3	0.1	0.4
21	-0.4	-0.7	-0.5	-0.5	-0.9
22	0.5	0.9	0.7	-0.5	0.4
23	-0.3	-0.7	0.2	0.2	-0.2
24	0.7	0.2	0.6	6.9	5.0
26	1.2	0.0	0.0	1.9	2.0
27	-1.8	-2.1	-2.0	-1.8	-3.4
28	-0.6	3.3	-0.4	-4.1	-0.2
29	-2.6	-0.6	1.3	2.4	0.0
	OFFICIAL CONTROL LABORATORIES (OCLs)				
51	-1.0	-1.9	-0.3	-1.1	-1.8
52	-0.7	-0.7	-0.8	-1.1	-1.5
53	-3.2	-0.5	11.7	0.2	1.8
61	-0.7	-1.3	-0.9	-1.1	-1.7
62	-5.0	-0.3	-5.0	-5.0	-9.2
63	-0.4	0.0	-1.5	-0.3	-0.9
71	-0.2	0.3	0.0	4.1	2.4
72	-0.1	-0.5	0.0	-0.7	-0.6
73	0.2	0.6	0.9	1.1	1.2
74	-0.5	-0.6	-0.7	-0.6	-1.1
75	-1.0	-0.9	-0.9	-0.7	-1.6
82	0.2	0.4	1.6	-0.3	0.6
91	-2.1	-0.1	3.2	2.4	1.2
92	0.0	-0.2	0.1	0.5	0.4
93	0.9	-0.3	0.3	1.5	1.5
99	0.8	2.3	0.1	3.9	3.4

Table 6: Compilation of zeta-scores calculated from the "final values", the reported corresponding expanded relative measurement uncertainties, as well as assigned values and expanded uncertainties of the analyte contents:

zeta-scores outside the satisfactory range (|zeta| > 2) are highlighted in red. Dark yellow highlighted cells indicate MU values that did not comply with the thresholds given by the "fitness-for-purpose" function U_f; green highlighted values indicate correct estimation of the uncertainty of the sum parameter

	BAA			BAP			BBF			CHR			SUM		
Assigned value +/- U, µg/kg	18.39 ± 1.2			5.38 ± 0.4			9.09 ± 0.3			16.52 ± 1.45			49.38 ± 2.01		
	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score
Lab code	µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%	
	National Reference Laboratories (NRLs)														
1	9.81	30	-5.4	5.89	30	0.6	8.48	30	-0.5	14	30	-1.1	38.2	30	-1.9
2	17.92	26	-0.2	5.3	34	-0.1	9.02	30	-0.1	19.79	22	1.4	52.02	15	0.7
3	14.797	36	-1.3	5.014	26	-0.5	12.085	42	1.2	22.826	34	1.6	54.721	35	0.6
4	27.39	17	3.7	4.91	18	-1.0	5.02	20	-7.8	21.6	20	2.2	58.93	38	0.9
5															
6	14.19	22	-2.5	4.18	19	-2.7	7.56	17	-2.4	13.25	27	-1.7	39.18	20	-2.5
7	18.09	16	0	5.06	17	-1	8.62	17	-1	16.42	16	-0.1	48.19	9	-0.5
8	19.2	15	0.5	4.4	15	-2.5	9	20	-0.1	19	25	1.0	51.6	20	0.4
9	8.1	23	-9.3	2.1	22	-10.7	3.7	27	-10.3	12.4	25	-2.4	26.3	24	-7.0
10	16.7	17	-1.1	4.5	19	-1.9	9.3	18	0.3	32.2	17	5.7	62.7	10	4.0
11	15.95	5	-3.4	4.94	5	-1.9	8.33	4	-3.3	15.5	7	-1.1	44.72	11	-1.8
12	22	20	1.6	6.6	20	1.8	9.6	20	0.5	21	20	2.0	59	20	1.6
13	13.85	20	-3.0	3.01	20	-6.6	10.36	20	1.2	18.39	20	0.9	45.61	20	-0.8
14															
15	16	20	-1.4	5	20	-0.7	8.5	20	-0.7	23	20	2.7	52	17	0.6
16	16	7	-2.9	4.2	4	-5.4	7.56	5	-6.7	15	6	-1.8	42.8	11	-2.5
17	15.3	25	-1.5	4.7	18	-1.5	7.8	27	-1.2	14.9	16	-1.2	42.8	44	-0.7
18	17.94	14	-0.3	5.48	13	0.2	9.41	14	0.5	16.69	18	0.1	49.52	9	0.1
19	15.08	20	-2.0	5	21.0	-0.3	10.56	16	1.7	18.33	22	0.8	49.164	22	0.0
20	19.4	24	0.4	5.7	22	0.5	9.7	29	0.4	16.7	19	0.1	51.6	12	0.7
21	16.87	15	-1.1	4.67	5	-3.1	8.25	15	-1.3	14.95	13	-1.3	44.73	8	-2.4
22	20.1	18	0.9	6.4	23	1.3	10.4	21	1.2	14.9	17	-1.1	51.8	10	0.9
23	17.15	20	-0.7	4.64	20	-1.5	9.44	20	0.4	17.09	20	0.3	48.32	11	-0.4
24	21.048	20	1.2	5.593	20	0.4	10.195	20	1.1	39.403	20	5.7	76.24	20	3.5
25															
26	22.97	16	2.4	5.39	12	0.0	9.17	12	0.1	22.81	18	2.9	60.34	18	2.0
27	11.9	22	-4.5	3.1	19	-6.4	5.4	23	-5.8	10.6	23	-4.2	31	13	-8.1
28	16.362	0	-3.4	9.012	2	17.1	8.342	0	-5.0	2.93	0	-18.7	48.087	1	-1.2
29	8.9	30	-6.5	4.7	30	-0.9	11.4	31	1.3	24.6	30	2.1	49.6	18	0.0
	Official Control Laboratories (OCLs)														
51	14.6	20	-2.4	3.3	20	-5.4	8.6	20	-0.6	13	20	-2.4	39.5	20	-2.4
52	15.97	20	-1.4	4.57	20	-1.6	7.64	20	-1.9	12.95	20	-2.4	41.21	20	-1.9
53	6.77	25	-11.2	4.85	25	-0.8	30.43	25	5.6	17.27	25	0.3	59.31	25	1.3
61	15.9	25	-1.2	4	26	-2.5	7.4	32	-1.4	12.9	25	-2.0	40.1	27	-1.7
62				5	41	-0.4									
63	17.1	5	-1.8	5.4	1	0.1	6.4	1	-17.5	15.4	5	-1.4	44.3	9	-2.2
71	17.5	25	-0.4	5.7	25	0.4	9	25	-0.1	30	25	3.5	62.5	25	1.7
72	18.142	5	-0.3	4.845	1	-2.6	9.094	3	0.0	14.202	4	-3.0	46.311	14	-0.9
73	19.26	20	0.4	6.05	20	1.1	10.67	20	1.5	20.05	20	1.7	56.03	20	1.2
74	16.5	13	-1.5	4.74	21	-1.2	7.82	18	-1.8	14.5	13	-1.7	43.57	23	-1.1
75	14.60	22	-2.2	4.40	22	-1.9	7.40	22	-2.0	14.1	22	-1.4	40.70	22	-1.9
81															
82	19.00	29	0.2	5.83	26	0.6	12	24	2.0	15.67	31	-0.3	52.5	29	0.4
91	10.80	20	-6.1	5.26	20	-0.2	15	25	3.1	24.5	20	3.1	55.6	20	1.1
92	18.50	20	0.1	5.2	20	-0.3	9.3	26	0.2	18.3	20	0.9	51.3	20	0.4
93	21.60	53	0.6	5	40	-0.4	9.6	27	0.4	21.3	57	0.8	57.5	47	0.6
98															
99	21.27	3	4.1	7.94	6	8.1	9.24	5	0.5	29.41	6	11.9	67.85	12	4.3

The compliance of the reported uncertainty with the maximum thresholds given by the "fitness-for-purpose" function U_f was assessed and non-complying uncertainties are highlighted in yellow. However, attention should be paid to the unrealistically low uncertainties, reported by some participants. For some of the participants this might be due to the erroneous reporting of the absolute instead of the required relative measurement uncertainty.

Comparing the precision estimated from the results of the three replicate analyses with the uncertainty reported with the final values, it becomes obvious that some laboratories based their uncertainty estimates purely on the standard deviation of the three replicate analyses. The relative expanded uncertainty reported by the participants for all the parameters and samples varied widely - between 1.1% and 57% with the two extremes of 13 values less than 5 % and 6 values above 40% (Figure 4).

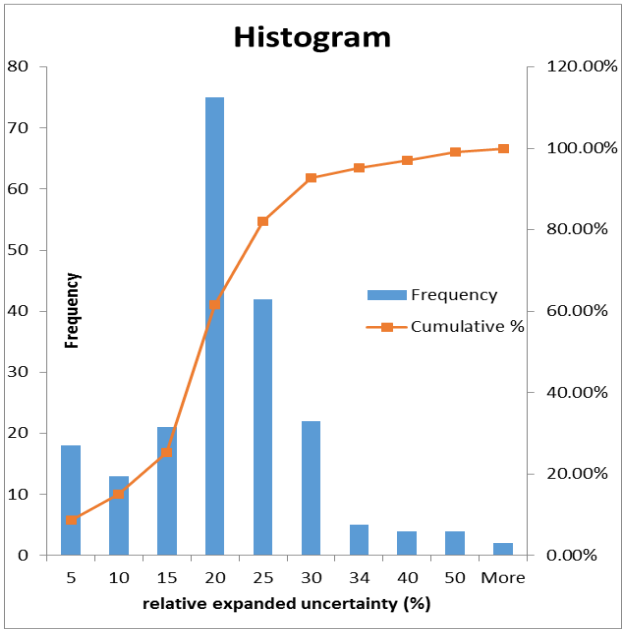


Figure 4 Histogram of the relative expanded uncertainties allocated to the reported test results for the 4 markers PAHs in smoked fish

Serious was the mismatch between the reported relative uncertainties of the sum parameter and the values derived from the propagation of measurement uncertainties reported for the individual analytes by applying the law or error propagation. Uncertainties of the sum parameter were mostly much above scientifically sound values. For illustration, the participant with laboratory code 1 reported for all four individual analytes relative expanded measurement uncertainties of 30 %. A coverage factor of two was provided with the uncertainty statement. Consequently, the absolute standard uncertainties derived thereof are for BAA 1.47 µg/kg, BAP 0.88 µg/kg, BBF 1.27 µg/kg, and CHR 2.10 µg/kg.

The law of error propagation foresees the propagation of absolute uncertainties in case the calculated uncertainty relates to a value that is formed by the addition of individual data, as shown in Equation 4.

Equation 4 $$u_{sum} = \sqrt[2]{u_{BAA}^2 + u_{BAP}^2 + u_{BBF}^2 + u_{CHR}^2}$$

Inserting the above given values of standard uncertainties in Equation 4 provides the standard uncertainty of the sum of four PAHs (2.99 µg/kg). Multiplying this value with a coverage factor of two and expressing it as relative uncertainty (relative to 38.2 µg/kg) results in a value of about 16 %, which is almost half of the reported relative expanded uncertainty of 30 %. The uncertainties of the sum of four PAHs of only one fourth of the

participants agreed with the values derived via the law of error propagation. The respective uncertainties are highlighted in Table 6 in green.

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

Another point to pay attention to is the way of reporting results in terms of number of significant figures. Inconsistencies were noted in the number of significant figures of reported measurement results and associated uncertainties. The EURL PAH will address this issue again at the coming workshop as a harmonised way of reporting results makes part of the proper implementation of EU legislation.

As could be seen from the Kernel density plots the distributions of results are close to a Gaussian distribution. The major modes are close to the assigned (reference) value and the robust mean calculated from the results of the participants. This supports the conclusion that the measurement of PAHs in smoked fish samples is from the statistical point of view under control.

Consequently, participants whose data are outside the satisfactory performance area shall perform root cause analysis. Participants outside the satisfactory performance area are required to report reasons for the deviation to the EURL PAH.

5.4 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire filled in by the participants (ANNEX 9). Data is presented as reported.

Most of the participants have already experience with the determination of PAHs in smoked fish, as smoked fish is a regulated food matrix. Six participants do not analyse this matrix in routine, while 6 other participants have less than 5-10 samples/year.

More than half of the participants (24) used GC with different types of mass spectrometric detectors and 17 laboratories used HPLC-FLD for determination of PAHs. The analysis of all data revealed that laboratory performance was not linked to any analytical technique or sample preparation method used.

The survey on the instrument calibration revealed that 11 participant did not use internal standards. However, those are mainly laboratories applying HPLC-FLD as measurement technique. Three participants reported the application of standard addition technique.

Most participants (except lab 10) reported results corrected for recovery (on purpose, or implicitly corrected by internal standards). Concerning uncertainty, most of the participants report it always together with the test results, 5 participants would provide it only when the results exceed the ML, or on request of the customer.

Concerning the way of uncertainty estimation most of the participant calculated uncertainty budget, eight participants add to this budget the measurement of replicates (precision), while two participants mentioned only precision experiment as bases for their uncertainty estimation. Six participants use the results from the interlaboratory comparison as background for their uncertainty estimation.

For 21 participants the MU depends on the analyte and on the matrix, for 6 participants depends only on analytes and is the same for all matrices for 4 participants MU does not depend neither on analyte nor the matrix.

Sixteen participants determined their LOD/LOQ based on measurements of a standard deviation in blank or low contaminated matrix sample, six participants (including 4 NRLs) wrongly estimated their LOD/LOQ based on S/N or calibration in pure solvent.; five participants – based on S/N in matrix and six – on calibration in matrix. Compliance with legislation was evaluated on basis of requirements set in Regulation (EC) No 333/2007

as amended by Regulation (EU) No 836/2011 [8]. Only one NRL and one OCL reported non-compliant LOD/LOQ data.

5.5 Compliance assessment

As important as the correct analysis of the test sample is the interpretation of results. The assigned analyte contents of the smoked fish test material exceeded the maximum level specified for BAP and the sum of four PAHs as laid down in paragraph 6.1.5 of the Commission Regulation (EU) No 835/2011. The respective maximum levels (ML) for BAP and for the sum of the four PAHs from 1.9.2014 are 2.0 µg/kg and 12.0 µg/kg .

The EURL asked the participants in this study to assess, based on their analysis results, the compliance of the sample with the current legislative limits (valid from 1.09.2014). Figure 5 presents the distribution of the reported results with associated uncertainties for BaP and the sum of four PAHs in relation to the maximum levels defined in legislation (indicated by red lines and the derogated maximum levels - dotted lines).

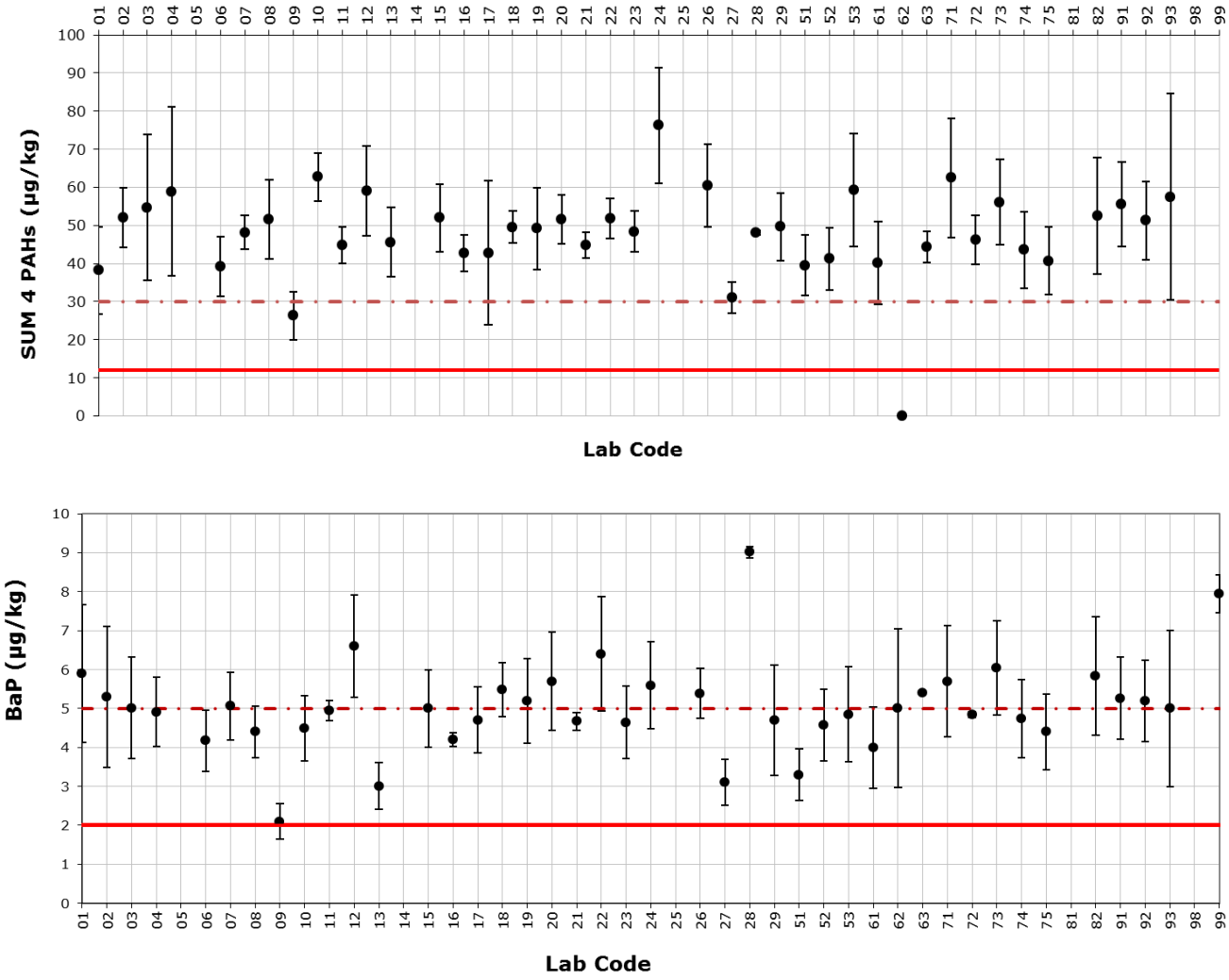


Figure 5. Distribution of the results reported by the participants and the associated expanded measurement uncertainties for BaP and the SUM PAHs in relation to the MLs.

The solid red lines represent the current maximum levels (MLs) valid from 1.08.2014 while the dotted red line represent the old MLs of 5.0 µg /kg for BAP and 30.0 µg/kg for the sum of four PAHs respectively.

The decision criterion for non-compliance is specified in Commission Regulation (EC) No 333/2007 [7]. A lot or sub-lot shall be rejected if the content value of this lot or sub-lot is beyond reasonable doubt above the respective maximum level given in legislation, taking into account the expanded measurement uncertainty and correction for recovery. It translates in a content value that is derived from the measured and recovery corrected content value by subtraction of the expanded uncertainty. This situation is provided in Figure 5 if the lower end of the error bar (representing the expanded measurement uncertainty) associated with the reported result (black dot) is above the red line.

Thirty five laboratories out of 40 laboratories classified the test sample correctly as non-compliant. Lab 72 assessed the sample as compliant although the reported results were clearly above the new (and the old) MLs. Another participant (19) answered positively on the compliance question, although correctly explained that "Yes, test result is clearly above ML regarding uncertainty". Two participants (2, 26) did not reply to the questionnaire and two more (4, 91) did not assess the compliance with the legislative limits.

Due to the high analyte contents of the test sample, which exceeded the MLs significantly, it was not surprising that around 88 % of the participants, who replied to the questionnaire, assessed the compliance of the test sample with EU legislation correctly.

6. 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.

Conclusion

Forty participants reported analysis results. The performance of most participants was satisfactory. More than 83 % of the results reported by NRLs and OCLs respectively obtained satisfactory performance ratings.

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

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

References

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

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

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

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

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

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

6 EFSA, Polycyclic Aromatic Hydrocarbons in Food, Scientific Opinion of the Panel on Contaminants in the Food Chain, (Question N° EFSA-Q-2007-136), Adopted on 9 June 2008, http://www.efsa.Europa eu/sites/

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

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

9 Commission Regulation (EU) No 1327/2014 of 12 December 2014 amending Regulation (EC) No 1881/2006 as regards maximum levels of polycyclic aromatic hydrocarbons (PAHs) in traditionally smoked meat and meat products and traditionally smoked fish and fishery products Text with EEA relevance http://eur-lex.europa.eu/legal-content/EN/TXT/ ?uri=CELEX:32014R1327

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

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

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

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

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

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

List of abbreviations and definitions

BAA -	benz[*a*]anthracene
BAP -	benzo[*a*]pyrene
BBF -	benzo[*b*]fluoranthene
CHR -	chrysene
EC -	European Commission
EFSA -	European Food Safety Authority
EU –	European Union
EURL PAHs -	European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons
ILC –	inter-laboratory comparison
IRMM -	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC -	Joint Research Centre
LOD -	Limit of Detection
LOQ -	Limit of Quantitation
ML -	maximum level
NIST	National Institute of Standards and Technology
NRL -	National Reference Laboratory
OCL -	official food control laboratory
PAHs -	Polycyclic aromatic hydrocarbons
PT -	proficiency test
SUM4PAH	sum of the four markers PAHs

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ANNEX 1: Announcement of the PT on the IRMM webpage

EU-RL 2014 PT PAH in smoked fish

Proficiency Test on the determination of 4 marker PAHs in smoked fish

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

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 smoked fish.

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 test sample for the determination of the EU marker PAHs will consist of an amber glass vial containing about 20 g of homogenised smoked herring test sample

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

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

General outline

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

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

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

Performance assessment:

The performance of the participants in the determination of PAHs in smoked fish 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 σ_r - values of the individual analytes, applying the law of uncertainty propagation.

Registration

Via invitation and submitting a filled in RDF registration form.

Schedule

Registration deadline	Sample dispatch	Reporting of results	Draft Report
04 May 2015	Mid- May 2015	4 weeks after dispatch	September 2015

Contacts

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

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, 17/04/2015
Ref. Ares(2015) 1645873 – 17/04/2015

Inter-laboratory comparison on the determination of four EU marker PAHs in smoked fish

Dear Madam/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EURL PAH on the determination of the 4 marker PAHs in smoked fish is **open until 4 May 2015**.

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

In support to the NRLs, and to facilitate fulfilling their tasks as defined 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 an amber glass vial containing approximately 30 g of smoked fish test sample

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

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

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

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

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

Timing:

- **Deadline for registration: 4 May 2015**
- Dispatch of samples: **end-May.** A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser
- Deadline for reporting of results: **4 weeks after the dispatch of the samples.**

Registration procedure:

You are invited to register via following link:
https://ec.europa.eu/eusurvey/runner/EURL_PAH_2015_PT_PAH_somoked_fish

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

Participants are invited to indicate the preferred solvent type of the standard solution (either toluene or acetonitrile) in the Registration Form as well as any justify additional requests.

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

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

1) *NRL enrols OCLs and covers participation fee.*
   The NRL submits to the EURL a 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 must 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.

Should you require further clarification, please do not hesitate to contact the EURL team via:

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

With kind regards,

Stefanka Bratinova

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

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

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

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

ANNEX 3: Registration form

EURL PAH 2015 Proficiency Test on the determination of 4 marker PAHs in smoked fish

Fields marked with * are mandatory.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

EURL PAH 2015 PT PAH in smoked fish - Registration

This inter-laboratory comparison targets the analysis of the 4 EU marker PAHs (benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, and chrysene) in a smoked fish. The set of test samples will be distributed in the mid-May and will consisting of an amber glass vial containing about 20 g of smoked fish.

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

In addition, a solution of PAHs in solvent will be supplied to participants with disclosed concentration of the analytes, in order to allow participants to verify their instrument calibration. Therefore, results have not to be reported for this material.

Participants are requested to choose either toluene or acetonitrile as solvent for the solution of PAHs in solvent.

This interlaboratory comparison is organised under accreditation to ISO 17043.

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

The PARTICIPATION FEE is 300 Euro for Official Food Control Laboratories per participation

*Organisation

Department

Address

City

*Country

*Name of the contact person

*Email

*NRL or OCL

- NRL
- OCL

Who is the enrolling laboratory (respectively to whom the invoce should be sent)

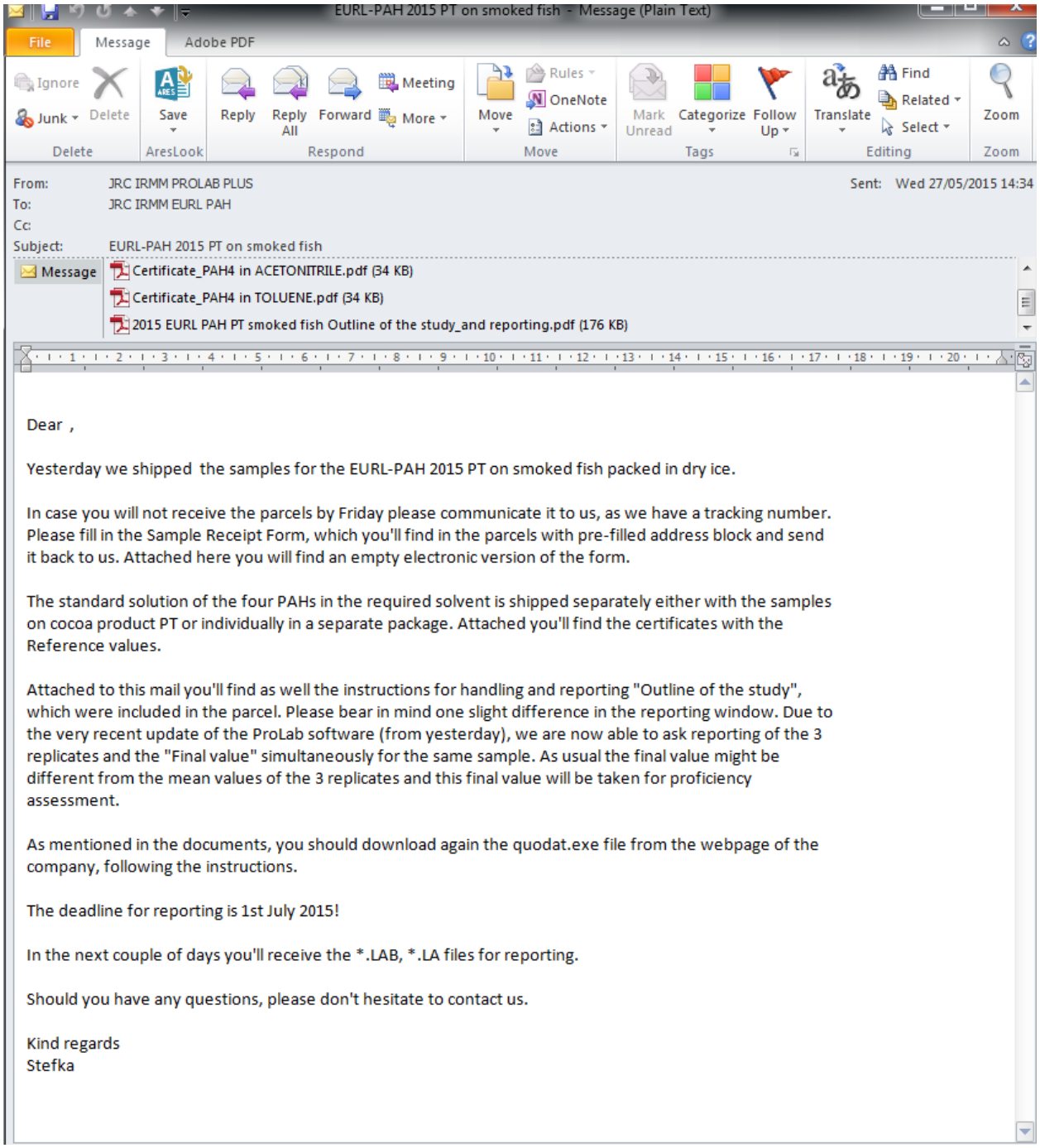
- enrolled by OCL itself (invoice sent to the avovementioned address)
- enrolled by the respective NRL (invoice sent to the respective NRL)

*Prefered solvent for the standard solution

- acetonitrile
- toluene

Any comment or request (not more than 100 characters)

ANNEX 4: Announcement of material dispatch



ANNEX 5: Documents sent to participants - OUTLINE and REPORTING INSTRUCTIONS

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements (Geel)

Geel, 25 May 2015

EURL-PAH 2015 PT- PAHs in smoked fish

Dear Madame/Sir,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of four EU marker PAHs in smoked fish 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, chrysene) and their sum. The participants are requested to report results on all of them.

Each participant is provided with amber glass vials containing a portion of smoked fish, naturally contaminated with PAHs 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 1st July 2015 at the latest following the instructions provided further on in this document.

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

Additionally participants are asked to perform compliance assessment according to the CURRENT legislative limits.

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

Test material and analytes

1. One amber vial, labelled as *"EU-RL PAHs PT 2015 interlaboratory comparison-430, 4 EU PAHs in smoked fish"* containing about 30 g of a naturally contaminated homogenised smoked herring. The analyte content shall be determined in triplicate. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value".

   Store the smoked fish sample in the freezer below -18°C, protected of light.

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

   The ampoule with the solution of 4 EU PAHs in solvent is dispatched separately.

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

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

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

Reporting the results

Data generated by the participants will be collected by using software RingDat, supplementary to ProLab software, used until now for professional data handling and statistical analyses of interlaboratory tests results.
You will receive by mail some files for reporting results. You should follow the following instructions:

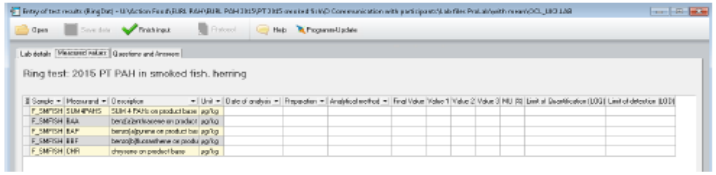
1. Please download the updated data entry program RingDat free from the QuoData web page using following link: http://quodata.de/ringdat_en.php
User: *ringdat*
Password: *prolabdata*

   The RingDat have to be downloaded again, even if you have it from last year's PT. It is updated (version 2015.4.21.0 and later) and gives additional possibilities for the answers in the questionnaire.

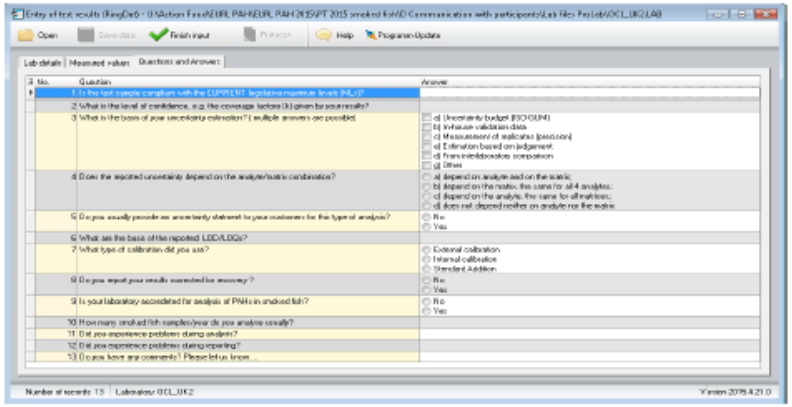
2. Save to the same folder the two lab specific files with the extension **"*.LAB"** and **"*.LA2"**, generated by the ProLab software and provided to each laboratory individually (personal files) by mail.

3. Start the RingDat.exe program and open **"*.LAB"** file for reporting the results. A table will appear with cells for every measurand/sample combination
   - the name of each laboratory and the samples are codified by the software, so that each participant will receive samples with unique codified numbers (i.e., 058);
   - The **"*.LA2"** file contains information about the participant – laboratory name and laboratory code;
   - The **"*.LAB"** file is unique to each laboratory (personal) and contains information about the samples and measurands, that have to be analysed and reported.
   - First tab contains the detailed information for the laboratory
   - Second tab contains table for entering the results. You could filter the entries by sample or by measurand. The cells marked with red are mandatory to be filled
   - Third tab contains a general questionnaire.

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



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



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

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

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

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

With kind regards,

Stefanka Bratinova
EURL-PAHs

SAMPLE RECEIPT

EUROPEAN COMMISSION
DIRECTORATE-GENERAL - JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

Confirmation of the receipt of the samples: RECEIPT FORM

2015 PT- PAHs in smoked fish

Lab Code	«Lab_Code»
Organization	«Description»
Affiliation	«Name»
Address	«Street»
City	«ZIP» «City»
Country	«Country»
Contact person	«Salutation» «Contact_person»

Content of the parcel

1. One amber glass vial containing about 30 g of smoked herring
2. One inter-laboratory comparison sample receipt form (= this form), which is e-mailed as well to be filed and send electronically
3. Instructions for handling and reporting

IF NOT ANALYSED IMMEDIATELY AFTER RECEIVING THE PARCEL,
PLEASE PUT THE TEST SAMPLES IN THE FREEZER at -18°C.

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

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

Date of the receipt of the test materials	
Items are missing	YES ☐ / NO ☐
If YES, please list missing items according to the list above	
All items have been received undamaged	YES ☐ / NO ☐
If NO, please list damaged items according to the list above (in case of samples, please specify the code too)	
Serial number of the smoked fish sample you received	
Ampoule number of the standard solution	

Date

Signature field

Retiesweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
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mail: jrc-irmm-eurl-PAH@ec.europa.eu

ANNEX 6: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 26/05/2015

Standard solution specification sheet	**PAH4 in ACETONITRILE**
Date of production: 04/04/2014	Total volume: 1 mL
Expiry date: *October 2015*	

Standard solution composition:

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

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

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

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

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

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

TOLUENE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 25/05/2015

Standard solution specification sheet	**PAH4 in TOLUENE**
Date of production: 04/04/2014	Total volume: 1 mL
Expiry date: *October 2015*	

Standard solution composition:

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

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

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

Solvent: Toluene

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

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

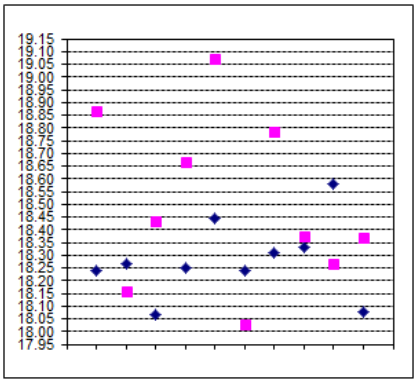
ANNEX 7: Homogeneity of the smoked fish test material

Analyte: **BAA**

	n =	10		
	mean =	18.3911	22%	**= σ-trg(%)**
0.037559917	**s_x =**	0.1938	4.0460	**= σ-trg**
√MSW =	**s_w =**	0.2792		
	s_s =	0.0377	1.2138	**= 0,3*s**

ISO-13528	passed		
F =	0.96359419	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	-0.0014	2.8486	= F1*(0,3*s)²+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 06	18.24	18.86	-0.62	37.10	18.55
Ampoule 19	18.27	18.16	0.11	36.43	18.21
Ampoule 22	18.07	18.44	-0.37	36.50	18.25
Ampoule 34	18.25	18.67	-0.42	36.92	18.46
Ampoule 42	18.44	19.07	-0.63	37.51	18.76
Ampoule 53	18.24	18.03	0.21	36.27	18.13
Ampoule 68	18.31	18.79	-0.48	37.10	18.55
Ampoule 80	18.33	18.37	-0.04	36.71	18.35
Ampoule 81	18.58	18.26	0.31	36.84	18.42
Ampoule 93	18.08	18.37	-0.29	36.45	18.22



$\sum$**(diff)²** = 1.55915912

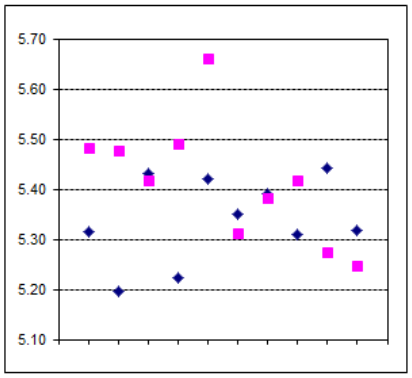
var(sum)/2 = 0.07512 =MSB

Analyte: **BAP**

	n =	10		
	mean =	5.3780	22%	**= σ-trg(%)**
0.004824251	**s_x =**	0.0695	1.1832	**= σ-trg**
√MSW =	**s_w =**	0.1186		
	s_s =	0.0470	0.3549	**= 0,3*s**

ISO-13528	passed		
F =	0.68557148	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	-0.0022	0.2511	= F1*(0,3*s)²+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 06	5.32	5.48	-0.17	10.80	5.40
Ampoule 19	5.20	5.48	-0.28	10.67	5.34
Ampoule 22	5.43	5.42	0.01	10.85	5.42
Ampoule 34	5.22	5.49	-0.27	10.71	5.36
Ampoule 42	5.42	5.66	-0.24	11.08	5.54
Ampoule 53	5.35	5.31	0.04	10.66	5.33
Ampoule 68	5.39	5.38	0.01	10.77	5.39
Ampoule 80	5.31	5.42	-0.11	10.73	5.36
Ampoule 81	5.44	5.27	0.17	10.72	5.36
Ampoule 93	5.32	5.25	0.07	10.56	5.28



$\sum$**(diff)²** = 0.28147327

var(sum)/2 = 0.00965 =MSB

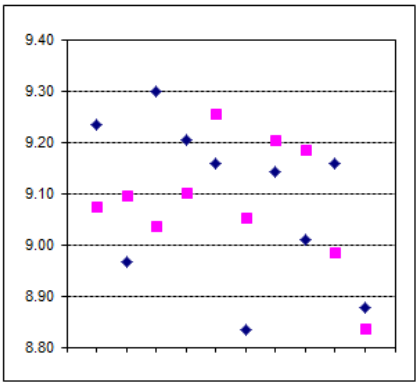
Analyte: **BBF**

	n =	10		
	mean =	9.0855	22%	**= σ-trg(%)**
0.012669274	**s_x =**	0.1126	1.9988	**= σ-trg**
√MSW =	**s_w =**	0.1107		
	s_s =	0.0809	0.5996	**= 0,3*s**

ISO-13528	passed		
F =	2.0686747	3.02038295	= Fcrit
	passed		

IUPAC		
(MSB-MSW)/2	0.0065	0.6884 = F1*(0,3*s)^2+F2*MSW
	passed	

Bottle	Result a	Result b	diff	sum	avg
Ampoule 06	9.23	9.07	0.16	18.31	9.15
Ampoule 19	8.97	9.10	-0.13	18.06	9.03
Ampoule 22	9.30	9.04	0.26	18.34	9.17
Ampoule 34	9.20	9.10	0.10	18.31	9.15
Ampoule 42	9.16	9.25	-0.10	18.41	9.21
Ampoule 53	8.84	9.05	-0.22	17.89	8.94
Ampoule 68	9.14	9.20	-0.06	18.35	9.17
Ampoule 80	9.01	9.19	-0.18	18.19	9.10
Ampoule 81	9.16	8.98	0.18	18.14	9.07
Ampoule 93	8.88	8.84	0.04	17.71	8.86



$\sum$(diff)^2 = 0.24497374

var(sum)/2 = 0.02534 =MSB

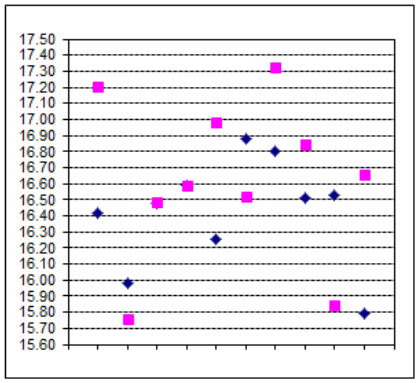
Analyte: **CHR**

	n =	10		
	mean =	16.5217	22%	**= σ-trg(%)**
0.120261437	**s_x =**	0.3468	3.6348	**= σ-trg**
√MSW =	**s_w =**	0.3834		
	s_s =	0.2162	1.0904	**= 0,3*s**

ISO-13528	passed		
F =	1.6362153	3.02038295	= Fcrit
	passed		

IUPAC		
(MSB-MSW)/2	0.0468	2.3839 = F1*(0,3*s)^2+F2*MSW
	passed	

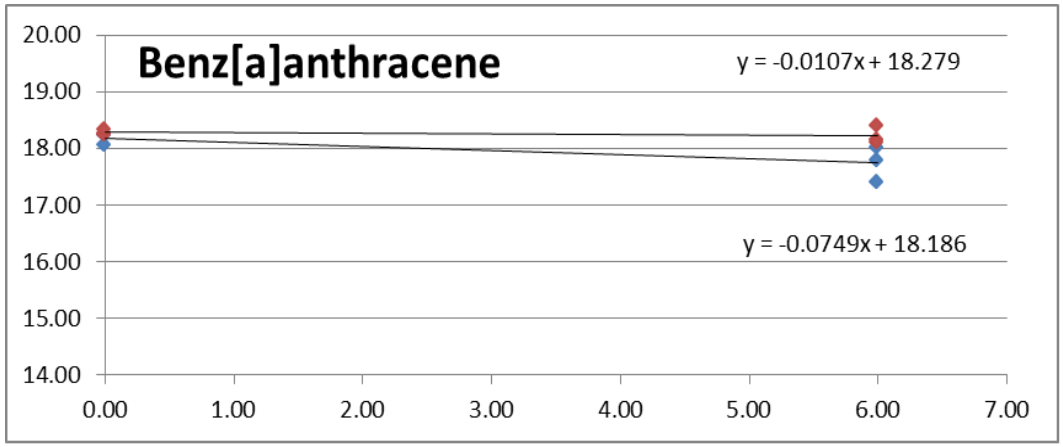
Bottle	Result a	Result b	diff	sum	avg
Ampoule 06	16.42	17.20	-0.78	33.62	16.81
Ampoule 19	15.98	15.75	0.22	31.73	15.87
Ampoule 22	16.47	16.49	-0.01	32.96	16.48
Ampoule 34	16.59	16.59	0.00	33.18	16.59
Ampoule 42	16.25	16.99	-0.73	33.24	16.62
Ampoule 53	16.88	16.52	0.36	33.40	16.70
Ampoule 68	16.80	17.33	-0.53	34.13	17.06
Ampoule 80	16.52	16.85	-0.33	33.36	16.68
Ampoule 81	16.53	15.84	0.69	32.37	16.18
Ampoule 93	15.79	16.66	-0.87	32.44	16.22

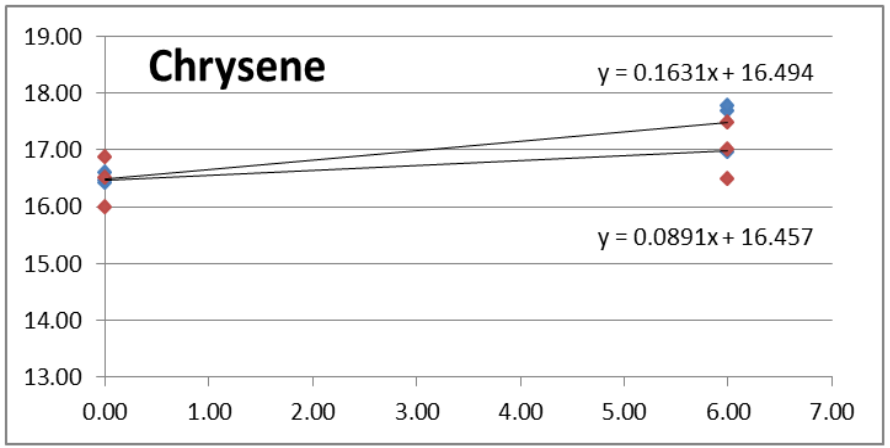


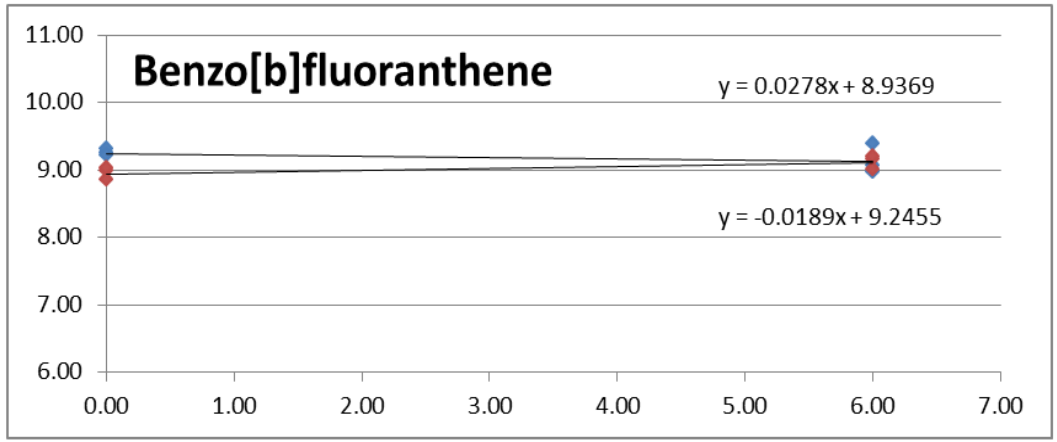
$\sum$(diff)^2 = 2.93999052

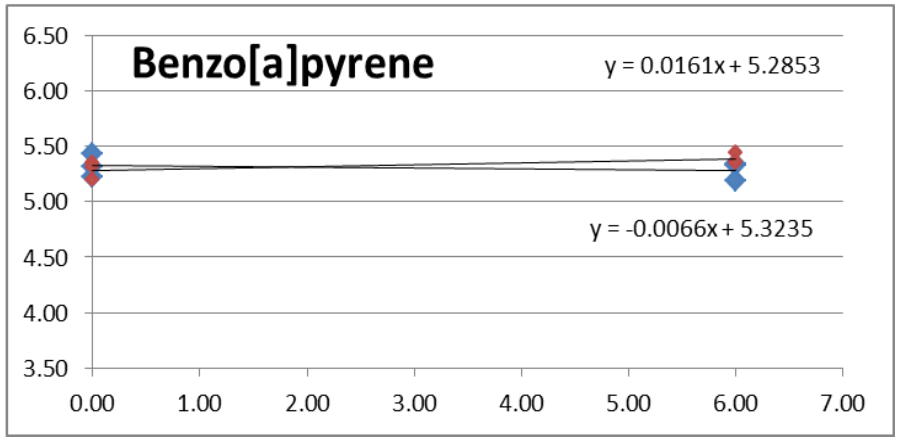
var(sum)/2 = 0.24052 =MSB

ANNEX 8. Stability of the smoked fish test material for the period of the study









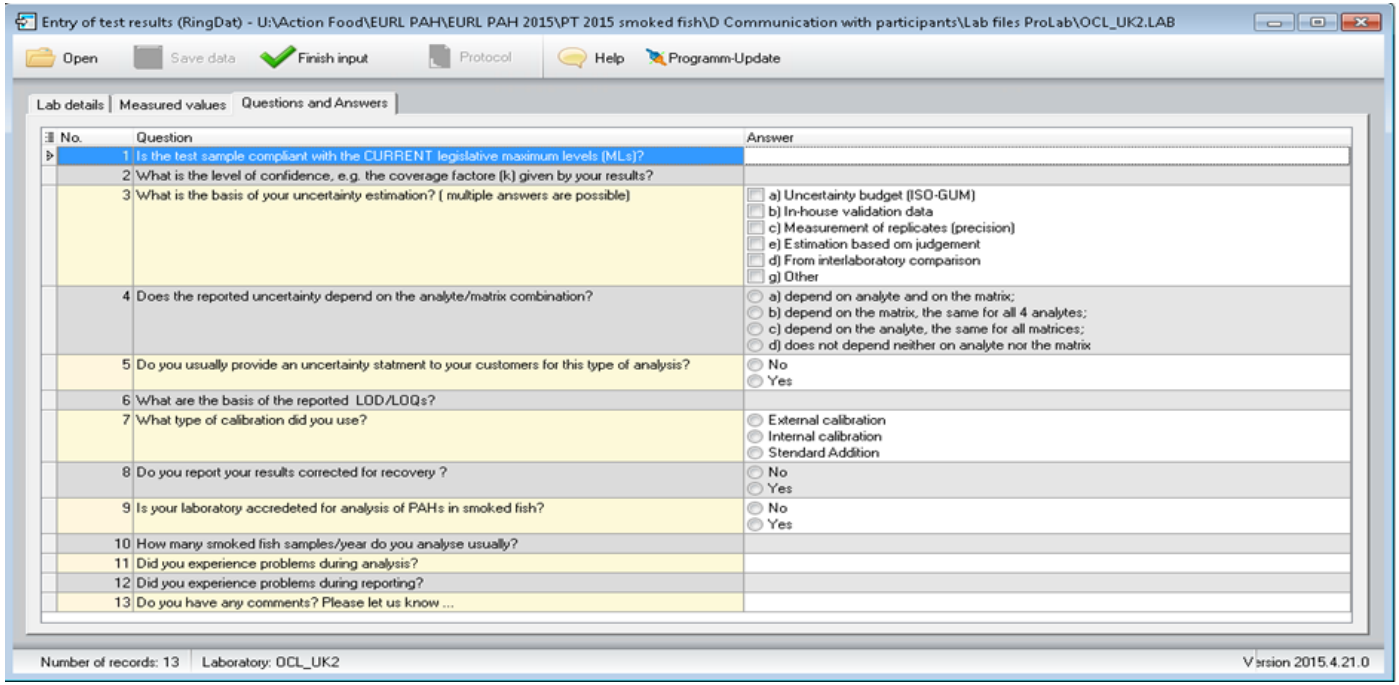
Better conditions: temperature -80°C ;

Recommended conditions: freezer -20°C

ANNEX 9. Questionnaire and answers from the participants

Ring test : 2015 PT PAH in smoked fish, herring (13 questions, 487 answers)

1	Compliance with the ML	Is the test sample compliant with the CURRENT legislative maximum levels (MLs)?	38 Answers	ComboBox
2	Level of confidence	What is the level of confidence, e.g. the coverage factore (k) given by your results?	35 Answers	TextEdit
3	Uncertainty estimate	What is the basis of your uncertainty estimation? (multiple answers are possible)	40 Answers	CheckGroup
4	Uncertainty dependance	Does the reported uncertainty depend on the analyte/matrix combination?	39 Answers	RadioGroup
5	Reporting uncertainty	Do you usually provide an uncertainty statment to your customers for this type of analysis?	39 Answers	RadioGroup
6	Basis for LOD/LOQ	What are the basis of the reported LOD/LOQs?	40 Answers	CheckGroup
7	Calibration	What type of calibration did you use?	39 Answers	RadioGroup
8	Recovery rate	Do you report your results corrected for recovery ?	40 Answers	RadioGroup
9	Laboratory accredeted	Is your laboratory accredeted for analysis of PAHs in smoked fish?	40 Answers	RadioGroup
10	Previous experience	How many smoked fish samples/year do you analyse usually?	39 Answers	TextEdit
11	Problems analysis	Did you experience problems during analysis?	37 Answers	TextEdit
12	Problems reporting	Did you experience problems during reporting?	36 Answers	TextEdit
13	Comment	Do you have any comments? Please let us know ...	25 Answers	TextEdit



Participants with Lab Codes 2 and 26 did not reply to the questionnaire

Lab Code	1. Compliance with the ML	2. Level of confidence	3. Uncertainty estimate
01	No (please explain) ...	2	Uncertainty budget
03	No, neither BaP nor sum	k = 2	Uncertainty budget Other
04		No	Uncertainty budget Estimation based om judgement
06	No (please explain) ... Concentrations of BaP and PAH4 above maximum limits (regulation 835/2011)	k=2, level of confidence of 95%	Uncertainty budget
07	No - exceeds ML of 30ug/kg PAH 4 even when taking MU into consideration.	2k	Uncertainty budget
08	No (please explain) ...Taking uncertainty of measurement into account, maximum levels for both BaP and Sum PAH4 are exceeded.	95%, coverage factor k=2	Uncertainty budget From interlaboratory comparison
09	No. The sample is compliant (after considering the measurement uncertianty) for BaP, but not for the sum	25%	Measurement of replicates (precision)
10	No (please explain) ...	2	Uncertainty budget
11	No (please explain) ...We don't have informatoin about the species of the fish, but even if is spratt, the sum of the 4 PAHs exceeds beyond doubt the legal limit of 30 µg/kg. (otherwise the limit is 2 and 12 µg/kg for BaP and the sum of 4PAHs respectively)	2	Uncertainty budget
12	No, the amount of SUMPAH and BaP including the MU exceed the MLs	k=2	Uncertainty budget
13	No (please explain) ...BaP > 2.0 ug/kg; 4PAH > 12.0 ug/kg	95%; k=2	Uncertainty budget
15	No: BaP - MU > 2 µg/kg ; Sum PAK4 - MU > 12 µg/kg	2	Uncertainty budget Measurement of replicates (precision)
16	No (please explain) ...B(a)p2, result4,2 (3,85-4,54), PAH4:12, result 42,8 (39,8-45,9)	2	Uncertainty budget
17	No, regarding the new MLs (b(a)p 2,0 µg/kg, PAH4 sum 12,0 µg/kg) our results show higher concentrations taking into account the MU	2	Uncertainty budget From interlaboratory comparison
18	No, the sample does not comply with legislative maximum levels	2	Measurement of replicates (precision)
19	Yes, test result is clearly above ML regarding uncertainty	2	Uncertainty budget
20	No. The sum of PAH4 exceeds the current and derogated ML. The BaP exceeds the current ML but not the derogated ML that applies in this jurisdiction.	2	Uncertainty budget
21	No (the measured levels of benzo(a) pyrene and sum 4PAHs exceed the respective current MLs taken into account the MU)	95	Uncertainty budget Measurement of replicates (precision)
22	No (because the results of the sum PAH exceeding the limit of 12 ug/kg)	k=2, 95%	Uncertainty budget
23	No (please explain) Sample non complying with EU maximum limits on 4 PAHs (summary of benzo(a)pyrene, chrysene, benzo(a)anthracene and benzo(b)fluoranthene) and on benzo(a)pyrene separetely set for smoked herring which are 12ug/kg and 2 ug/kg respectively, if the sample consists only of muscle meat.	2	Uncertainty budget In-house validation data Other
24	Yes for BaP, No for SUM4PAHs		Uncertainty budget
27	No (please explain) ...Measured values of BAP and SUM4PAHs minus values of their expanded uncertainty are above maximum levels from the Commission Regulation (EU) No 835/2011	k=2	Uncertainty budget Measurement of replicates (precision) From interlaboratory comparison
28	No, the sample contamination si higher than the MLs		Uncertainty budget
29	No (please explain) ... BAP 4.7 ± 1.4 > 2.0 ug/kg and sum >12 ug/kg	95%	Uncertainty budget Estimation based om judgement
51	No (please explain) ... sum is too high (ML is 12)	2	Uncertainty budget Measurement of replicates (precision)
52	No: exeeding current ML Reg. 1881/2006	95%	Measurement of replicates (precision)
53	No. Explanation: MRL for BaP (2 µg/kg) and MRL for Sum BaP, BaA, BbF, CHR (12 µg/kg) are exceeded.	95%	Uncertainty budget Measurement of replicates (precision) Estimation based om judgement
61	No (please explain) ...	2	Uncertainty budget
62	No. BaP > 2,0 µg/kg.	95 % (k=2)	Uncertainty budget Measurement of replicates (precision) From interlaboratory comparison
63	No (please explain) ...	2	Uncertainty budget Measurement of replicates (precision)
71	No (please explain) ...Higher content the MRL	2	Uncertainty budget From interlaboratory comparison
72	Yes	95% (k=2)	Uncertainty budget
73	No (please explain) ...benzo (a) pyrene and sum 4PAHs greater than the maximum level (reg (UE) 835/2011)	95 % (k=2)	Uncertainty budget From interlaboratory comparison
74	No. >maximum level for benzoapyrene and sum of 4 HAP.	2	Measurement of replicates (precision)
75	no, the sample test is no compliant with the legislative Mls		
82	No (please explain) ...Exceeds limits of 2 for BAP and 12 for total even when MU is taken into account		Uncertainty budget Measurement of replicates (precision)
91		2	Uncertainty budget Uncertainty budget
92	benuo[a]pyren: not compliance; Sum 4 PAH: not compliance	K=2	
93	No (please explain) ...According to (EC) 1881/2006 (6.1.5) MRL for Benzo(a)pyreenh is 2.0 ug/kg and for the sum 12,0 ug/kg		Uncertainty budget
99	No (BAP is above 2 ppb (above 5ppb in Croatia due to derrogation), sumPAH is above 12 ppb (above 30 ppb due to derrogation)	95 k=2	Uncertainty budget

Lab Code	4. Uncertainty dependance	5. Reporting uncertainty	6. Basis for LOD/LOQ
01	Depend on the analyte and on the matrix;	Yes	Calibration approach in pure solvent
03	Depend on the analyte and on the matrix;	Yes	S/N approach in pure solvent
04	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	S/N approach in similar matrix
06	Depend on the analyte, the same for all matrices	Yes	Measurement of the blank/low contaminated matrix samples
07	Depend on the analyte and on the matrix;	No	Measurement of the blank/low contaminated matrix samples Measurement of the blank/low contaminated matrix samples
08	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
09	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	S/N approach in similar matrix
10	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
11	Depend on the analyte and on the matrix;	Yes	Calibration approach in similar matrix
12	Depend on the analyte and on the matrix;	No	S/N approach in similar matrix
13	Depend on the analyte and on the matrix;	Yes	Calibration approach in pure solvent S/N approach in similar matrix
15	Depend on the analyte and on the matrix;	Yes	Calibration approach in pure solvent S/N approach in similar matrix
16	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
17	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
18	Depend on the analyte and on the matrix;	Yes	S/N approach in pure solvent
19	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
20	Does not depend neither on the analyte nor on the matrix	Yes	Measurement of the blank/low contaminated matrix samples S/N approach in pure solvent
21	Depend on the analyte and on the matrix;	Yes	Calibration approach in similar matrix
22	Does not depend neither on the analyte nor on the matrix	Yes	Measurement of the blank/low contaminated matrix samples S/N approach in pure solvent
23	Depend on the analyte and on the matrix;	Yes	Calibration approach in similar matrix
24	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	Calibration approach in pure solvent S/N approach in similar matrix
27	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
28	Depend on the analyte, the same for all matrices	Yes	Measurement of the blank/low contaminated matrix samples
29	Depend on the analyte, the same for all matrices		Calibration approach in pure solvent
51	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	S/N approach in pure solvent
52	Does not depend neither on the analyte nor on the matrix	Yes	Calibration approach in similar matrix
53	Does not depend neither on the analyte nor on the matrix	Yes	Calibration approach in similar matrix
61	Depend on the analyte, the same for all matrices	Yes	S/N approach in similar matrix
62	Depend on the analyte, the same for all matrices	No	Calibration approach in pure solvent Measurement of the blank/low contaminated matrix samples
63	Depend on the analyte and on the matrix;	No	Calibration approach in similar matrix
71	Depend on the analyte and on the matrix;	Yes	Calibration approach in similar matrix S/N approach in similar matrix
72	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	Measurement of the blank/low contaminated matrix samples
73	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	S/N approach in similar matrix
74	Depend on the analyte, the same for all matrices	Yes	Calibration approach in similar matrix
75			
82	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples
91	Depend on the matrix, the same for all Does not depend neither on the analyte nor on the matrix analytes	Yes	Measurement of the blank/low contaminated matrix samples
92			
93	Depend on the analyte and on the matrix;	No	Calibration approach in pure solvent
99	Depend on the analyte and on the matrix;	Yes	Measurement of the blank/low contaminated matrix samples

Lab Code	7. Calibration	8. Recovery rate	9. Laboratory accredeted	10. Previous experience	11. Problems analysis
01	External calibration	No	Yes	0	Yes.
03	External calibration	Yes	Yes	5-10	no
04	External calibration	Yes	Yes	50	interference for BAA, BBF, CHR
06	Internal calibration	Yes	Yes	20	No
07	Internal calibration	Yes	Yes	>20	Low sample mass in original vial so requested second vial.
08	Internal calibration	Yes	Yes	10-50	No
09	Standard Addition	No	Yes	none	yes - very few testing material, analysis could not be repeated (standard addition)
10	External calibration	Yes	No	10 samples	NO
11	Internal calibration	Yes	Yes	50 smoked fish and 50 smoked spratt samples /year	No
12	Internal calibration	Yes	Yes	5	no
13	Internal calibration	No	Yes	~40	No
15	External calibration	Yes	Yes	< 20	no
16	Internal calibration	Yes	Yes	40	No
17		No	Yes	20	no
18	External calibration	Yes	Yes		
19	Internal calibration	Yes	Yes	15	no
20	Internal calibration	Yes	Yes	30	No
21	Internal calibration	No	Yes	10	no
22	Internal calibration	No	No	50	No
23	Standard Addition	Yes	Yes	20-30	The HPLC analysis resulted to unclear peaks (puritty and similarity of fluorescence spectra limited) and forced us to carry out analysis by using GC-MS
24	Internal calibration	Yes	Yes	500	No
27	Internal calibration	Yes	Yes	30	No
28	Internal calibration	Yes	No	0 samples, until the method validation for meat products will be finished	yes, the chromatogram was not as "clean" as for the other products
29	External calibration	Yes	No	10	
51	External calibration	Yes	Yes	0	yes, BAA and CHR could not be sufficiently separated from fat by GPC, not enough sample material to optimize GPC conditions
52	Internal calibration	No	Yes	20	Matrix peak coelution with IS benzo(a)anthracene switched to IS benzo(b)chrysene
53	Internal calibration	Yes	Yes	<20	No
61	Internal calibration	Yes	Yes	100	no
62	Internal calibration	No	Yes	Very occasionally	
63	Internal calibration	Yes	Yes	80 (smoked and non-smoked fish)	No
71	Standard Addition	Yes	Yes	> 50 samples	no
72	Internal calibration	No	Yes	50	no
73	Internal calibration	Yes	Yes	5	no
74	Internal calibration	Yes	Yes	20	recovery rates under 50%(about 45%)
75			no for smoked fish	10	/
82	External calibration	Yes	Yes	less than 50	no
91	External calibration	Yes	Yes	20	No
92			yes	yes	concentration to high; Sample intake must be reduce to be in the calibration range
93	Internal calibration	No	Yes	0	No
99	External calibration	Yes	Yes	50	No

Lab Code	12. Problems reporting	13. Comment
01	No.	
03	no	uncertainty estimation based on control chart rsd
04	No	
06	No	
07	No	We report MU on request to customers. For official control MU reported as standard.
08	No	
09	no	/
10	NO	The sample amount was 15 g instead of 30 g
11	I can't read the end of the sentences in the questionarre.	
12	no	no
13	No	
15	no	no
16	No	
17	no	no
18		Nº 3: The estimation of uncertainty is based not only in the precision, but also considering bias factor contribution. Nº 6: LOQ was calculated s/r, but LOD was estimated on the lowest in house validated concentration. Nº 10: Depending if any survey study is carried out on this kind of products. Nº 13: In the information sheet accompanying the sample was said that the amount of sample was 30g, however the amount of sample received was 18 g approximately.
19	no	
20	No	The amount of sample supplied (16g) is small given the warning in the accompanying letter that the sample is highly contaminated.
21	no	
22	No	No
23	No	This kind of sample with such interfence in peak purity in HPLC has never been analysed in our lab before.
24	No	no
27	No	No
28	we don't have the uncertainty calculated for each PAH,only for BAP and SUM, so I completed the column with 0	Our validated method is based on the SE EN ISO 15753. We need to mention that we didn't participate in any training for the detection of PAH's and we would like to know if there is any posibility to participate in a trainig organised by you. Our laboratory is acredited with SE EN ISO 17025/2005 . PAHs could be acreditated only after we participate in an interlaboratory comparison with acceptable results.
29		MU% is for single determination or for average??? we report for average.
51	no	more sample material would be great
52	not till now	
53	No	Actual sample amount (appr. 15 gramms) significantly below the announced 30 gramms.
61	no	no
62		We are accredeted only for BaP. Only BaP is quantified.
63	No	
71	no	
72	no	no
73	no	
74	No	No
75	/	/
82	no	no
91	No	
92		The sample contains also the same amount of Triphenylene! If it is not separated from Chrysene the reported amount of Chrysene will be around 35 µg/kg.
93	Yes/no	
99	No	/

Annex 10. Method performance LOD and LOQ

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..

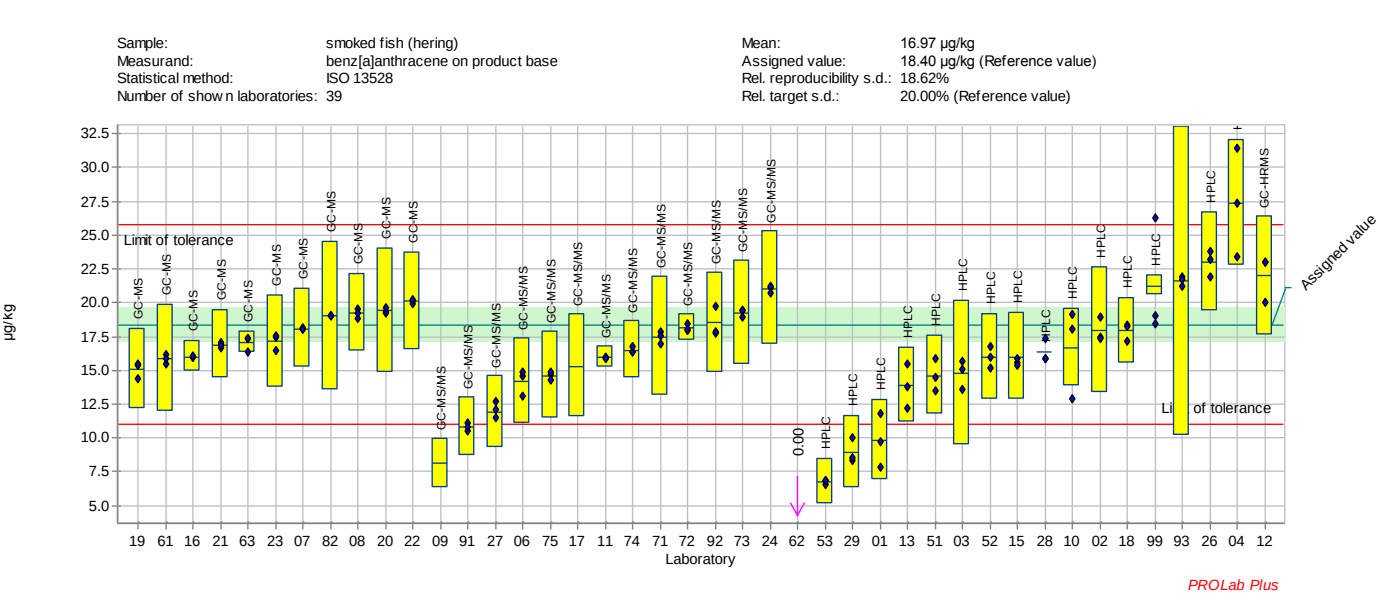
	BaA		BaP		BbF		CHR	
Lab Code	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]2	LOQ [µg/kg]3	LOD [µg/kg]3	LOQ [µg/kg]4	LOD [µg/kg]4	LOQ [µg/kg]2
1	0.15	0.5	0.05	0.2	0.05	0.2	0.15	0.5
2	0.03	0.05	0.03	0.05	0.05	0.1	0.03	0.05
3	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4
4	0.12	0.36	0.08	0.24	0.11	0.33	0.03	0.09
5								
6	0.03	0.09	0.03	0.09	0.03	0.09	0.03	0.09
7	0.05	0.05	0.08	0.08	0.06	0.06	0.07	0.07
8	0.18	0.05	0.24	0.07	0.21	0.06	0.12	0.03
9	0.03	0.1	0.07	0.1	0.02	0.1	0.03	0.1
10	0.17	0.56	0.15	0.48	0.15	0.48	0.16	0.52
11	0.06	0.19	0.06	0.2	0.05	0.17	0.08	0.28
12	0	0.1	0	0.1	0	0.1	0	0.1
13	0.06	0.2	0.06	0.2	0.06	0.2	0.2	0.5
14								
15	0.06	0.2	0.06	0.2	0.1	0.3	0.03	0.1
16	0.1	0.2	0.1	0.3	0.1	0.3	0.1	0.3
17	0.26	0.78	0.26	0.78	0.26	0.78	0.26	0.78
18	0.03	0.4	0.02	0.4	0.13	0.4	0.06	0.4
19	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5
20	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
21	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
22	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5
23	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
24	0.02	0.5	0.03	0.5	0.03	0.5	0.02	0.5
25								
26	0.5	0.25	0.16	0.08	0.4	0.2	0.5	0.25
27	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
28	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7
29	0.33	1	0.33	1	0.33	1	0.33	1
51	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5
52	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5
53	0.15	0.5	0.15	0.5	0.15	0.5	0.15	0.5
61	1	0.5	1	0.5	1	0.5	1	0.5
62			0.2	0.5				
63	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
71	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2
72	0.04	0.04	0.09	0.09	0.07	0.07	0.09	0.09
73	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
74	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
75	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1
81								
82	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5
91	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
92	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1
93	0.1	0.02	0.1	0.01	0.1	0.04	0.1	0.04
98								
99	0.22	0.57	0.23	0.65	0.12	0.26	0.25	0.54

ANNEX 11: Data reported by participants

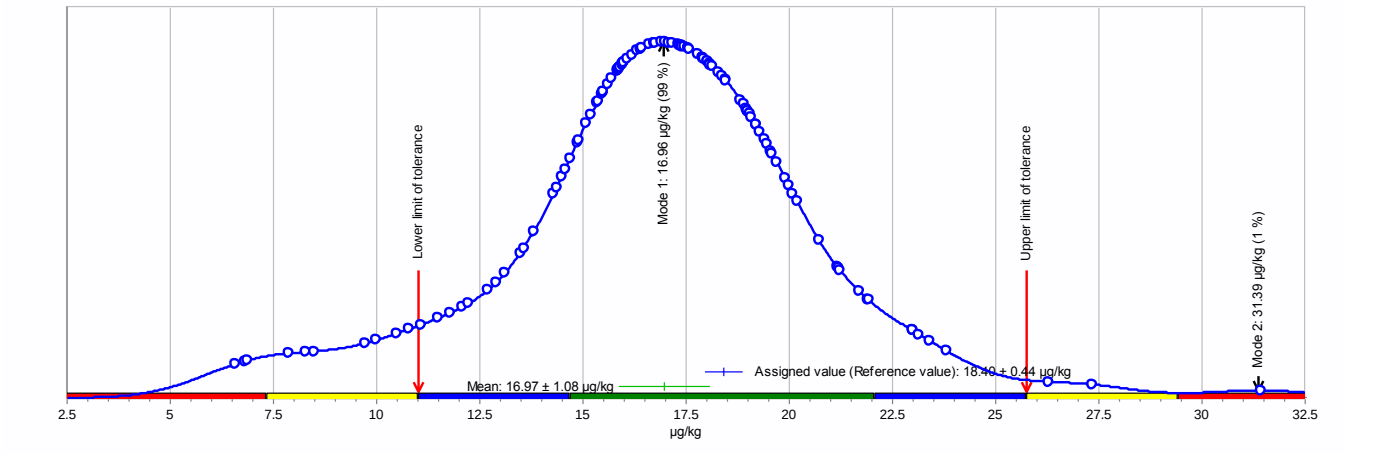
The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores. "Mean values" and "Rel. reproducibility s.d." represent the robust mean values and the robust standard deviations of the participants data, calculated according to the ISO 13528 algorithm. Very slight differences in the mean values on both graphs are possible as on the Kernel density plot mean values are calculated based on the "final values" reported by the participants while on the Distribution graphs they are calculated based on the three replicate results.

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

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

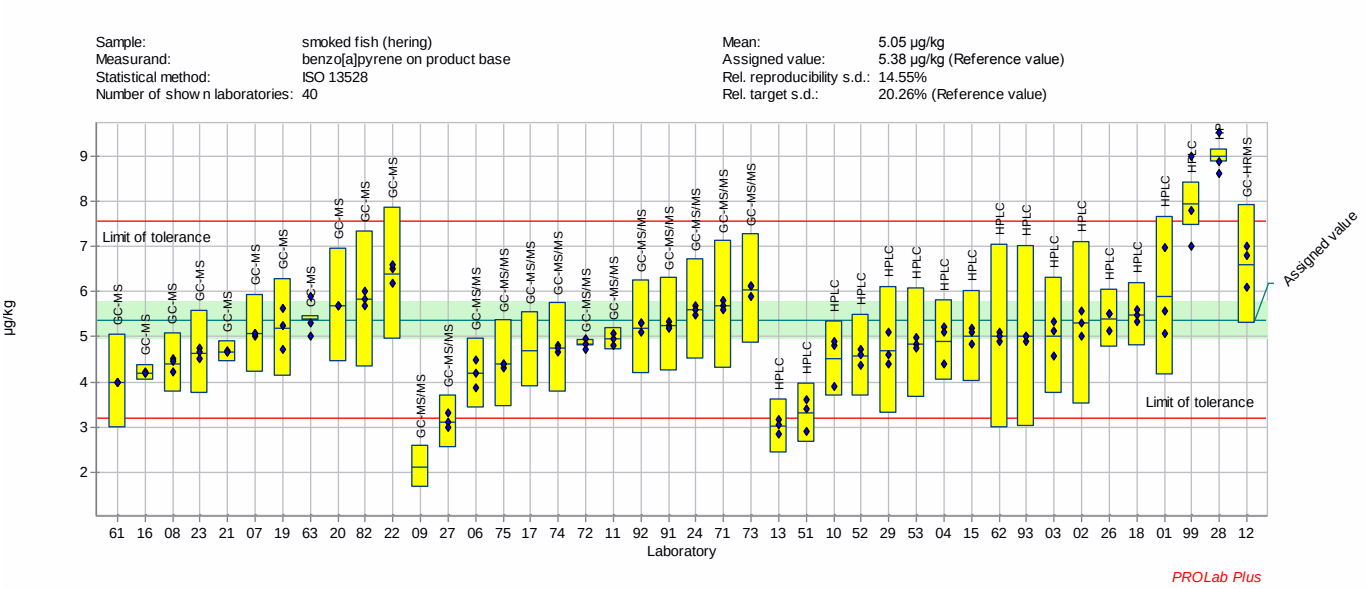


Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA) of the smoked fish test sample. Assigned value is 18.4 µg/kg**.**
Due to a software problem, the reported significant zeros after the comas are missing

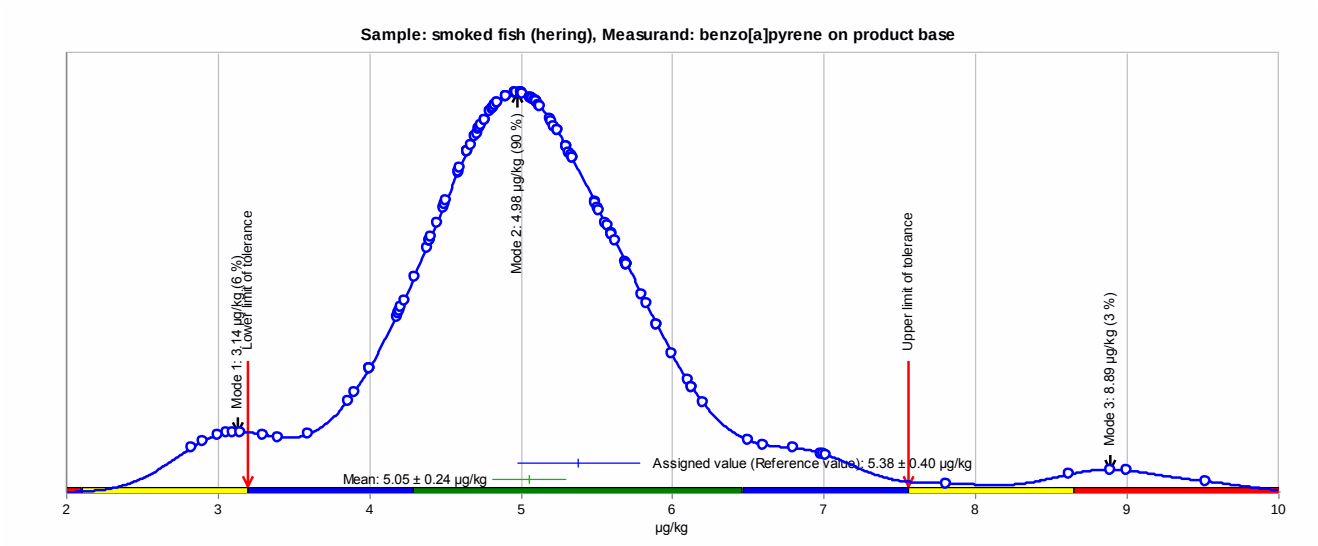
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	BAA	11.8	7.87	9.75	9.81	30	HPLC
2	BAA	18.97	17.42	17.36	17.92	26	HPLC
3	BAA	13.581	15.714	15.095	14.797	36	HPLC
4	BAA	23.4	31.43	27.36	27.39	17	HPLC
5	BAA						
6	BAA	14.58	14.87	13.13	14.19	22.3	GC-MS/MS
7	BAA	18.15	18.08	18.03	18.09	16	GC-MS
8	BAA	18.83	19.57	19.21	19.2	15	GC-MS
9	BAA				8.1	23	GC-MS/MS
10	BAA	18.1	19.1	12.9	16.7	17.2	HPLC
11	BAA	16.01	15.98	15.86	15.95	4.8	GC-MS/MS
12	BAA	23	23	20	22	20	GC_HRMS
13	BAA	15.47	13.82	12.25	13.85	20	HPLC
14	BAA						
15	BAA	15.62	15.37	15.84	16	20	HPLC
16	BAA	16	16	16.1	16	7.3	GC-MS
17	BAA				15.3	25	GC-MS/MS
18	BAA	17.17	18.37	18.29	17.94	13.6	HPLC
19	BAA	15.36	15.51	14.37	15.08	20	GC-MS
20	BAA	19.2	19.3	19.6	19.4	23.9	GC-MS
21	BAA	16.62	17.08	16.91	16.87	15	GC-MS
22	BAA	20.1	19.9	20.2	20.1	18	GC-MS
23	BAA	16.44	17.47	17.55	17.15	20	GC-MS
24	BAA	21.167	21.245	20.732	21.048	20	GC-MS/MS
25	BAA						
26	BAA	23.16	21.93	23.83	22.97	16	HPLC
27	BAA	11.5	12.7	12.1	11.9	22.3	GC-MS/MS
28	BAA	15.896	17.321	15.869	16.362	0	HPLC
29	BAA	8.3	10	8.5	8.9	30	HPLC
51	BAA	14.5	15.9	13.5	14.6	20	HPLC
52	BAA	16.75	15.97	15.2	15.97	20	HPLC
53	BAA	6.82	6.59	6.89	6.77	25	HPLC
61	BAA	16.2	15.5	15.9	15.9	25	GC-MS
62	BAA				0	0	HPLC
63	BAA	17.4	16.4	17.4	17.1	4.6	GC-MS
71	BAA	17	17.9	17.6	17.5	25	GC-MS/MS
72	BAA	18.472	17.934	18.02	18.142	5.443	GC-MS/MS
73	BAA	19.4	18.9	19.47	19.26	20	GC-MS/MS
74	BAA	16.4	16.33	16.77	16.5	13	GC-MS/MS
75	BAA	14.7	14.9	14.3	14.6	22	GC-MS/MS
81	BAA						
82	BAA	19	19	19	19	29	GC-MS
91	BAA	10.5	11.1	10.8	10.8	20	GC-MS/MS
92	BAA	17.8	19.7	17.9	18.5	20	GC-MS/MS
93	BAA	21.2	21.9	21.7	21.6	53	HPLC
98	BAA						
99	BAA	26.29	19.05	18.46	21.27	3.4	HPLC

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

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



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

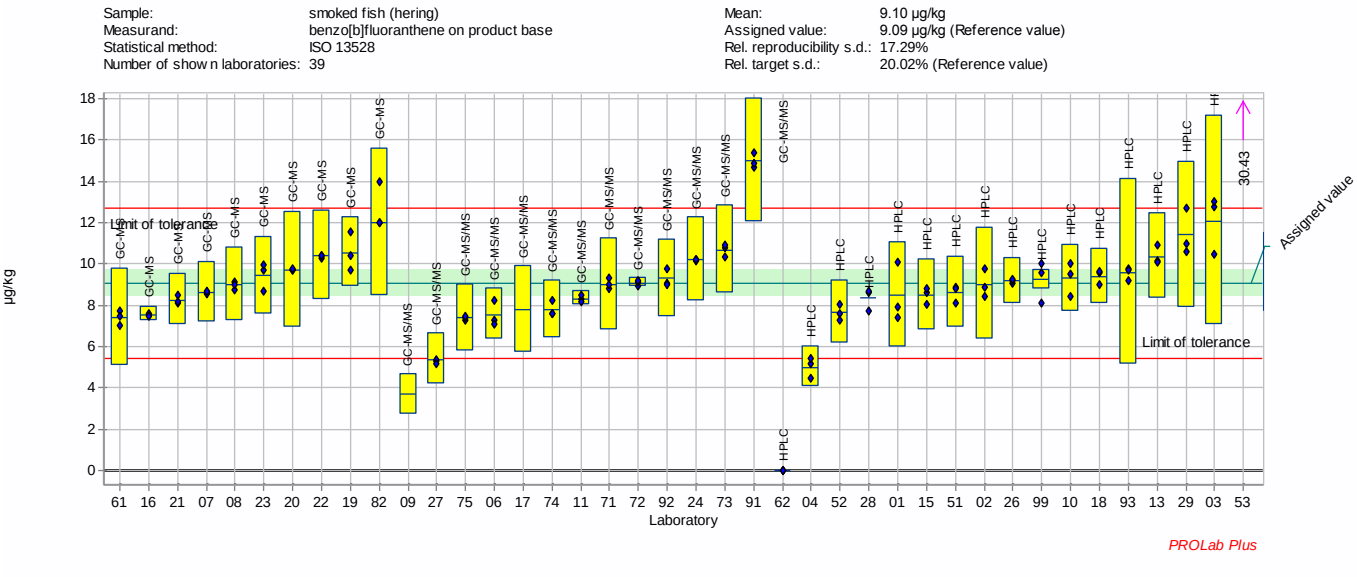


Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP) of the smoked fish test sample. Assigned value is 5.38 µg/kg**.**
Due to a software problem, the reported significant zeros after the comas are missing

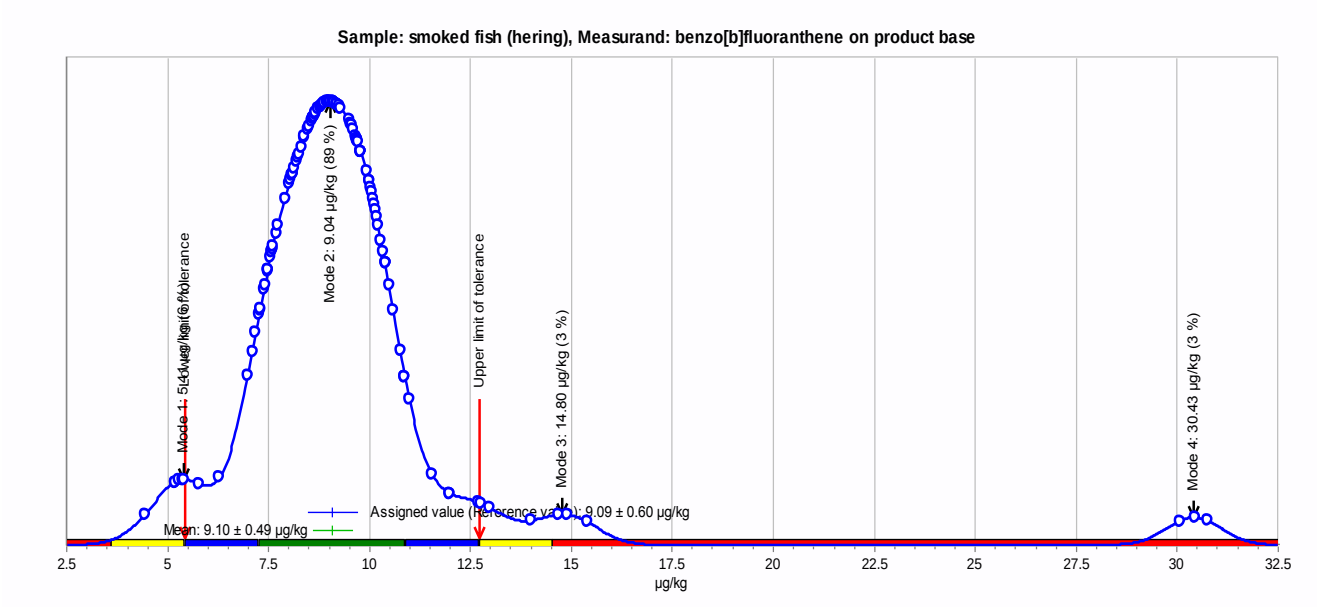
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	BAP	6.98	5.06	5.56	5.89	30	HPLC
2	BAP	5.57	5.32	5	5.3	34	HPLC
3	BAP	5.117	4.586	5.339	5.014	26	HPLC
4	BAP	5.22	4.41	5.09	4.91	18	HPLC
5	BAP						
6	BAP	4.49	4.19	3.86	4.18	18.8	GC-MS/MS
7	BAP	5.01	5.08	5.08	5.06	17	GC-MS
8	BAP	4.23	4.51	4.45	4.4	15	GC-MS
9	BAP				2.1	22	GC-MS/MS
10	BAP	3.9	4.8	4.9	4.5	18.6	HPLC
11	BAP	4.81	5.07	4.96	4.94	5.2	GC-MS/MS
12	BAP	7	6.8	6.1	6.6	20	GC_HRMS
13	BAP	3.15	3.06	2.83	3.01	20	HPLC
14	BAP						
15	BAP	5.19	4.85	5.1	5	20	HPLC
16	BAP	4.18	4.21	4.2	4.2	4.1	GC-MS
17	BAP				4.7	18	GC-MS/MS
18	BAP	5.34	5.49	5.6	5.48	12.7	HPLC
19	BAP	4.71	5.62	5.24	5.19	21	GC-MS
20	BAP	5.7	5.7	5.7	5.7	22.17	GC-MS
21	BAP	4.7	4.65	4.65	4.67	5	GC-MS
22	BAP	6.2	6.5	6.6	6.4	23	GC-MS
23	BAP	4.74	4.67	4.5	4.64	20.03	GC-MS
24	BAP	5.692	5.492	5.596	5.593	20	GC-MS/MS
25	BAP						
26	BAP	5.13	5.52	5.51	5.39	12	HPLC
27	BAP	3.3	3.1	3	3.1	18.9	GC-MS/MS
28	BAP	8.891	9.523	8.622	9.012	1.583	HPLC
29	BAP	4.6	5.1	4.4	4.7	30	HPLC
51	BAP	2.9	3.4	3.6	3.3	20	HPLC
52	BAP	4.73	4.59	4.38	4.57	20	HPLC
53	BAP	4.83	4.76	4.97	4.85	25	HPLC
61	BAP	4	4	4	4	26	GC-MS
62	BAP	5.1	4.9	5	5	40.7	HPLC
63	BAP	5.9	5	5.3	5.4	1.1	GC-MS
71	BAP	5.8	5.7	5.6	5.7	25	GC-MS/MS
72	BAP	4.96	4.849	4.725	4.845	1.454	GC-MS/MS
73	BAP	6.13	5.9	6.13	6.05	20	GC-MS/MS
74	BAP	4.65	4.82	4.76	4.74	21	GC-MS/MS
75	BAP	4.4	4.3	4.4	4.4	22	GC-MS/MS
81	BAP						
82	BAP	5.83	5.7	6	5.83	26	GC-MS
91	BAP	5.33	5.24	5.2	5.26	20	GC-MS/MS
92	BAP	5.3	5.1	5.3	5.2	20	GC-MS/MS
93	BAP	4.9	5	5	5	40	HPLC
98	BAP						
99	BAP	9	7.01	7.81	7.94	6.2	HPLC

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

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



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

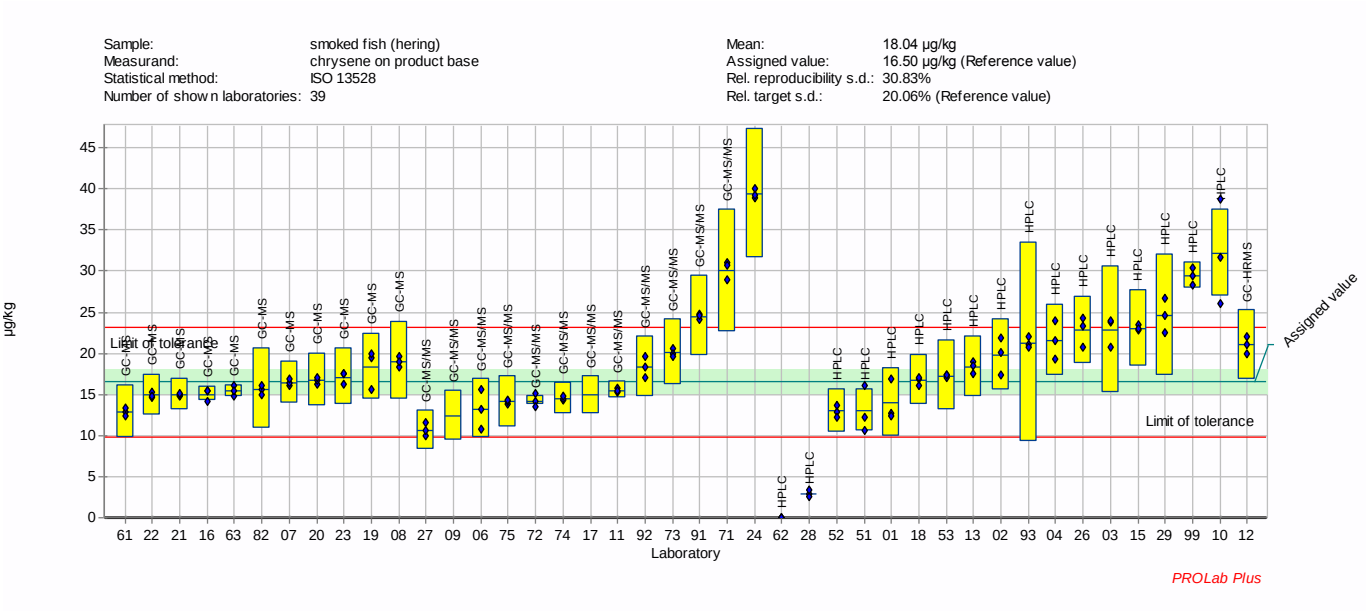


Results, as reported by the participants, for the content of benzo[*b*]-fluoranthene (BBF) of the smoked fish test sample. Assigned value is 9.09 µg/kg.
Due to a software problem, the reported significant zeros after the comas are missing

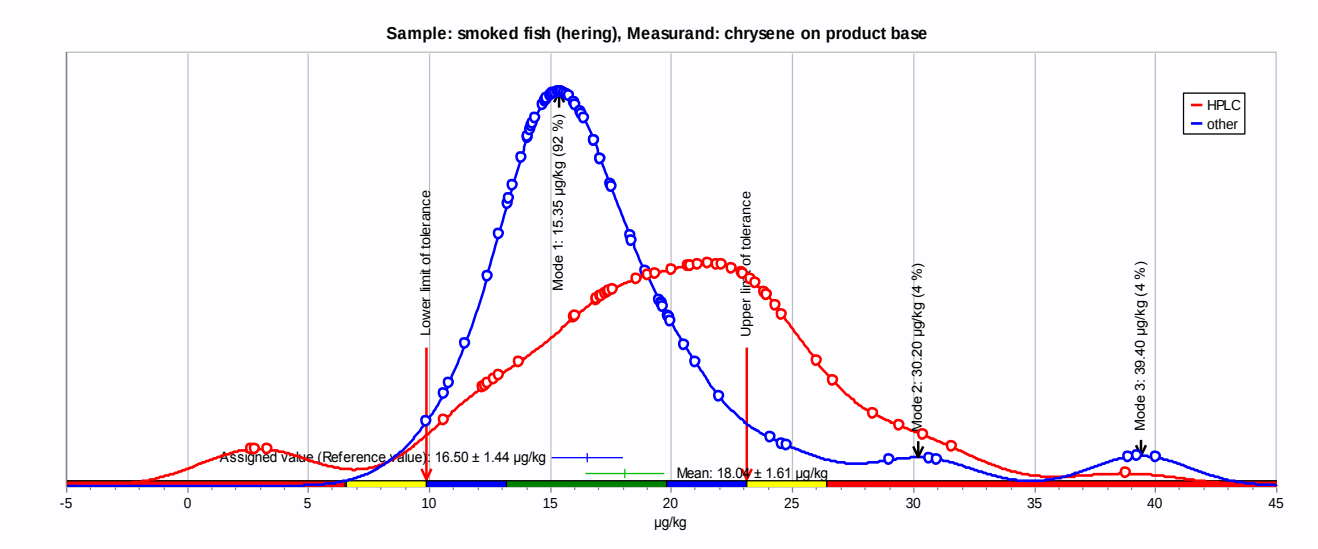
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	BBF	10.1	7.92	7.42	8.48	30	HPLC
2	BBF	8.86	9.8	8.41	9.02	30	HPLC
3	BBF	10.492	12.774	12.99	12.085	42	HPLC
4	BBF	4.46	5.19	5.42	5.02	20	HPLC
5	BBF						
6	BBF	8.26	7.31	7.11	7.56	16.5	GC-MS/MS
7	BBF	8.61	8.57	8.68	8.62	17	GC-MS
8	BBF	8.75	9.13	8.98	9	20	GC-MS
9	BBF				3.7	27	GC-MS/MS
10	BBF	8.4	10	9.5	9.3	17.5	HPLC
11	BBF	8.32	8.2	8.48	8.33	4.2	GC-MS/MS
12	BBF	10	9.6	9.1	9.6	20	GC_HRMS
13	BBF	10.89	10.13	10.06	10.36	20	HPLC
14	BBF						
15	BBF	8.629	8.829	8.059	8.5	20	HPLC
16	BBF	7.57	7.6	7.49	7.56	4.5	GC-MS
17	BBF				7.8	27	GC-MS/MS
18	BBF	9.02	9.55	9.67	9.41	14.3	HPLC
19	BBF	10.4	9.73	11.56	10.56	16	GC-MS
20	BBF	9.7	9.7	9.8	9.7	29.08	GC-MS
21	BBF	8.09	8.51	8.15	8.25	15	GC-MS
22	BBF	10.3	10.4	10.4	10.4	21	GC-MS
23	BBF	8.67	9.71	9.94	9.44	20.01	GC-MS
24	BBF	10.16	10.191	10.233	10.195	20	GC-MS/MS
25	BBF						
26	BBF	9.05	9.21	9.26	9.17	12	HPLC
27	BBF	5.3	5.4	5.2	5.4	22.7	GC-MS/MS
28	BBF	7.75	8.605	8.672	8.342	0	HPLC
29	BBF	10.6	12.7	11	11.4	31	HPLC
51	BBF	8.9	8.8	8.1	8.6	20	HPLC
52	BBF	8.03	7.6	7.28	7.64	20	HPLC
53	BBF	30.08	30.76	30.44	30.43	25	HPLC
61	BBF	7.7	7	7.5	7.4	32	GC-MS
62	BBF						HPLC
63	BBF	7.2	5.8	6.3	6.4	1.1	GC-MS
71	BBF	8.8	9.3	9	9	25	GC-MS/MS
72	BBF	8.943	9.148	9.191	9.094	2.728	GC-MS/MS
73	BBF	10.77	10.89	10.35	10.67	20	GC-MS/MS
74	BBF	7.61	7.63	8.23	7.82	18	GC-MS/MS
75	BBF	7.3	7.4	7.5	7.4	22	GC-MS/MS
81	BBF						
82	BBF	12	12	14	12	30	GC-MS
91	BBF	15.4	14.7	14.9	15	20	GC-MS/MS
92	BBF	9.1	9.8	9	9.3	20	GC-MS/MS
93	BBF	9.8	9.2	9.7	9.6	47	HPLC
98	BBF						
99	BBF	8.1	10.04	9.56	9.24	5.3	HPLC

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

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



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

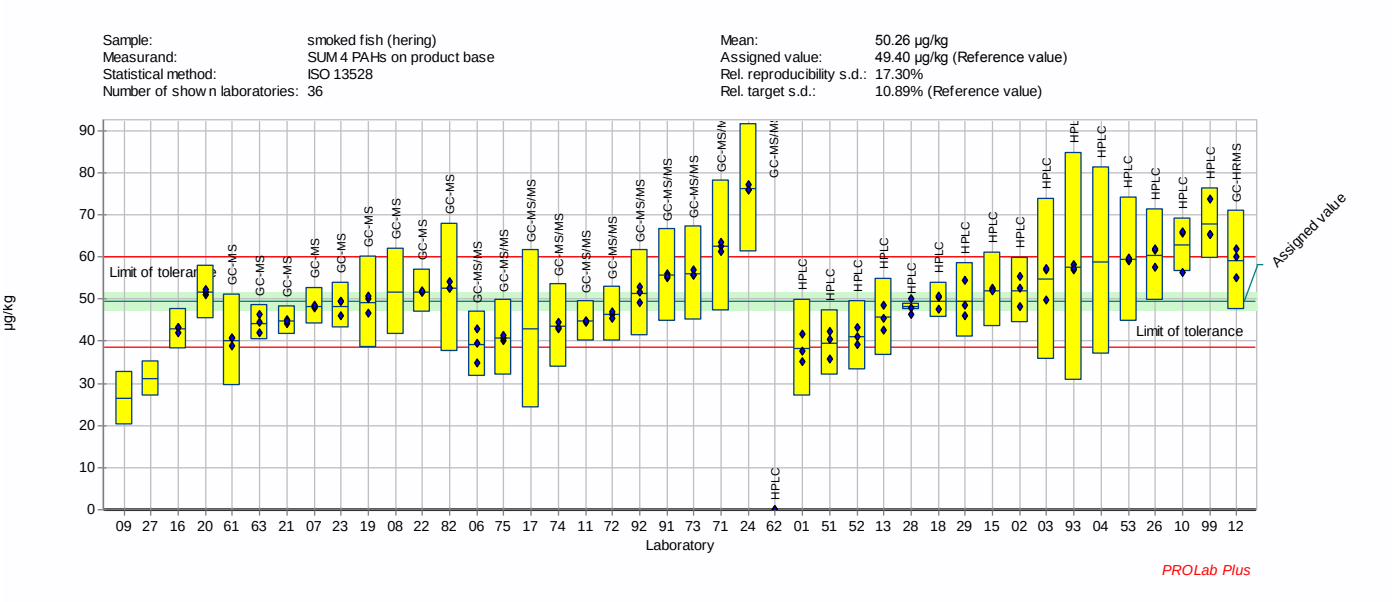


Results, as reported by the participants, for the content of chrysene (CHR) of the smoked fish test sample. Assigned value is 16.5 µg/kg.
Due to a software problem, the reported significant zeros after the comas are missing

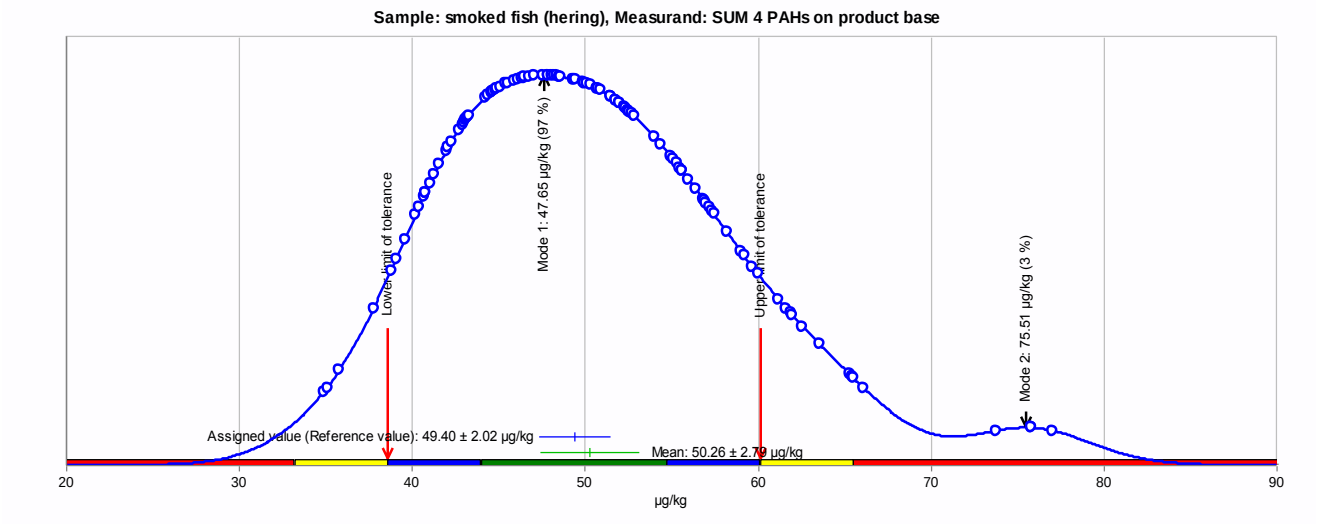
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	CHR	12.7	16.9	12.4	14	30	HPLC
2	CHR	21.89	20.04	17.43	19.79	22	HPLC
3	CHR	20.701	23.847	23.93	22.826	34	HPLC
4	CHR	19.33	23.96	21.53	21.6	20	HPLC
5	CHR						
6	CHR	15.67	13.24	10.83	13.25	27.4	GC-MS/MS
7	CHR	16.07	16.39	16.81	16.42	16	GC-MS
8	CHR	18.39	19.59	18.93	19	25	GC-MS
9	CHR				12.4	25	GC-MS/MS
10	CHR	26	31.6	38.8	32.2	16.6	HPLC
11	CHR	15.78	15.34	15.38	15.5	6.8	GC-MS/MS
12	CHR	22	21	20	21	20	GC_HRMS
13	CHR	19.02	18.57	17.57	18.39	20	HPLC
14	CHR						
15	CHR	22.91	23.48	22.97	23	20	HPLC
16	CHR	15.4	15.5	14.2	15	5.9	GC-MS
17	CHR				14.9	16	GC-MS/MS
18	CHR	16.05	16.92	17.11	16.69	18.3	HPLC
19	CHR	19.52	19.87	15.6	18.33	22	GC-MS
20	CHR	16.3	16.8	17.1	16.7	19.29	GC-MS
21	CHR	14.85	14.88	15.11	14.95	12.5	GC-MS
22	CHR	15.2	14.7	14.8	14.9	17	GC-MS
23	CHR	16.26	17.52	17.48	17.09	20	GC-MS
24	CHR	40.05	38.898	39.26	39.403	20	GC-MS/MS
25	CHR						
26	CHR	24.32	20.82	23.29	22.81	18	HPLC
27	CHR	9.9	11.5	10.6	10.6	23.1	GC-MS/MS
28	CHR	2.824	2.628	3.336	2.93	0	HPLC
29	CHR	22.5	26.7	24.6	24.6	30	HPLC
51	CHR	16	12.3	10.6	13	20	HPLC
52	CHR	13.72	12.88	12.24	12.95	20	HPLC
53	CHR	17.3	17.1	17.4	17.27	25	HPLC
61	CHR	12.9	12.4	13.3	12.9	25	GC-MS
62	CHR				0	0	HPLC
63	CHR	16	14.8	15.4	15.4	4.5	GC-MS
71	CHR	31	30.7	29	30	25	GC-MS/MS
72	CHR	14.071	13.463	15.071	14.202	4.261	GC-MS/MS
73	CHR	20.55	19.92	19.68	20.05	20	GC-MS/MS
74	CHR	14.26	14.41	14.84	14.5	13	GC-MS/MS
75	CHR	13.8	14.1	14.3	14.1	22	GC-MS/MS
81	CHR						
82	CHR	15.67	16	15	15.67	31	GC-MS
91	CHR	24.8	24.1	24.6	24.5	20	GC-MS/MS
92	CHR	17.1	18.3	19.6	18.3	20	GC-MS/MS
93	CHR	21.1	22.1	20.8	21.3	57	HPLC
98	CHR						
99	CHR	30.41	28.35	29.46	29.41	5.5	HPLC

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

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



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



Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH) of the smoked fish test sample. Assigned value is 49.4 µg/kg.
Due to a software problem, the reported significant zeros after the comas are missing

LCode	Measurant	Final value, µg/kg	Uncertainty, %	Analytical technique
1	SUM4PAHS	38.2	30	HPLC
2	SUM4PAHS	52.02	15	HPLC
3	SUM4PAHS	54.721	35	HPLC
4	SUM4PAHS	58.93	37.6	HPLC
5	SUM4PAHS			
6	SUM4PAHS	39.18	20.1	GC-MS/MS
7	SUM4PAHS	48.19	9	GC-MS
8	SUM4PAHS	51.6	20	GC-MS
9	SUM4PAHS	26.3	24	
10	SUM4PAHS	62.7	10.1	HPLC
11	SUM4PAHS	44.72	10.7	GC-MS/MS
12	SUM4PAHS	59	20	GC_HRMS
13	SUM4PAHS	45.61	20	HPLC
14	SUM4PAHS			
15	SUM4PAHS	52	17	HPLC
16	SUM4PAHS	42.8	11.2	
17	SUM4PAHS	42.8	44	GC-MS/MS
18	SUM4PAHS	49.52	8.5	HPLC
19	SUM4PAHS	49.164	22	GC-MS
20	SUM4PAHS	51.6	12.4	
21	SUM4PAHS	44.73	7.6	GC-MS
22	SUM4PAHS	51.8	10	GC-MS
23	SUM4PAHS	48.32	11.12	GC-MS
24	SUM4PAHS	76.24	20	GC-MS/MS
25	SUM4PAHS			
26	SUM4PAHS	60.34	18	HPLC
27	SUM4PAHS	31	13.2	
28	SUM4PAHS	48.087	1.372	HPLC
29	SUM4PAHS	49.6	18	HPLC
51	SUM4PAHS	39.5	20	HPLC
52	SUM4PAHS	41.21	20	HPLC
53	SUM4PAHS	59.31	25	HPLC
61	SUM4PAHS	40.1	27	GC-MS
62	SUM4PAHS	0	0	HPLC
63	SUM4PAHS	44.3	9.3	GC-MS
71	SUM4PAHS	62.5	25	GC-MS/MS
72	SUM4PAHS	46.311	13.893	GC-MS/MS
73	SUM4PAHS	56.03	20	GC-MS/MS
74	SUM4PAHS	43.57	23	GC-MS/MS
75	SUM4PAHS	40.7	22	GC-MS/MS
81	SUM4PAHS			
82	SUM4PAHS	52.5	29	GC-MS
91	SUM4PAHS	55.6	20	GC-MS/MS
92	SUM4PAHS	51.3	20	GC-MS/MS
93	SUM4PAHS	57.5	47	HPLC
98	SUM4PAHS			
99	SUM4PAHS	67.85	12.3	HPLC

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