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Four marker PAHs in spiked olive oil

Donata Lerda, Philippe Verlinde, Thomas Wenzl

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Contact information
Thomas Wenzl
Address: Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, B-2440 Geel, Belgium
E-mail: jrc-irmm-crl-pah@ec.europa.eu
Tel.: +32 14 571 320
Fax: +32 14 571 783

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

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Donata Lerda*, Philippe Verlinde and Thomas Wenzl

EC-JRC-IRMM
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*co-ordinator

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1 Summary

This report presents the results of the ninth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EU-RL 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 olive oil spiked with 15+1 EU priority PAHs. It was conducted in accordance with ISO Standard 17043 and the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.
In agreement with National Reference Laboratories, the test material used in this exercise was commercial olive oil spiked with 15 + 1 EU priority PAHs. The spiked oil was prepared gravimetrically and values obtained from preparation were used to benchmark the results reported by participants.
Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States were admitted as participants.
The participants were free to choose the method of analysis. The four EU marker PAHs were chosen as target analytes as limits for their sum were recently introduced in European legislation. The performance of the participating laboratories in the determination of the target PAHs in olive oil was expressed by both z-scores and zeta-scores.
Participants also received a solution of PAHs in solvent of their choice (either toluene or acetonitrile) with disclosed content for the verification of their instrument calibration.

A summary of the performance of the participants in the determination of the four marker PAHs in the olive oil test material is given in the following table.

Participant group	Reporting laboratories	Calculated z-scores	z-scores ≤ |2|	z-scores ≤ |2|	Calculated zeta-scores	zeta-scores ≤ |2|	zeta-scores ≤ |2|
#	#	#	#	%	#	#	%
NRLs	25	125	120	96	120	94	78
OCLs	24	115	101	88	95	75	79

However, in some cases bias was discovered. It is therefore recommended to investigate this further.

2 Introduction

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

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

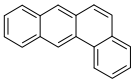
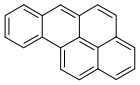
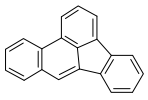
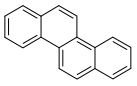
In 2002 the European Commission's Scientific Committee on Food identified 15 individual PAHs as being of major concern for human health. These 15 EU priority PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene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

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

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

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

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

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

3 Scope

As specified in Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules [ii], one of the core duties of EU-RLs is organising inter-laboratory comparison tests (ILCs).
This inter-laboratory comparison study aimed to evaluate the comparability of analysis results reported by National Reference Laboratories (NRLs) and EU official food control laboratories (OCLs) for the four EU marker PAHs in olive oil. The appropriateness of the reported measurement uncertainty was also tested as this parameter is important in the compliance assessment of food with EU maximum levels.
The ILC was designed and evaluated according to ISO Standard 17043:2010 and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, further denoted as Harmonized Protocol [ix, x].

4 Participating Laboratories

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

Table 2: List of participating National Reference Laboratories

Institute	***Country***
AGES - Österreichische Agentur für Gesundheit und Ernährungssicherheit, Kompetenzzentrum Cluster Chemie	AUSTRIA
Scientific Institute of Public Health	BELGIUM
SGL - State General Laboratory, Environmental and other Food Contamination Laboratory	CYPRUS
Nàrodní referenční laboratoř pro polycyklické aromatické uhlovodíky - Státní veterinární ústav Praha	CZECH REPUBLIC
Division of Food Chemistry, National Food Institute, Technical University of Denmark	DENMARK
Danish Plant Directorate, Laboratory for Feed and Fertilizers	DENMARK
Tartu Laboratory of Health Protection Inspectorate	ESTONIA
EVIRA - Finnish Food Safety Authority	FINLAND
LABERCA - Laboratoire d'Etude des Résidus et des Contaminants dans les Aliments	FRANCE
BVL - Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	GERMANY
GCSL - General Chemical State Laboratory - Food Division - Laboratory	GREECE
Central Agricultural Office, Food & Feed Safety Directorate, Food Residues Toxicological Dept.	HUNGARY
Central Agricultural Office, Food and Feed Safety Directorate, Feed Investigation NRL	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
RIKILT- Institute of Food Safety	NETHERLANDS
NIFES - National Institute of Nutrition and Seafood Research	NORWAY
National Institute of Public Health - National Institute of Hygiene	POLAND
IP – INRB -Instituto Nacional dos Recursos Biológicos	PORTUGAL
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

One of the 27 NRLs did not register and one did not report results for this PT.

Table 3: List of participating Official Food Control Laboratories

Institute	*Country*
ANALYTEC	AUSTRIA
Institut Dr. Wagner	AUSTRIA
LARECO	BELGIUM
Federaal Agentschap voor de veiligheid van de voedselketen - FAVV	BELGIUM
Laboratorium ECCA NV	BELGIUM
VITO - Vlaamse Instelling voor Technologisch Onderzoek	BELGIUM
Health Board - Tallin	ESTONIA
Laboratoire de l'Environnement et de l'Alimentation de Vendée	FRANCE
LDA 22	FRANCE
Laboratoire Departemental de la Sarthe	FRANCE
LDA 56	FRANCE
La Drome Laboratoire (LDA26)	FRANCE
IDAC	FRANCE
CVUA-OWL	GERMANY
Thueringer Landesamt fuer Lebensmittelsicherheit und Verbraucherschutz	GERMANY
CVUA Rheinland	GERMANY
Bavarian Food Savety Agency	GERMANY
Chemisches Untersuchungsamt der Stadt Hagen	GERMANY
Arpa Puglia	ITALY
Istituto G. Caporale	ITALY
ASL Milano	ITALY
State Veterinary and Food Institution	SLOVAKIA
Leicestershire & Staffordshire Scientific Services	UNITED KINGDOM
Minton Treharne & Davies Ltd	UNITED KINGDOM

All the 24 registered OCLs reported results, however for one participant they were not rated due to analytical problems reported by the participant.

5 Time frame

The ILC was agreed with the NRLs at the EU-RL PAH workshop in Brussels on the 6th of April 2011. It was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on the 18th of August 2011 (see ANNEX 2). Test samples were dispatched (see ANNEX 3) on the 4th of October 2011 and the deadline for reporting of results was set to the 11th of November 2011.
The documents sent to the participants are presented in ANNEX 4.

6 Confidentiality

The identities of participants are kept confidential unless the participant provides a letter of consent to the PT organiser giving permission to disclose his/her details and results to a third party.

7 Test materials

7.1 Preparation

The test materials of this PT round was olive oil spiked with 15+1 EU priority PAHs, in the following denoted as OIL. This matrix is mimicking the food category 6.1.1 "Fats and oils" specified in Commission Regulation (EC) No 1881/2006, with a maximum level for BAP and for the sum of the four PAHs (in the following indicated as SUM) of 2.0 µg/kg and 10.0 µg/kg respectively.

Participants also received a solution of the 15+1 EU Priority PAHs in either acetonitrile or toluene (according to their choice, see ANNEX 3) with disclosed concentrations, which allowed them to check their instrument calibration against an independent reference. Participants received the technical specifications (see ANNEX 5) of the chosen solution together with the test material.

The test material was prepared at the EU-RL PAH laboratories from four litres of olive oil, checked for absence of PAHs prior to the test material preparation. It was spiked with a PAH standard solution containing besides the four EU marker PAHs also other PAHs. The standard solution was prepared from neat certified reference materials (purchased from BCR®, Institute for Reference Materials and Measurements, Geel, Belgium, except CPP - purchased from Biochemisches Institut für Umweltkarzinogene, Großhansdorf, Germany, BCL - purchased from Dr. Ehrenstorfer, Germany, and DIP - purchased from Campro Scientific, Germany). Single standard stock solutions of each analyte were produced by substitution weighing of neat substance on a microbalance and dissolution in toluene. These standard stock solutions were mixed and diluted further gravimetrically with toluene to obtain the solution used for spiking the olive oil. After spiking, the test sample was homogenised over night by intensive stirring. Portions of about 20 g spiked olive oil test material were sealed under inert atmosphere in 25 ml amber glass ampoules.

7.2 Homogeneity and stability

Homogeneity of the olive oil test sample was evaluated according to ISO Standard 13528. Ten ampoules of the olive oil test material were selected randomly and analysed by online-donor acceptor complex chromatography high performance liquid chromatography with fluorescence detection. The test material was rated sufficiently homogeneous (see ANNEX 6).

The stability of the test materials was evaluated by analysing the test material after the deadline for reporting of results by online-donor acceptor complex chromatography high performance liquid chromatography with fluorescence detection. Significant differences of the analyte contents between the analysis results and the preparation concentrations were not found. Hence stability of the samples over the whole study period can be assumed.

7.3 Assigned value and standard deviation for proficiency assessment

The gravimetrical preparation concentrations, corrected for the purity of the reference materials were applied as assigned values for the proficiency assessment. The assigned values of the target PAHs are listed in **Table 4.**
The uncertainties of the assigned values were calculated taking into account the purity of the reference materials used and the weighing operation carried-out.

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 [9]. 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 SUM parameter from the σ_P - values of the individual analytes applying the law of error propagation.

Equation 1 $$U_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2}$$

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.

Table 4: Analyte contents of the olive oil test material

		Assigned value#	U	σ_P	
Analyte	**Analyte short name**	**µg/kg**	**µg/kg**	**µg/kg**	**%**
Benz[*a*]anthracene	BAA	2.79	0.02	0.58	20.7
Benzo[*a*]pyrene	BAP	2.27	0.03	0.48	21.1
Benzo[*b*]fluoranthene	BBF	5.32	0.05	1.07	20.2
Chrysene	CHR	2.77	0.03	0.57	20.7
Sum of the four marker PAHs	SUM	13.15	0.07	1.43	10.9

gravimetrical preparation concentration of the material for the individual analytes, respectively sum of the individual concentrations for the SUM parameter
σ_p standard deviation for proficiency assessment.
U expanded uncertainty of the assigned value (k=2). For the individual analytes 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 the test material; for the SUM is equal to the combined standard uncertainty of the four analytes.

8 Design of the proficiency test

The design of the PT foresaw triplicate analyses of the test sample and reporting of the individual results of replicate analyses for the single analytes, in the following denoted as OIL_REP. Additionally a "value for proficiency assessment", in the following denoted as "final value - OIL_FIN", was requested for both the single analytes and the sum of the four PAHs. Both OIL_REP results and OIL_FIN results had to be reported corrected for recovery (and recovery had to be stated in the questionnaire together with other parameters of the method applied); OIL_FIN results had also to be accompanied by the respective expanded measurement

uncertainty (with a coverage factor of 2). The OIL_FIN results were the values used for performance assessment.
Participants were asked to report besides analysis results also details of the applied analysis method (see ANNEX 7).
Each participant received at least one ampoule of a solution of the target PAHs in the chosen solvent (2 ml), with disclosed content, and at least one ampoule of OIL (20 ml).

9 Evaluation of Laboratories

9.1 General

The results reported by participants are listed in ANNEX 8. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed (see the Outline in ANNEX 4).

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the olive oil test material, which was expressed by z-scores and zeta-scores.
The compliance with legislation of method performance characteristics for the determination of the four marker PAHs was evaluated as well.

9.2 Evaluation criteria

z-Scores

z-scores were calculated based on the OIL_FIN values. Equation 2 presents the formula for calculation of z-scores.

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

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

zeta-Scores

In addition to z-scores, zeta-scores were calculated. In contrast to z-scores, zeta-scores describe the agreement of the reported result with the assigned value within the respective uncertainties. zeta-Scores were calculated according to Equation 3.

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

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

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

calculated.
Unsatisfactorily large zeta-scores might be caused by underestimated measurement uncertainties, large bias, or a combination of both. On the contrary, satisfactory zeta scores might be obtained even with high bias if the uncertainty is sufficiently high. However, legislation specifies maximum tolerable standard uncertainties. Uncertainties exceeding them are not considered fit-for-purpose. Therefore, the uncertainties reported by the participants for the four PAHs were checked whether they comply with the thresholds provided by the "fitness-for-purpose" function. The results reported by the participants and the maximum tolerated LOD of 0.3 µg/kg were applied for the calculation of respective threshold values. For the SUM parameter the agreement between reported standard measurement uncertainties and the combined standard uncertainty of the four EU marker PAHs was evaluated. The latter was derived via the law of error propagation from the uncertainties reported for the individual analytes. Non-compliant reported uncertainties are highlighted in Table 7 and Table 8.

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

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

9.3 Evaluation of results

The participants were requested to report for the four analytes the results of replicate measurements and a "value for proficiency assessment" (OIL_FIN), which is the result they wish to be applied for the calculation of performance indicators. z-Scores and zeta-scores were attributed only to these results. The individual results of replicate analyses were not rated.

Each laboratory had to report a total of 17 results (12 results for replicate measurements plus 5 values for proficiency assessment), therefore the expected number of results of registered participants was 833. The 48 participants in the study reported in total 804 results, which equals to about 97 %.
The results of participant M637 were not rated due to analytical problems reported by the participant. About 96 % and about 88% of the results reported from NRLs and OCLs respectively obtained a satisfactory z-score.

In Figures 1 and 2 overviews of the z-scores assigned to the results are given for NRLs and OCLs respectively. The larger the triangles, the larger were the differences to the assigned values. Red triangles indicate z-scores above an absolute value of three, whereas yellow triangles represent z-scores in the questionable performance range. For questionable and unsatisfactory scores, the corresponding score values are presented next to the triangles. All of the three non-satisfactory results of NRLs were reported by two participants; whereas in the case of OCLs all nine non-satisfactory results were reported by three laboratories only, e.g. the performance of participant D023 was not satisfactory for all target analytes.

The numerical values of the calculated z-scores are compiled in **Tables 5 and 6** for NRLs and OCLs respectively. z-Scores with an absolute value of above 2 are given in bold, red font.

Tables 7 and 8 present the respective zeta-scores. As for the z-scores, data outside the

satisfactory performance range are given in bold, red font. The assessment of the performance of the participants based on the reported measurement uncertainty gave a less favourable picture. Only 78% and 79% respectively (for NRLs and OCLs) of the zeta-scores calculated for the four individual analytes and the SUM are within the range given by |zeta| ≤ 2. It has to be noted that the magnitude of the zeta-scores were for many participants much higher than the z-scores attributed to the same results. Consequently the laboratories perform according to internationally agreed standards, which form the basis for the z-scores, but seem to have partially difficulties in deducing realistic measurement uncertainty values. The establishment of proper measurement uncertainty values caused problems especially for the SUM parameter. The majority of participants reported for this parameter measurement uncertainty values different from the value which is derived by the law of error propagation.
Hence the EU-RL PAHs will continue to pay in the ILCs to come special attention to this parameter, as it has major implications on the assessment of compliance of food with European legislation.

The graphical representations of the distribution of results for the individual analytes are given in ANNEX 8 together with the results of replicate analyses.
For each analyte the figure shows the individual analysis results of the three replicate determinations. The assigned value is shown as green dotted line. The blue boxes represent the expanded uncertainties reported by participants for the "value for proficiency assessment". The arithmetic mean of the results of the individual participant is indicated in the blue boxes by a blue line. The red dotted lines represent deviations from the assigned value of ± 2 σ_p.

Figure 1: Graphical presentation of z-scores corresponding to the "values for proficiency assessment" reported by the **NRLs** for the contents of BAA, BAP, BBF, CHR, and the SUM parameter in the spiked olive oil test material.
Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented above the triangles for the last two performance categories.

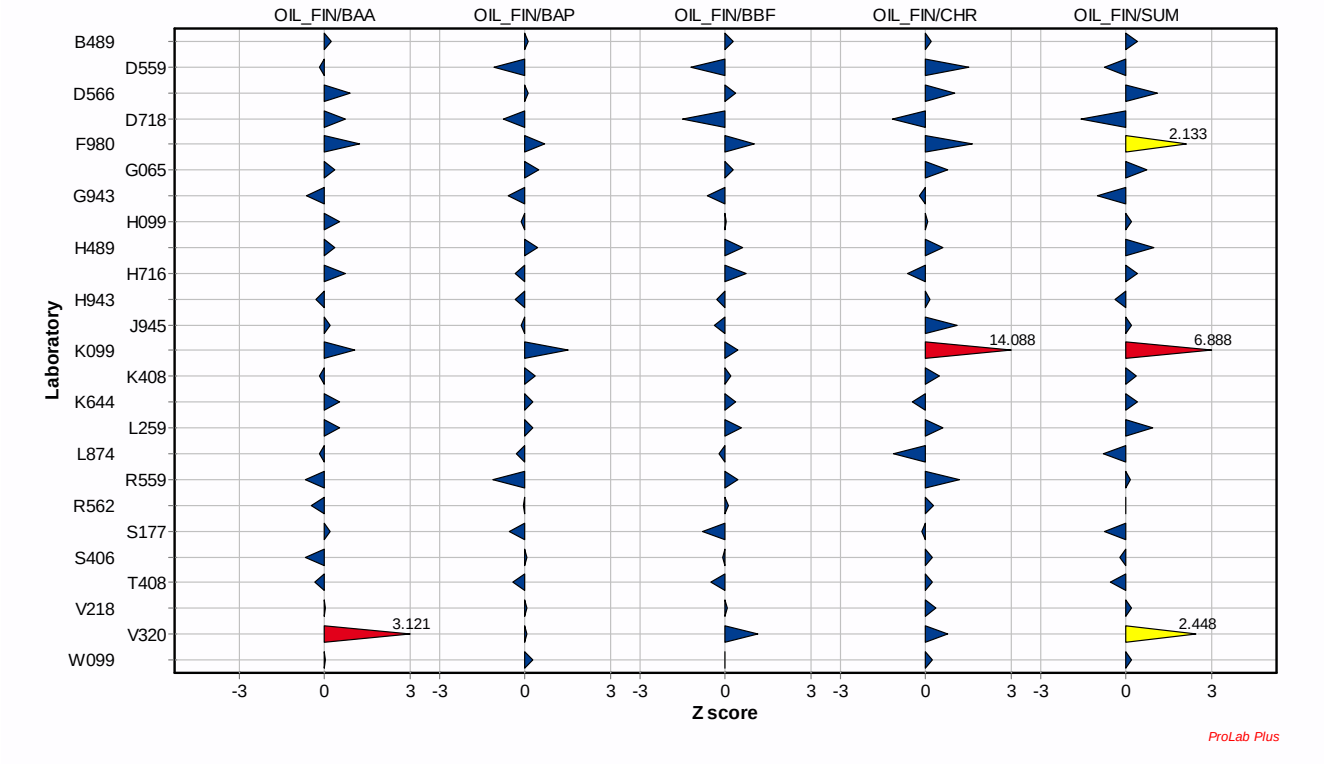


Figure 2: Graphical presentation of z-scores corresponding to the "values for proficiency assessment" reported by the **OCLs** for the contents of BAA, BAP, BBF, CHR, and the SUM in the spiked olive oil test material.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented above the triangles for the latter performance category.

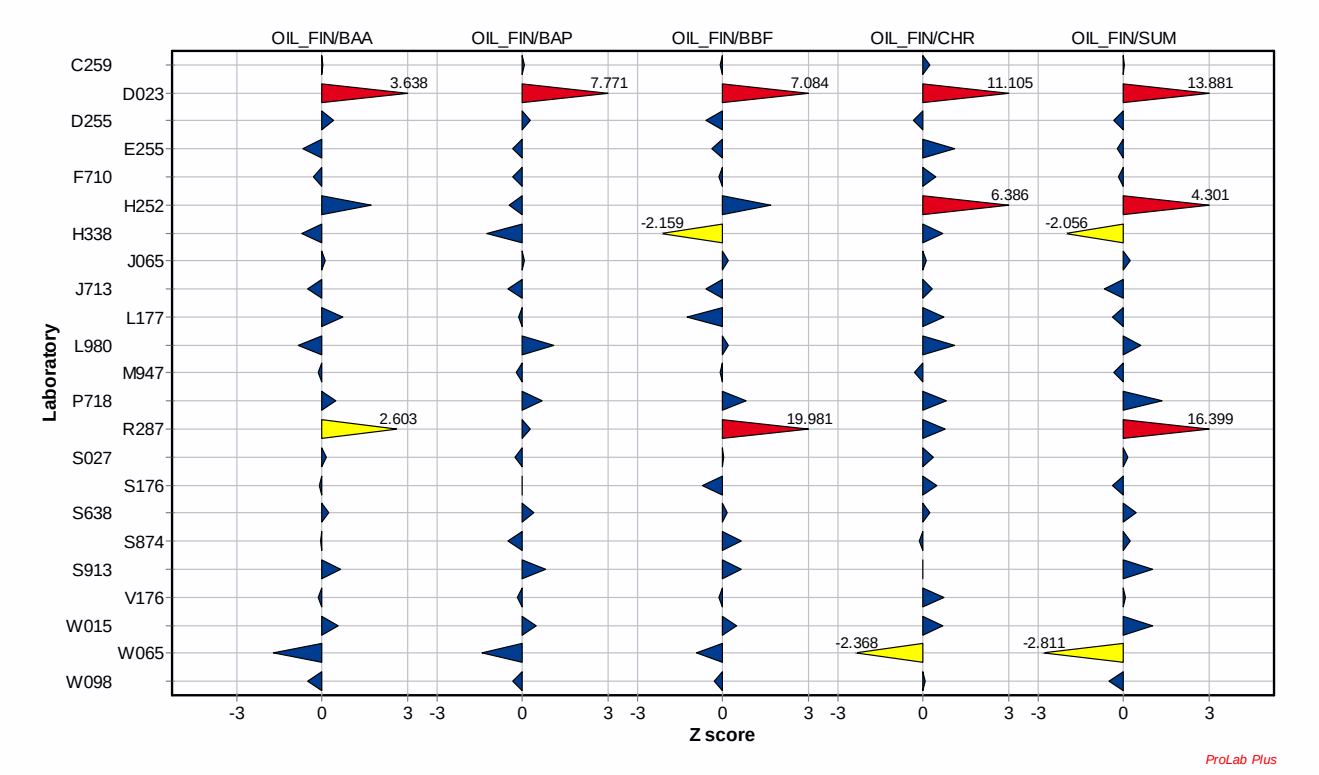


Table 5: Compilation of **z-scores calculated from the "results for proficiency assessment" reported by the NRLs** for test material OIL: z-scores outside the satisfactory range (|z| > 2) are indicated by red font.

		BAA		BAP		BBF		CHR		SUM	
Assigned value	µg/kg	2.79		2.27		5.32		2.77		13.15	
σ_P	µg/kg	0.58		0.48		1.07		0.57		1.43	
		Result	z-score	Result	z-score	Result	z-score	Result	z-score	Result	z-score
Lcode		µg/kg		µg/kg		µg/kg		µg/kg		µg/kg	
B489		2.91	0.21	2.31	0.08	5.62	0.28	2.87	0.18	13.71	0.39
D559		2.68	-0.19	1.75	-1.08	4.02	-1.21	3.63	1.51	12.08	-0.75
D566		3.30	0.88	2.31	0.08	5.70	0.36	3.35	1.02	14.7	1.08
D718		3.20	0.71	1.9	-0.77	3.7	-1.51	2.1	-1.18	10.9	-1.57
F980		3.50	1.22	2.6	0.69	6.4	1.01	3.7	1.63	16.2	**2.13**
G065		3.00	0.36	2.5	0.48	5.6	0.26	3.2	0.75	14.2	0.73
G943		2.42	-0.64	1.99	-0.58	4.64	-0.64	2.65	-0.21	11.69	-1.02
H099		3.08	0.50	2.196	-0.15	5.325	0.00	2.803	0.06	13.404	0.18
H489		2.99	0.34	2.47	0.42	5.97	0.61	3.1	0.58	14.53	0.97
H716		3.20	0.71	2.1	-0.35	6.1	0.73	2.4	-0.65	13.7	0.38
H943		2.62	-0.29	2.11	-0.33	5	-0.30	2.86	0.16	12.59	-0.39
J945		2.90	0.19	2.2	-0.15	4.9	-0.39	3.4	1.11	13.4	0.17
K099		3.40	1.05	3	1.52	5.8	0.45	10.8	**14.09**	23	**6.89**
K408		2.68	-0.19	2.44	0.35	5.5	0.17	3.05	0.49	13.67	0.36
K644		3.10	0.53	2.4	0.27	5.7	0.36	2.5	-0.47	13.7	0.38
L259		3.10	0.53	2.4	0.27	5.9	0.54	3.1	0.58	14.5	0.94
L874		2.68	-0.19	2.12	-0.31	5.09	-0.21	2.12	-1.14	12.01	-0.80
R559		2.40	-0.67	1.72	-1.15	5.78	0.43	3.43	1.16	13.33	0.13
R562		2.51	-0.48	2.25	-0.04	5.44	0.11	2.92	0.26	13.11	-0.03
S177		2.89	0.17	2	-0.56	4.47	-0.79	2.69	-0.14	12.05	-0.77
S406		2.40	-0.67	2.3	0.06	5.2	-0.11	2.9	0.23	12.8	-0.24
T408		2.58	-0.36	2.06	-0.44	4.78	-0.50	2.91	0.25	12.33	-0.57
V218		2.81	0.03	2.29	0.04	5.37	0.05	2.96	0.33	13.43	0.20
V320		4.60	**3.12**	2.3	0.06	6.55	1.15	3.21	0.77	16.65	**2.45**
W099		2.80	0.02	2.4	0.27	5.3	-0.02	2.9	0.23	13.4	0.17

Table 6: Compilation of **z-scores calculated from the "results for proficiency assessment" reported by the OCLs** for test material OIL: z-scores outside the satisfactory range (|z| > 2) are indicated by red font.

		BAA		BAP		BBF		CHR		SUM	
Assigned value	µg/kg	2.79		2.27		5.32		2.77		13.15	
σ_P	µg/kg	0.58		0.48		1.07		0.57		1.43	
		Result	z-score	Result	z-score	Result	z-score	Result	z-score	Result	z-score
Lcode		µg/kg		µg/kg		µg/kg		µg/kg		µg/kg	
C259		2.80	0.02	2.3	0.06	5.2	-0.11	2.9	0.23	13.2	0.03
D023		4.90	**3.64**	6	**7.77**	12.9	**7.08**	9.1	**11.11**	33	**13.88**
D255		3.01	0.38	2.39	0.25	4.69	-0.59	2.58	-0.33	12.67	-0.34
E255		2.40	-0.67	2.1	-0.35	4.9	-0.39	3.4	1.11	12.8	-0.24
F710		2.62	-0.29	2.1	-0.35	5.16	-0.15	3.01	0.42	12.89	-0.18
H252		3.78	1.71	2.05	-0.46	7.1	1.66	6.41	**6.39**	19.3	**4.30**
H338		2.38	-0.71	1.67	-1.25	3.01	**-2.16**	3.15	0.67	10.21	**-2.06**
J065		2.85	0.10	2.3	0.06	5.51	0.18	2.82	0.09	13.48	0.23
J713		2.50	-0.50	2.02	-0.52	4.7	-0.58	2.94	0.30	12.15	-0.70
L177		3.21	0.72	2.21	-0.13	3.97	-1.26	3.19	0.74	12.58	-0.40
L980		2.30	-0.84	2.8	1.10	5.5	0.17	3.4	1.11	14	0.59
M947		2.71	-0.14	2.16	-0.23	5.19	-0.12	2.59	-0.32	12.64	-0.36
P718		3.07	0.48	2.59	0.67	6.19	0.81	3.22	0.79	15.07	1.34
R287		4.30	**2.60**	2.4	0.27	26.7	**19.98**	3.2	0.75	36.6	**16.40**
S027		2.88	0.15	2.137	-0.28	5.353	0.03	2.968	0.35	13.335	0.13
S176		2.72	-0.12	2.26	-0.02	4.57	-0.70	3.03	0.46	12.6	-0.38
S638		2.91	0.21	2.45	0.38	5.48	0.15	2.91	0.25	13.75	0.42
S874		2.75	-0.07	2.03	-0.50	5.99	0.63	2.68	-0.16	13.46	0.22
S913		3.17	0.66	2.65	0.79	6	0.64	2.76	-0.02	14.58	1.00
V176		2.71	-0.14	2.19	-0.17	5.16	-0.15	3.17	0.70	13.23	0.06
W015		3.12	0.58	2.5	0.48	5.836	0.48	3.157	0.68	14.617	1.03
W065		1.79	-1.72	1.59	-1.42	4.33	-0.93	1.42	**-2.37**	9.13	**-2.81**
W098		2.50	-0.50	2.1	-0.35	5	-0.30	2.8	0.05	12.4	-0.52

Table 7: Compilation of **zeta-scores calculated from the "results for proficiency assessment" reported by the NRLs** for test material OIL, the combined reported standard measurement uncertainty, and the uncertainty of the analyte content of the test material:
zeta-Scores outside the satisfactory range (|zeta| > 2) are indicated by bold red font. Yellow highlighted cells indicate measurement uncertainty values that either did not comply with the thresholds given by the "fitness-for-purpose" function (BAA, BAP, BBF, and CHR), or were not in agreement with the uncertainty value derived from the uncertainties of the individual analytes (SUM parameter).

		BAA			BAP			BBF			CHR			SUM		
Assigned value	µg/kg	2.79			2.27			5.32			2.77			13.15		
σ_p	µg/kg	0.58			0.48			1.07			0.57			1.43		
		Result	u	zeta-score	Result	u	zeta-score	Result	u	zeta-score	Result	u	zeta-score	Result	u	zeta-score
Lcode		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg	
B489		2.91	0.07	1.70	2.31	0.03	1.19	5.62	0.07	**4.04**	2.87	0.11	0.90	13.71	0.67	0.83
D559		2.68	0.27	-0.41	1.75	0.175	**-2.96**	4.02	0.4	**-3.24**	3.63	0.365	**2.35**	12.08	1.205	-0.89
D566		3.30	n.r.		2.31	n.r.		5.70	n.r.		3.35	n.r.		14.7	n.r.	
D718		3.2	0.2	**2.05**	1.9	0.15	**-2.45**	3.7	0.25	**-6.45**	2.1	0.2	**-3.34**	10.9	0.85	**-2.64**
F980		3.5	0.35	**2.03**	2.6	0.25	1.32	6.4	0.6	1.80	3.7	0.35	**2.65**	16.2	1.6	1.91
G065		3	0.25	0.84	2.5	0.25	0.92	5.6	0.85	0.33	3.2	0.2	**2.14**	14.2	1.55	1.11
G943		2.42	0.135	**-2.73**	1.99	0.11	**-2.52**	4.64	0.23	**-2.94**	2.65	0.17	-0.70	11.69	0.875	-1.67
H099		3.08	0.5175	0.56	2.196	0.305	-0.24	5.325	0.687	0.01	2.803	0.388	0.08	13.404	1.898	0.26
H489		2.99	0.235	0.85	2.47	0.25	0.80	5.97	0.51	1.27	3.1	0.25	1.32	14.53	1.255	1.10
H716		3.2	0.6	0.68	2.1	0.2	-0.85	6.1	1.1	0.71	2.4	0.8	-0.74	13.7	1.5	0.37
H943		2.62	0.385	-0.44	2.11	0.325	-0.49	5	0.985	-0.32	2.86	0.26	0.35	12.59	3.8	-0.49
J945		2.9	0.55	0.20	2.2	0.15	-0.46	4.9	0.3	-1.40	3.4	0.1	**6.23**	13.4	0.8	0.31
K099		3.4	0.55	1.11	3	0.05	**13.98**	5.8	0.15	**3.16**	10.8	2.95	**3.71**	23	3	**3.28**
K408		2.68	0.295	-0.37	2.44	0.245	0.69	5.5	0.55	0.33	3.05	0.335	0.83	13.67	2.87	0.69
K644		3.1	0.4	0.77	2.4	0.25	0.52	5.7	0.5	0.76	2.5	0.4	-0.67	13.7	0.8	0.69
L259		3.1	0.3	1.03	2.4	0.25	0.52	5.9	0.6	0.97	3.1	0.3	1.10	14.5	0.8	1.69
L874		2.68	0.23	-0.48	2.12	0.16	-0.93	5.09	0.355	-0.65	2.12	0.17	**-3.81**	12.01	0.915	-1.24
R559		2.4	0.175	**-2.22**	1.72	0.095	**-5.72**	5.78	0.13	**3.47**	3.43	0.56	1.18	13.33	0.49	0.37
R562		2.51	0.325	-0.86	2.25	0.385	-0.05	5.44	0.815	0.15	2.92	0.32	0.47	13.11	1.835	-0.04
S177		2.89	0.175	0.57	2	0.175	-1.54	4.47	0.37	**-2.29**	2.69	0.185	-0.43	12.05	1.815	-2.28
S406		2.4	0.24	-1.62	2.3	0.23	0.13	5.2	0.52	-0.23	2.9	0.29	0.45	12.8	0.68	-0.51
T408		2.58	0.175	-1.20	2.06	0.15	-1.39	4.78	0.375	-1.44	2.91	0.225	0.62	12.33	0.495	-1.65
V218		2.81	0.315	0.06	2.29	0.215	0.09	5.37	0.445	0.11	2.96	0.405	0.47	13.43	1.35	0.21
V320		4.6	0.345	**5.24**	2.3	0.115	0.26	6.55	0.82	1.50	3.21	0.32	1.37	16.65	2.08	3.67
W099		2.8	0.2	0.05	2.4	0.1	1.29	5.3	0.4	-0.05	2.9	0.2	0.65	13.4	0.5	0.50

n.r.: not reported

Table 8: Compilation of **zeta-scores calculated from the "results for proficiency assessment" reported by the OCL**s for test material OIL, the combined reported standard measurement uncertainty, and the uncertainty of the analyte content of the test material:
zeta-Scores outside the satisfactory range (|zeta| > 2) are indicated by bold red font. Yellow highlighted cells indicate measurement uncertainty values that either did not comply with the thresholds given by the "fitness-for-purpose" function (BAA, BAP, BBF, and CHR), or were not in agreement with the uncertainty value derived from the uncertainties of the individual analytes (SUM parameter).

		BAA			BAP			BBF			CHR			SUM		
Assigned value	µg/kg	2.79			2.27			5.32			2.77			13.15		
σ_P	µg/kg	0.58			0.48			1.07			0.57			1.43		
		Result	u	zeta-score	Result	u	zeta-score	Result	u	zeta-score	Result	u	zeta-score	Result	u	zeta-score
Lcode		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg	
C259		2.8	0.3	0.03	2.3	0.25	0.12	5.2	0.5	-0.24	2.9	0.3	0.43	13.2	2.65	0.07
D023		4.9	1.05	**2.13**	6	1.3	**3.08**	12.9	2.85	**2.93**	9.1	2	**3.47**	33	7	**5.14**
D255		3.01	0.14	1.53	2.39	0.12	1.02	4.69	0.23	**-2.69**	2.58	0.14	-1.36	12.67	0.63	-0.76
E255		2.4	0.24	-1.62	2.1	0.16	-1.07	4.9	0.37	-1.14	3.4	0.34	1.85	12.8	1.28	-0.27
F710		2.62	n.r.		2.1	n.r.		5.16	n.r.		3.01	n.r.		12.89	n.r.	
H252		3.78	0.88	1.28	2.05	0.61	-0.50	7.1	1.49	1.25	6.41	1.36	**2.82**	19.3	2.28	**2.69**
H338		2.38	n.r.		1.67	n.r.		3.01	n.r.		3.15	n.r.		10.21	n.r.	
J065		2.85	0.285	0.21	2.3	0.23	0.13	5.51	0.55	0.35	2.82	0.28	0.18	13.48	2.696	0.12
J713		2.5	0.25	-1.16	2.02	0.2	-1.25	4.7	0.47	-1.32	2.94	0.295	0.58	12.15	1.215	-0.82
L177		3.21	0.45	0.93	2.21	0.2	-0.30	3.97	0.3	**-4.48**	3.19	0.45	0.93	12.58	1.25	-0.46
L980		2.3	n.r.		2.8	n.r.		5.5	n.r.		3.4	n.r.		14	n.r.	
M947		2.71	0.155	-0.52	2.16	0.155	-0.71	5.19	0.235	-0.55	2.59	0.29	-0.62	12.64	0.815	-0.63
P718		3.07	0.75	0.44	2.59	0.65	0.59	6.19	1.55	0.70	3.22	0.8	0.68	15.07	3.75	0.96
R287		4.3	0.75	**2.01**	2.4	0.4	0.32	26.7	4.65	**4.60**	3.2	0.55	0.78	36.6	6.4	**4.93**
S027		2.877	0.387	0.22	2.137	0.204	-0.65	5.353	0.586	0.06	2.968	0.358	0.55	13.335	3.094	0.23
S176		2.72	0.273	-0.26	2.26	0.2275	-0.04	4.57	0.458	-1.64	3.03	0.304	0.85	12.6	0.655	-0.84
S638		2.91	0.305	0.39	2.45	0.245	0.73	5.48	0.575	0.28	2.91	0.29	0.48	13.75	0.75	0.80
S874		2.75	n.r.		2.03	n.r.		5.99	n.r.		2.68	n.r.		13.46	n.r.	
S913		3.17	0.08	**4.71**	2.65	0.086	**4.35**	6	0.074	**8.71**	2.76	0.099	-0.10	14.58	0.339	**4.20**
V176		2.71	0.3	-0.27	2.19	0.25	-0.32	5.16	0.55	-0.29	3.17	0.3	1.33	13.23	0.74	0.11
W015		3.124	0.312	1.07	2.500	0.250	0.92	5.836	0.584	0.88	3.157	0.316	1.22	14.617	1.462	1.00
W065		1.79	0.09	**-11.04**	1.59	0.175	**-3.87**	4.33	1.47	-1.13	1.42	0.255	**-5.28**	9.13	0.5	**-8.02**
W098		2.5	0.3	-0.97	2.1	0.15	-1.13	5	0.55	-0.58	2.8	0.25	0.12	12.4	2.45	-1.08

n.r.: not reported

The figures in ANNEX 9 are an aid to allow laboratories to compare the performance of their method to those of other participants with respect to bias (closeness to the assigned value, plotted on the x-axis) and precision (the standard deviation for repeatability, plotted on the y-axis). A vertical solid green line depicts the assigned value; laboratories are represented by blue dots (mean value of the replicates and the associated standard deviation of the replicates). The light blue area indicates the satisfactory performance area, which is defined by the assigned value $\pm 2\sigma_P$ along the x-axis and by the average repeatability standard deviation of the results reported by the participants along the y-axis. The latter was obtained by analysis-of-variance of the data set received for each analyte.

Participants whose data are outside the satisfactory performance area should perform root cause analysis. It would be very much appreciated if they would report back to the EU-RL PAH the identified reason for the deviations.

8.6 Evaluation of compliance with legislation

The characteristics of the methods applied by participants and the results reported are listed in ANNEX 7 and 8 respectively.
Compliance with legislation was evaluated on basis of requirements set in Regulation (EC) No 333/2007 as amended by Regulation (EU) No 836/2011 [vii]. Non compliant values for LOD, LOQ, and recovery are indicated by bold red font.
Some laboratories reported lower limits of the working range of their analysis method which would prohibit the determination of the respective analyte at levels suitable for the implementation of legislation. These values are marked by bold red font as well.
The compliance of reported measurement uncertainties with provisions given in legislation was discussed before.

In general the number of non compliances was higher for OCLs than for NRLs.
This could be considered a positive outcome of the discussions during the EU-RL workshops.
NRLs are therefore encouraged to create awareness for these issues among the OCLs.

10 Follow-up actions for underperforming laboratories

All laboratories that got "questionable" or "non-satisfactory" performance ratings are urged to perform root cause analysis, and to implement corrective actions.
The NRLs not reporting were already contacted for explanation.
The EU-RL 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 (EU-RLs) activities. These laboratories shall perform as an immediate action root-cause-analysis, and shall report to the EU-RL PAH in writing the identified cause for their underperformance and corrective actions they are going to take. Additionally, they shall participate to an independent (non-EU-RL) proficiency test on the determination of PAHs in food and shall communicate the outcome of this exercise to the EU-RL PAH.

11 Conclusions

Forty-eight participants reported analysis results. One participant was excluded from the data evaluation due to reported analytical problems. The performance of most participants was good. In total 96 % and 88% of the results reported by NRLs and OCLs respectively obtained a satisfactory z-score. However significant bias can be concluded from the pattern of performance indicators of some laboratories.
zeta-Scores were calculated besides z-scores. They indicate the agreement of the reported result with the assigned value with respect to the stated measurement uncertainty. The outcome of this rating was worse than for the z-scores, which reveals that the measurement uncertainty estimates were in some cases not realistic.
The great majority of participants in this inter-laboratory comparison applied analytical methods which, with regard to performance characteristics, were compliant with EU legislation; however, some participants are encouraged to verify the compliance to legislation of both the method and the modality of data reporting in use at their laboratory.

12 Acknowledgements

The organisers would like to thank Beatriz de la Calle and Franz Ulberth (all from IRMM, Geel, Belgium) for their accurate revision of this report and all NRLs and OCLs for their cooperation.

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14 ANNEXES

ANNEX 1 – Announcement of the PT on the IRMM webpage

ANNEX 2 – Announcement via e-mail and invitation

ANNEX 3 – Announcement of material dispatch

ANNEX 4 – Documents sent to participants

ANNEX 5 – Technical specifications of the calibration solutions

ANNEX 6 – Homogeneity of the test material

ANNEX 7 – Questionnaire

ANNEX 8 – Data reported by participants

ANNEX 9 - Laboratory means and repeatability standard deviation

ANNEX 1: Announcement of the PT on the IRMM webpage

4 marker PAHs in edible oil

Proficiency Test on the Determination of 4 marker PAHs in edible oil

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

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 edible oil in view of forthcoming legislative updates on maximum levels of PAHs in food.

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

Participation is admitted to maximum 80 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 250** (two hundred fifty) per registration for OCLs, which do not have NRL status.

Test material and analytes

The test material is a commercial olive oil containing the target analytes (see Table 1). Participants will receive one amber glass ampoule containing about 20 g of the spiked olive oil. In addition, participants will get an ampoule with a solution of PAHs with disclosed analyte content, in, depending on their preference, either acetonitrile or toluene. This solution will be supplied to allow the participants verifying their instrument calibration against an independent standard.

Table 1: The target analytes of the comparison

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

General outline

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

Participants will also be asked to report a single value for scoring, the "finalvalue", 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 olive oil 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)No333/2007, assuming a value of 0.3 µg/kg for the limit of detection.
- For their sum, the target standard deviations will be obtained from the truncated Horwitz equation (σ = 22 % C, where C is the assigned value)

Registration

Registration shall be done via this link

Schedule

Registration deadline	Sample dispatch	Reporting of results	Report
16 September 2011	second half of September2011	6 weeks from sample dispatch	January 2012

Contacts

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

Latest update 30 August, 2011

ANNEX 2: Announcement of the PT via e-mail and invitation

From: LERDA Donata (JRC-GEEL) on behalf of JRC IRMM CRL PAH
Sent: 18 August 2011 10:42
To: *All NRLs*'
Cc: *Concerned IRMM staff*
Subject: Opening of registration for the second EU-RL PAHs 2011 proficiency test
Importance: High
Attachments: EU-RL PAHs PT oil 2011_Announcement of registration opening.pdf

Dear Madame / Sir,

The European Union Reference Laboratory for PAHs would like to inform you that the registration for the second 2011 proficiency test (PT) on PAHs will be open **from 22/08/2011 to midnight of 16/09/2011**.

The link for registration, reported also in the attached document, is
https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=760

Please note that the fields marked with a * are mandatory.
After confirmation you must provide us with a signed and stamped copy of the Registration Form, either by FAX or by e-mail as a PDF file (mail address: jrc-irmm-crl-pah@ec.europa.eu).

After the registration, you will be contacted for the selection of the solvent for the standard solution.

Dispatch of the samples will take place in the second half of September and you will receive an announcement of dispatch a few days before it will take place.
A detailed outline of the study will be included in the parcel of PT samples.

Results are expected to be reported within 6 weeks after dispatch. Please note that no extension of the deadline will be granted (the interface for reporting will be closed).
The link for reporting will be sent to you upon dispatch of the PT samples together with the **exact deadline for reporting**.

Information on the PT will also be soon available on the EU-RL PAHs webpage at the link:
http://irmm.jrc.ec.europa.eu/EURLs/EURL_PAHs/interlaboratory_comparisons/Pages/index.aspx

Please read carefully the document attached and in case you should need any clarification, do not hesitate contacting us. In particular, please note that the PT will also be open to the official food control laboratories (OCLs) and their participation is possible upon presentation from the respective NRL.
The NRLs are kindly requested to distribute as soon as possible this information to the OCLs under their responsibility and to send to the EU-RL the lists of the OCLs to be involved in the study by end of 30/08 the latest.

Thank you for the co-operation and best regards,

Donata

Donata Lerda
Food Safety and Quality Unit
Institute for Reference Materials and Measurements
(EC – JRC – IRMM)
Postal address: Retieseweg 111, B-2440 Geel, Belgium

Phone: +32 14 571 826
Fax: +32 14 571 783
e-mail: donata.lerda@ec.europa.eu

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 17/08/2011

JRC/IRMM/DDG.D6/ARES (2011)884553

Ninth Interlaboratory comparison of the EU-RL for Polycyclic Aromatic Hydrocarbons (PAHs)

Dear Madame/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EU-RL PAH on the determination of the 4 marker PAHs in olive oil will be **open from 22 August to 16 September 2011**.
Participation is mandatory and free of charge for **National Reference Laboratories** (NRLs) for PAHs. Confidentiality of participants and respective results is granted.

In support to the NRLs, to facilitate fulfilling their tasks as included in Regulation (EC) No 882/2004, **EU Official Food Control Laboratories** (OCLs) falling under the responsibility of the NRLs may participate in the study. **The participation fee for official food control laboratories is 250 Euro per participation.**

The target analytes are listed in the following Table.

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

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

Each participant will be provided with one amber glass ampoule containing ~ 20 g of olive oil.
Participants will also receive a standard solution in either acetonitrile or toluene with disclosed content; which might be used for verification of instrument calibration.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. 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

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

Timing:

- Deadline for registration: 16 September 2011
- Dispatch of samples: second half of September 2011. 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: six weeks from dispatch of samples. You will receive the link for entering the results upon reception of the PT samples

Registration procedure:

Participants shall register via this link:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=760

In order to register, laboratories must:

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

PT coordinator	**Second contact**
Donata LERDA	Philippe VERLINDE
Fax: 0032-14-571783 e-mail: jrc-irmm-crl-pah@ec.europa.eu	

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

Distribution of information:

The NRLs are kindly requested to distribute as soon as possible this information to the OCLs under their responsibility, and to assist the EU-RL in identifying laboratories that are eligible to participate in the study, e.g. by sending to the EU-RL the list of the OCLs to be involved in the study.

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

Two options:

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

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

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

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

With kind regards,

Thomas Wenzl
(Operating Manager of the EU-RL PAHs)

Cc: Donata Lerda, Beatriz de la Calle, Franz Ulberth

ANNEX 3: Announcement of material dispatch

From: LERDA Donata (JRC-GEEL) on behalf of JRC IRMM CRL PAH
Sent: 20 September 2011 14:15
To: *All NRLs and registered OCLs*
Cc: *Concerned IRMM staff*
Subject: EU-RL 2011 PT on PAHs in oil: solvent preference

Dear Madame/Sir,

Your laboratory registered for participating in the **proficiency test (PT) on the determination of** polycyclic aromatic hydrocarbons **(PAHs) in olive oil**.

Together with the oil test sample, you will get one ampoule with a **solution of the target analytes in either toluene or acetonitrile,** which might be used for checking the instrument calibration.

Please select the solvent type (toluene or acetonitrile) that is most suitable for your application, and reply to this email by mentioning the chosen solvent type in the subject line.

Please submit this information to us by **26/09/2011.**

Dispatch of the PT test samples is scheduled for **week 40** at the latest.

However, you will be informed in due time about the exact date of the dispatch of the test samples.

With best regards,

Donata

Donata Lerda
Food Safety and Quality Unit
Institute for Reference Materials and Measurements
(EC – JRC – IRMM)
Postal address: Retieseweg 111, B-2440 Geel, Belgium

Phone: +32 14 571 826
Fax: +32 14 571 783
e-mail: donata.lerda@ec.europa.eu

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
EU reference laboratory for polycyclic aromatic hydrocarbons

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 30/09/2011
EU-RL PAHs/DLE (2011)

Shipment of materials for the EU-RL PT-2011 on PAHs in olive oil

«Title» «Firstname» «Surname»
«Organisation» - «Department»
«Address»
«Zip» - «Town»
«Country»
«LName»

Dear «Title» «Firstname» «Surname»,

We are planning to dispatch the materials for the next proficiency test on **3rd of October 2011** via DHL.

Please be prepared to receive the samples and to store them in an appropriate way (**20ºC** for the olive oil sample and **cool, 4ºC, and dark** for the solutions).

We will inform you about the details of the shipment, the analyses to be made, and deadline for reporting as soon as the items will have left our premises.

With best regards,

Donata Lerda

From: LERDA Donata (JRC-GEEL) on behalf of JRC IRMM CRL PAH
Sent: 30 September 2011 15:28
Cc: *Concerned IRMM staff*
Bcc: *All NRLs and registered OCLs*
Subject: Ares(2011)1033394 - 29/09/2011: Reporting of results for EU-RL PAHs PT 2011 on PAHs in oil
Attachments: ARES(2011)990123_Outline PT PAH in oil 2011.pdf; PT OIL 2011 - reporting instructions.pdf

DG.D.6./DL/vs/ARES (2011) 1033394

Dear Madam / Sir,

The materials for the proficiency test will be **dispatched** next week either on **Monday 03/10 or Tuesday 04/10**. Please do not forget to **send back to us the sample receipt** as soon as you receive the parcel and to store the **oil sample at room temperature** and the **standard solution at 4 ºC and in the dark**.

Starting from **06/10/2011 at 00:00 AM** you will be enabled to enter your results.

Please find herein below the link to the web interface for reporting of results for this PT round.

https://web.jrc.ec.europa.eu/ilcReportingWeb

When you get to the web interface, please enter the PASSWORD key (11 digits) you received in the PT parcel: this will allow you to enter your results and to answer the questionnaire.
Remember to **save each page** of the results and to **submit them only when you have finished** entering the results for all the samples.

Please follow the instructions included in the parcel and reported in the documents herein attached.

The deadline for reporting is the **11th of November 2011** (last day: it will not be any longer possible to have access to the reporting interface from midnight of the 11th of November).

For questions on reporting and other subjects concerning the PT, please do not hesitate to contact this e-mailbox.
I or my colleagues will be available for the whole period.

Thank you for your collaboration.

Best regards,

Donata

Donata Lerda
Food Safety and Quality Unit
Institute for Reference Materials and Measurements
(EC – JRC – IRMM)
Postal address: Retieseweg 111, B-2440 Geel, Belgium

Phone: +32 14 571 826
Fax: +32 14 571 783
e-mail: donata.lerda@ec.europa.eu

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

ANNEX 4: Documents sent to participants

OUTLINE

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
European Reference Laboratory for Polycyclic Aromatic Hydrocarbons (PAH)

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Ares(2011)990123

Geel, 16/09/2011

Outline of the 9th Inter-laboratory comparison study organised by the EU-RL-PAH:

EU-RL-PAHs-09: ***Analysis of the four marker PAHs in olive oil***

General description

The test material is olive oil. Target analytes are the four marker PAHs (listed in Table 1). Additionally laboratories have to report their sum.

The EU-RL PAHs will check for the four target analytes the compliance of the performed analyses with provisions given in Regulation (EU) No 836/2011.

Participating laboratories will be scored for each of the four PAHs, plus for their sum.

Table 1: The target analytes of the comparison (four marker PAHs)

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

The PT was announced on the IRMM webpage and in addition to NRLs and OCLs, reference laboratories of EU Candidate Countries will be supplied with samples upon request.

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

The content of the parcel

Each participant will be provided with a set of samples that comprises:

- One ampoule, labelled as "OIL-2011 - XXX", containing about 20 g of *spiked olive oil*: The concentration of the individual analytes is in the range from about 0 to 5 µg/kg. This sample **is the test sample of the PT**.
- One ampoule, labelled as "ACN-OIL-2011-K/XXX" or as "TOL-OIL-2011-K/XXX" depending on the solvent you chose, acetonitrile or toluene respectively, containing about 2 ml of a solution of the *four marker PAHs in solvent (acetonitrile or toluene)*. The concentration of the individual analytes is reported in the respective specification sheet and is therefore **known to participants**. Please bear in mind that these solutions *do not contain any internal standards*.

Olive oil samples are to be stored at room temperature and solutions at 4°C in the dark

Participants will also receive:

- the a sample receipt form (to be filled in and sent back to the EU-RL as soon as possible)
- the outline of the study (a printout of this document)
- the participation (password) key (to be used for all following communication concerning this PT)
- specification sheets for the solutions of known content
- material safety data sheets for some of the analytes and for the solvents

Outline of the study

1. The laboratories are requested to perform **three (3) replicate analyses on the contaminated olive oil material.** The sample shall be analysed immediately after opening of the ampoule, and the three replicates should be analysed under repeatability condition. A **"final value", which is the value applied for scoring,** is also required for each analyte beside the results obtained from replicate analysis. In addition, participants are asked to report a value for the sum of the four target PAHs.

2. The **known solution of PAHs in solvent** may be used by participants as an external reference to check their instrument calibration.

For all samples the participating laboratories shall apply a method of their choice, taking into account that other PAHs than the four marker PAHs could be present.

The laboratories shall report the results by **11th November 2011 at the latest** via the ILC web interface using the participation (password) key they received after registration together with the hyperlink for reporting.

Scoring system

The assigned values will be obtained from the gravimetrical preparation of the materials. They will be verified by chemical analysis.

The target standard deviations will be set:

- for the four individual PAHs as equal to the value derived from the uncertainty function (Uf) according to Commission Regulation (EU) No 836/2011.
- for the sum of the four marker PAHs as equal to the combined standard uncertainty derived from the Uf of the four individual marker PAHs, according to the equation below:
- $$Uf(SUM) = \sqrt{U_f{}^2(BaA) + U_f{}^2(BaP) + U_f{}^2(BbF) + U_f{}^2(CHR)}$$

z-scores and zeta(ζ)-scores will be assigned for the marker PAHs (**BaA**, **BaP**, **BbF**, and **CHR**) (see Table 1 for full names) and their sum on the base of the reported final value. For these five measurands a non reported final value (an empty cell in the reporting system) will be considered as underperformance. In case the content was found to be below the LOD, the scoring will be calculated upon the concentration corresponding to the LOD reported.

In case of questions please do not hesitate to contact:

PT coordinator	**Second contact**
Donata LERDA	Philippe VERLINDE
Fax: 0032-14-571783 e-mail: jrc-irmm-crl-pah@ec.europa.eu	

With kind regards,

Thomas Wenzl

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

Cc: Almut Bitterhof, Michael Flueh, Franz Ulberth, Beatriz de la Calle, Philippe Verlinde

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
EU reference laboratory for polycyclic aromatic hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 16-09-2011

Reporting instructions

The link for reporting will be sent to registered participants immediately after dispatch of PT samples together with the opening date and closing date for reporting. **Please note that the deadline for reporting will not be extended.**

In the parcel participants will find their **password key** and the **participant secret code.** This last will be used in the report for generating Tables and graphics.

The password key is needed to get access to the interface for reporting of results and for filling in the questionnaire. **All characters of the key should be entered as they are** (e.g. keeping capital letters).

Please remember to save frequently your entries so to avoid any loss of data in case of malfunctioning of the server. **The filling in of all fields marked with a * is mandatory**.

As a support for the reporting steps, PDF preview is available for both data reporting and questionnaire.

Each page of the results reporting interface corresponds to a sample as they are listed in Table 2 below (use the arrows on top of the page to move across pages).

Table 2: The samples of the comparison

Page	Sample	Field name in the reporting interface
Page 1	Spiked olive oil replicates	OIL-REP replicate 1/2/3
Page 2	Spiked olive oil final value	OIL-FIN (for proficiency assessment) single value

The reporting page is structured like a table. To facilitate the compilation of results, it is also possible to download an excel template, in which results may be entered offline. This file has to be saved with a different name on the participant's PC, filled in (without modifying its structure!) and uploaded again in the interface.

After you entered the results directly, or via upload from the Excel table, you still have the possibility to modify entries, if deemed necessary. By clicking on the button "Validate and save" the interface verifies that all mandatory data were correctly entered by the participant.

After having validated all the data, by clicking on the button "Cancel" you are sent to the main page and proceed with the questionnaire.

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

After having completed the questionnaire and validated it, by clicking on the button "Cancel" you are sent to the main page.

From the main page you can print the PDF of the data entered and decide whether to modify them or to proceed with the **final submission** of your data, by clicking the button "Submit".

You shall then print and sign the final PDF and send it back by fax or by mail to the EU-RL mailbox (jrc-irmm-crl-pah@ec.europa.eu). **Reporting of proficiency test data finishes with sending of the signed printout.**

Reporting of RESULTS

Participants shall report:

- for the edible oil sample the **individual results** obtained by replicate analysis (in the web interface labelled as OIL-REP replicate 1/2/3) for the four individual analytes **BaP, BaA, BbF, and CHR** only. Results have to be reported in **µg/kg and corrected for recovery.** In case the concentration level detected should be below the LOD, please leave the cell empty
- for the edible oil sample a **"final value"**, which is the value which will be used for calculation of performance indicators (OIL-FIN (for proficiency assessment) in the web interface) applying following provisions:
  - the content of the four individual analytes **BaP, BaA, BbF, and CHR**, shall be expressed in **µg/kg.** The results have to be corrected for recovery and accompanied by their uncertainty. In case the content measured should be below the LOD, then the prefix "<" shall be entered instead of the default sign = in the field before the result and the numeric value of the LOD, expressed in µg/kg, shall be entered.
  - **the sum of the four marker PAHs**: the sum of the contents of the four marker PAHs shall be expressed in **µg/kg** and corrected for recovery, and has to be accompanied by its uncertainty

IMPORTANT: the choice of the final value (average of the replicates, robust mean of the replicates, etc.) is with the participant. Please note that participants will be scored upon the **final value for the target four marker PAHs and their sum.** Uncertainty has to be reported for the final values only. It has to be reported in µg/kg and should be expressed as **expanded uncertainty with a coverage factor of 2** (it is not necessary to enter the coverage factor k unless it is different from 2).

Questionnaire

Participants will be asked to report together with the results also relevant method performance characteristics, a description of the method and of the possible problems encountered when applying their method to this PT samples, and, additionally, some general information on their laboratory.

For the list of questions, please note that if a question mark is displayed beside the question, you can select it to receive additional information on the question and on what

the answer should include. Please also note that all fields marked with a * are mandatory.

Concerning the Table of method performances (*please use the acronyms listed in Table 1 for reporting*), please follow the following instructions:

- The LOD has to be reported in µg/kg (**IMPORTANT:** check that the LOD entered in this Table is the same as the LOD entered in the results in case the result was entered as < LOD)
- The LOQ has to be reported in µg/kg
- The lower limit of the working range has to be reported in µg/kg
- The higher limit of the working range has to be reported in µg/kg
- The recovery has to be reported in %

SAMPLE RECEIPT

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
EU reference laboratory for polycyclic aromatic hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

EU-RL-PAHs-09

Ninth Interlaboratory comparison of the EU-RL for Polycyclic Aromatic Hydrocarbons (PAHs)

Determination of 4 marker PAHs and their sum in olive oil

Confirmation of the receipt of the samples: RECEIPT FORM

Surname of Participant	
Name of Participant	
Affiliation	
Lab ID	
Country	

Content of the parcel

a) One amber glass ampoule containing about 20 g of spiked olive oil

b) One 5 ml brown glass ampoule with a standard solution of PAHs in solvent (acetonitrile or toluene) (concentrations known)

c) A specification sheet for the item b) content (standard solution)

d) Material safety data sheets for acetonitrile / toluene, cyclohexane and for the PAHs included in the study

e) One outline of the study + instructions

f) One paper sheet with the Laboratory ID (assigned for anonymous evaluation of data and for the PT report to be kept for all further communication) and the Participant key (for accessing to the webpage for reporting data)

g) One inter-laboratory comparison sample receipt form (= this form)

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

Date of the receipt of the test materials	
All items have been received undamaged	YES / NO
If NO, please list damaged items according to the letters associated at each item in the list above (in case of samples, please specify the numeric code too) Please write one item per row	
Items are missing	YES / NO
If YES, please list missing items according to the letters associated at each item in the list above Please write one item per row	
Serial number of the spiked olive oil sample you received	
Serial number of the standard solution(s) with known concentrations you received	

Signature .....

ATTENTION

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

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

or print it and send the printout by fax at the attention of Donata Lerda at the following number:

+32 – 014 - 571783

PARTICIPANT CODES

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
EU reference laboratory for polycyclic aromatic hydrocarbons

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Ref. Ares(2011)1004209 - 22/09/2011
Geel, 22 September 2011

Dear «Title» «Firstname» «Surname»
«Organisation» - «Department»
«Address»
«Zip» - «Town»
«Country»
«LName»

Please take note of the following codes for the participation to the EU-RL PAHs 2011 PT on 4 marker PAHs in olive oil.

1. To have access to the interface for reporting of results and for the questionnaire you will receive the link immediately after dispatching of materials. You will be asked to enter your participant code **(PASSWORD KEY)**, which is the following (case sensitive)

«Password_key»

2. In the sample receipt you will be asked to enter your secret code **(Lab ID)** which will be also used in the PT report to identify your laboratory and is obtained with the first letter and the last three numbers of your PARTKEY

«LCode»

In case of questions regarding the technical aspects, please do not hesitate to contact:

PT coordinator	**Second contact**
Donata LERDA – Tel 0032-14-571826	Philippe VERLINDE – Tel 0032-14-571625
Fax: 0032-14-571783 e-mail: jrc-irmm-crl-pah@ec.europa.eu	

Best regards,

ANNEX 5: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 11.08.2011

Standard solution specification sheet **Product ID: ACN-OIL-2011-K**

Date of production: 10/08/2011 Total volume: 3 mL

Expiry date: *February 2012*

Standard solution composition:

	Product name	CAS	Conc.*	Conc.*	U**
			(ng/g)	(ng/ml)	± %
1	5-methylchrysene	3697-24-3	64.2	50.1	1
2	Benz[*a*]anthracene	56-55-3	64.1	50.0	1
3	Benzo[*a*]pyrene	50-32-8	64.2	50.1	1
4	Benzo[*b*]fluoranthene	205-99-2	65.4	51.1	1
5	Benzo[*c*]fluorene	205-12-9	63.3	49.4	1
6	Benzo[*ghi*]perylene	191-24-2	65.5	51.2	1
7	Benzo[*j*]fluoranthene	205-82-3	64.8	50.6	1
8	Benzo[*k*]fluoranthene	207-08-9	64.9	50.7	1
9	Chrysene	218-01-9	64.3	50.2	1
10	Cyclopenta[*cd*]pyrene	27208-37-3	67.8	52.9	2
11	Dibenzo[*a,e*]pyrene	192-65-4	64.3	50.2	1
12	Dibenz[*a,h*]anthracene	53-70-3	64.3	50.2	1
13	Dibenzo[*a,h*]pyrene	189-64-0	64.6	50.4	1
14	Dibenzo[*a,i*]pyrene	189-55-9	65.6	51.2	3
15	Dibenzo[*a,l*]pyrene	191-30-0	64.8	50.6	1
16	Indeno[1,2,3-*cd*]pyrene	193-39-5	63.5	49.6	1

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

*** U is the expanded uncertainty calculated using the coverage factor 2 (corresponding to a confidence interval of 95%) multiplied by the combined standard uncertainty. 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 SOLUTION

Geel, 11.08.2011

Standard solution specification sheet **Product ID: TOL-OIL-2011-K**

Date of production: 10/08/2011 Total volume: 3 mL

Expiry date: *February 2012*

Standard solution composition:

	Product name	CAS	Conc.*	Conc.*	U**
			(ng/g)	(ng/ml)	± %
1	5-methylchrysene	3697-24-3	57.9	50.1	1
2	Benz[*a*]anthracene	56-55-3	57.9	50.1	1
3	Benzo[*a*]pyrene	50-32-8	58.0	50.1	1
4	Benzo[*b*]fluoranthene	205-99-2	59.0	51.0	1
5	Benzo[*c*]fluorene	205-12-9	57.2	49.4	1
6	Benzo[*ghi*]perylene	191-24-2	59.2	51.2	1
7	Benzo[*j*]fluoranthene	205-82-3	58.4	50.5	1
8	Benzo[*k*]fluoranthene	207-08-9	58.5	50.6	1
9	Chrysene	218-01-9	58.3	50.4	1
10	Cyclopenta[*cd*]pyrene	27208-37-3	60.8	52.5	2
11	Dibenzo[*a,e*]pyrene	192-65-4	57.9	50.1	1
12	Dibenz[*a,h*]anthracene	53-70-3	59.1	51.1	1
13	Dibenzo[*a,h*]pyrene	189-64-0	58.1	50.2	1
14	Dibenzo[*a,i*]pyrene	189-55-9	59.4	51.4	3
15	Dibenzo[*a,l*]pyrene	191-30-0	58.6	50.7	1
16	Indeno[1,2,3-*cd*]pyrene	193-39-5	57.3	49.6	1

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

*** U is the expanded uncertainty calculated using the coverage factor 2 (corresponding to a confidence interval of 95%) multiplied by the combined standard uncertainty. 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

ANNEX 6: Homogeneity of the test material

Analyte: **BAA**

	n =	10		
	mean =	3.0455	21%	**= σ-trg(%)**
0.032880278	**s_x =**	0.1813	0.6414	**= σ-trg**
ÖMSW =	**s_w =**	0.1913		
	s_s =	0.1208	0.1924	**= 0,3*s**

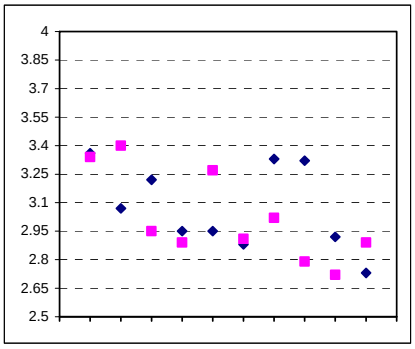
ISO-13528 passed

F = 0 3.02038295 = Fcrit
passed

IUPAC

(MSB-MSW)/2 0.0146 0.1066 = F1*(0,3*s)^2+F2*MSW
passed

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	3.36	3.34	0.02	6.7	3.35
Ampoule 026	3.07	3.4	-0.33	6.47	3.235
Ampoule 039	3.22	2.95	0.27	6.17	3.085
Ampoule 077	2.95	2.89	0.06	5.84	2.92
Ampoule 095	2.95	3.27	-0.32	6.22	3.11
Ampoule 102	2.88	2.91	-0.03	5.79	2.895
Ampoule 120	3.33	3.02	0.31	6.35	3.175
Ampoule 159	3.32	2.79	0.53	6.11	3.055
Ampoule 174	2.92	2.72	0.2	5.64	2.82
Ampoule 187	2.73	2.89	-0.16	5.62	2.81



∑(diff)^2 = 0.7317
var(sum)/2 = 0.06576 =MSB

Analyte: **BAP**

	n =	10		
	mean =	2.6485	21%	**= σ-trg(%)**
0.017116944	**s_x =**	0.1308	0.5578	**= σ-trg**
ÖMSW =	**s_w =**	0.1814		
	s_s =	0.0259	0.1673	**= 0,3*s**

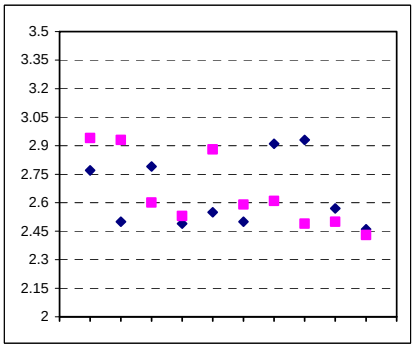
ISO-13528 passed

F = 0 3.02038295 = Fcrit
passed

IUPAC

(MSB-MSW)/2 0.0007 0.0859 = F1*(0,3*s)^2+F2*MSW
passed

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	2.77	2.94	-0.17	5.71	2.855
Ampoule 026	2.5	2.93	-0.43	5.43	2.715
Ampoule 039	2.79	2.6	0.19	5.39	2.695
Ampoule 077	2.49	2.53	-0.04	5.02	2.51
Ampoule 095	2.55	2.88	-0.33	5.43	2.715
Ampoule 102	2.5	2.59	-0.09	5.09	2.545
Ampoule 120	2.91	2.61	0.3	5.52	2.76
Ampoule 159	2.93	2.49	0.44	5.42	2.71
Ampoule 174	2.57	2.5	0.07	5.07	2.535
Ampoule 187	2.46	2.43	0.03	4.89	2.445



∑(diff)^2 = 0.6579
var(sum)/2 = 0.03423 =MSB

Analyte: **BBF**

	n =	10		
	mean =	5.8080	20%	**= σ-trg(%)**
0.109156667	**s_x =**	0.3304	1.1732	**= σ-trg**
ÖMSW =	**s_w =**	0.3751		
	s_s =	0.1970	0.3520	**= 0,3*s**

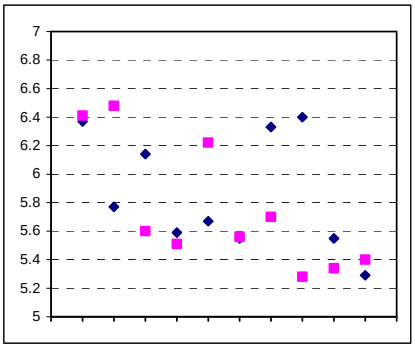
ISO-13528 passed

F = 0 3.02038295 = Fcrit
passed

IUPAC
(MSB-MSW)/2 0.0388 0.3750 = F1*(0,3*s)^2+F2*MSW
passed

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	6.37	6.41	-0.04	12.78	6.39
Ampoule 026	5.77	6.48	-0.71	12.25	6.125
Ampoule 039	6.14	5.6	0.54	11.74	5.87
Ampoule 077	5.59	5.51	0.08	11.1	5.55
Ampoule 095	5.67	6.22	-0.55	11.89	5.945
Ampoule 102	5.55	5.56	-0.01	11.11	5.555
Ampoule 120	6.33	5.7	0.63	12.03	6.015
Ampoule 159	6.4	5.28	1.12	11.68	5.84
Ampoule 174	5.55	5.34	0.21	10.89	5.445
Ampoule 187	5.29	5.4	-0.11	10.69	5.345

∑(diff)^2 = 2.8138
var(sum)/2 = 0.21831 =MSB



Analyte: **CHR**

	n =	10		
	mean =	3.0490	21%	**= σ-trg(%)**
0.044215556	**s_x =**	0.2103	0.6318	**= σ-trg**
ÖMSW =	**s_w =**	0.2128		
	s_s =	0.1469	0.1895	**= 0,3*s**

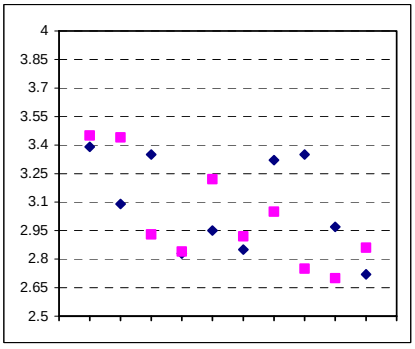
ISO-13528 passed

F = 0 3.02038295 = Fcrit
passed

IUPAC
(MSB-MSW)/2 0.0216 0.1133 = F1*(0,3*s)^2+F2*MSW
passed

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	3.39	3.45	-0.06	6.84	3.42
Ampoule 026	3.09	3.44	-0.35	6.53	3.265
Ampoule 039	3.35	2.93	0.42	6.28	3.14
Ampoule 077	2.83	2.84	-0.01	5.67	2.835
Ampoule 095	2.95	3.22	-0.27	6.17	3.085
Ampoule 102	2.85	2.92	-0.07	5.77	2.885
Ampoule 120	3.32	3.05	0.27	6.37	3.185
Ampoule 159	3.35	2.75	0.6	6.1	3.05
Ampoule 174	2.97	2.7	0.27	5.67	2.835
Ampoule 187	2.72	2.86	-0.14	5.58	2.79

∑(diff)^2 = 0.9058
var(sum)/2 = 0.08843 =MSB



ANNEX 7: Questionnaire

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Milc questionnaire

Comparison for 2011 second EU-RL PAHs PT: four marker PAHs in olive oil

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

Submission Form

Performance criteria for the method

The values reported in this Table will be evaluated for the four individual analytes with reference to the requirements set in Regulation (EC) No 333/2007 for BaP. In case you reported for one or more analyte(s) a value below the LOD (e.g. <0.20 µg/kg), please check the consistency of the value reported in the results with the value reported in the Table below.

Questions/Response table	*LOD [µg/kg]*	*LOQ [µg/kg]*	*Recovery [%]*	*Linear working range lower limit [µg/kg]*	*Linear working range higher limit [µg/kg]*
BaA					
BaP					
BbF					
CHR					

1. **Did you find the instructions distributed for this PT adequate?** *

- a) Yes
- b) No

1.1. If NO, please report about possible lacking information *

2. **Did you experience any specific problem related to the organisation of this PT?**

- a) yes
- b) no

2.1. If YES, please describe here the main problems you were confronted with (e.g. registration, reporting of results, questionnaire, content of the parcel, material quantity/stability/packaging, instructions concerning the samples, etc) *

3. **Did your laboratory quantify PAHs in EDIBLE OIL before?** *

- a) yes
- b) no

3.1. If YES, for how long? (expressed in years) *

- a) <1
- b) 1-4
- c) 4-8
- d) 8-15
- e) >15
- f) other

3.1.1. If OTHER, please specify *

3.2. If YES, how many samples per year does your laboratory analyse for THIS FOOD CATEGORY? *

- a) < 10
- b) 10-50
- c) 50-100
- d) > 100
- e) other

3.2.1. If OTHER, please specify *

4. **Is your laboratory accredited for the determination of PAHs in food?** *

- a) yes
- b) no

4.1. If YES, please specify the food matrix included in the accreditation scope *

- a) Oils and fats (6.1.1)
- b) Smoked meats and smoked meat products (6.1.2)
- c) Muscle meat of smoked fish and smoked fishery products (6.1.3)
- d) Muscle meat of fish (6.1.4)
- e) Crustaceans, cephalopods, other than smoked (6.1.5)
- f) Bivalve molluscs (6.1.6)
- g) Processed cereal-based foods and baby foods for infants and young (6.1.7)
- h) Infant formulae and follow-on formulae (6.1.8)
- i) Dietary foods for special medical purposes (6.1.9)
- j) OTHER
- k) All the matrices listed above
- l) the following of the matrices listed above

4.1.1. If OTHER, please specify *

4.1.2. If you chose "the following of the matrices listed above", please report the corresponding codes *

4.2. If YES, please specify the PAHs included in the accreditation scope *

- a) BaP
- b) 4 marker PAHs
- c) 15+1 EU priority PAHs
- d) 16 EPA PAHs
- e) other

4.2.1. If OTHER, please specify *

5. **How did you prepare the sample?** *

- a) Dilution
- b) No preparation
- c) Other

5.1. If OTHER, please describe *

6. **Which extraction method did you use?** *

- a) Saponification
- b) Pressurized liquid extraction
- c) Soxhlet extraction
- d) No extraction
- e) Other

6.1. If OTHER, please describe *

7. **Which was the MAIN purification step of your method?** *

- a) Donor-Acceptor Complex Chromatography (DACC)
- b) Size-Exclusion Chromatography
- c) Solid Phase Extraction (SPE)
- d) Solvent partitioning
- e) Other

7.1. If OTHER, please describe *

8. **Which was the instrumental detection method you applied?** *

- a) HPLC-FLD
- b) UHPLC-FLD
- c) HPLC-FLD-UV
- d) UHPLC-FLD-UV
- e) HPLC-MS
- f) UHPLC-MS
- g) HPLC-MS/MS
- h) UHPLC-MS/MS
- i) GC-FID
- j) GC-MS
- k) GC-HRMS
- l) GC-MS/MS
- m) Other

8.1. If OTHER, please describe *

9. **In case you applied a gaschromatographic technique, please describe the analytical column used (stationary phase, length, internal diameter, film thickness)**

10. **In case you applied a liquid chromatographic technique, please describe the analytical column used (stationary phase, particle size, length, internal diameter)**

11. **Did you encounter any problems during the analysis of the sample?** *

- a) Yes
- b) No

11.1. If YES, please describe *

12. **In the following field you may add any further information about this PT and the analysis of the samples**

METHOD PERFORMANCE PARAMETERS

With reference to Commission Regulation (EC) No 333/2007 as amended by Commission Regulation (EU) No 836/2011, non-compliant method performance characteristics are marked in the tables in bold red font. Threshold values for the evaluation were LOD ≥ 0.30 µg/kg, LOQ ≥ 0.90 µg/kg, and recovery outside the range of 50 % - 120 %. Levels of the lower limit of the working range, which are not considered fit-for-purpose for the implementation of legislation, are marked by bold red font too.

Questionnaire Table – BAA NRLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
B489	0.0014	0.4	98.5	0.06	10
D559	0.1	0.5	90	0.5	20
D718	0.07	0.2	85	0.2	10
F980	0.1	0.3	90	0.3	20
G065	0.3	0.6	97.8	0.2	20
G943	0.07	0.21	95	0.21	20
H099	0.2	0.4	78	0.5	25
H489	0.02	0.02	69	0.005	10
H716	0.3	0.8	94	1	13
H943	0.06	0.21	75	0.5	5
J945	0.1	0.3	100	0.4	17
K099	0.1	0.5	81	1.2	20
K408	0.09	0.3	85	0.1	10
K644	0.1	0.33	81.1	1	20
L259	0.3	**1**	100	0.5	20
L874	0.1	0.5	100	0.1	50
R559	0.08	0.25	112	0.25	75
R562	0.025	0.05	98	0	20
S177	0.12	0.24	81.4	0.24	25
S406	0.07	0.21	105	0.8	50
T408	0.2	0.6	110	0.6	8
V218	0.01	0.03	77	0.1	40
V320	0.006	0.012	83	0.012	30
W099	0.1	0.3	73	0.1	40

n.r.: not reported

Questionnaire Table – BAA OCLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
C259	0.1	0.1	91	0.1	10
D023	0.2	0.6	90	1	20
D255	0.03	0.05	89	0.2	20
E255	0.2	0.5	90	**5**	500
F710	**<0.5**	**<1**	80	1	40
H252	**0.9**	0.3	101	0.9	50
H338	<0.05	0.1	56	n.r.	n.r.
J065	0.07	0.2	82	0.2	200
J713	0.03	0.1	74.5	0.1	5
L177	**0.5**	**<=1**	97	0.8	60
L980	**0.5**	**1**	n.r.	n.r.	n.r.
M637	**300***	**400***	n.r.	**300***	2000
M947	0.02	0.11	72.9	0.1	10
P718	**0.33**	**1**	70.3	1	40
R287	**0.5**	**1**	100	1	20
S027	0.029	0.098	93	**5.79**	2316
S176	0.1	0.3	100	0.1	5
S638	0.2	0.5	88	**3**	10
S874	**0.5**	**1.8**	98	0.2	5
S913	0.05	0.1	63.8	0.1	4.5
V176	0.02	0.2	100.1	0.2	10
W015	0.1	0.3	110	1	10
W065	0.1	0.2	100	0.1	10
W098	0.06	0.12	89	0.15	19.5

n.r.: not reported
* Participant reported instrument problems

Questionnaire Table – BAP NRLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
B489	0.001	0.41	98.8	0.06	10
D559	0.04	0.2	90	0.2	10
D718	0.07	0.2	93	0.2	10
F980	0.1	0.3	90	0.3	20
G065	0.3	0.7	98.3	0.2	20
G943	0.05	0.15	96	0.15	20
H099	0.2	0.4	94	0.5	25
H489	0.14	0.14	91	0.005	10
H716	0.3	0.8	95	1	13
H943	0.04	0.14	61	0.5	5
J945	0.1	0.2	81	0.4	17
K099	0.1	0.5	91	1.2	20
K408	0.18	0.59	99	0.1	10
K644	0.1	0.33	71.2	1	20
L259	0.2	**1**	85	0.5	20
L874	0.1	0.5	98	0.1	50
R559	0.08	0.25	90	0.25	75.15
R562	0.025	0.05	98	0	20
S177	0.1	0.2	70.7	0.2	25
S406	0.08	0.24	101	0.8	50
T408	0.1	0.3	112	0.4	8
V218	0.01	0.03	74	0.1	40
V320	0.013	0.026	96	0.026	30
W099	0.1	0.3	67	0.1	40

Questionnaire Table – BAP OCLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
C259	0.1	0.1	91	0.1	10
D023	0.2	0.6	90	1	20
D255	0.03	0.05	89	0.2	20
E255	0.2	0.5	90	**5**	500
F710	**<0.5**	**<1**	80	1	40
H252	**0.9**	0.3	101	0.9	50
H338	<0.05	0.1	56	n.r.	n.r.
J065	0.07	0.2	82	0.2	200
J713	0.03	0.1	74.5	0.1	5
L177	**0.5**	**<=1**	97	0.8	60
L980	**0.5**	**1**	**n.r.**	n.r.	n.r.
M637	**300***	**400***	**n.r.**	**300***	2000
M947	0.02	0.11	72.9	0.1	10
P718	**0.33**	**1**	70.3	1	40
R287	**0.5**	**1**	100	1	20
S027	0.029	0.098	93	**5.79**	2316
S176	0.1	0.3	100	0.1	5
S638	0.2	0.5	88	**3**	10
S874	**0.5**	**1.8**	98	0.2	5
S913	0.05	0.1	62.9	0.1	4.5
V176	0.02	0.2	100.1	0.2	10
W015	0.1	0.3	110	1	10
W065	0.1	0.2	100	0.1	10
W098	0.06	0.12	89	0.15	19.5

n.r.: not reported
* Participant reported instrument problems

Questionnaire Table – BBF NRLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
B489	0.0055	0.41	100.3	0.06	10
D559	0.04	0.2	90	0.2	10
D718	0.07	0.2	102	0.2	10
F980	0.1	0.3	90	0.3	20
G065	0.3	0.5	96	0.2	20
G943	0.15	0.45	95	0.45	40
H099	0.2	0.4	95	0.5	25
H489	0.07	0.07	85	0.005	10
H716	0.3	0.8	88	1	13
H943	0.23	0.75	70	0.5	5
J945	0.1	0.3	84	0.4	17
K099	0.1	0.5	85	1.2	20
K408	0.11	0.38	107	0.1	10
K644	0.1	0.33	76.4	1	20
L259	0.2	1	108	0.5	20
L874	0.1	0.5	100	0.1	50
R559	0.09	0.26	83	0.26	76.65
R562	0.05	0.1	101	0	20
S177	0.16	0.32	82.7	0.32	25
S406	0.15	0.45	100	0.8	50
T408	0.3	0.9	118	0.9	8
V218	0.01	0.03	81	0.1	40
V320	0.008	0.016	85	0.016	30
W099	0.1	0.3	70	0.1	40

n.r.: not reported

Questionnaire Table – BBF OCLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
C259	0.1	0.1	90	0.1	10
D023	0.3	0.9	90	1	20
D255	0.29	0.49	86	0.2	20
E255	0.2	0.5	95	**5**	500
F710	**<0.5**	**<1**	88.9	1	40
H252	**0.9**	0.3	91	0.9	50
H338	<0.05	0.1	43	n.r.	n.r.
J065	0.07	0.2	104	0.2	200
J713	0.03	0.1	94	0.1	5
L177	**0.5**	**<=1**	87.9	0.8	60
L980	**0.5**	**1**	n.r.	n.r.	n.r.
M637	**300***	**400***	n.r.	**300***	2000
M947	0.05	0.24	93.8	0.1	10
P718	**0.33**	**1**	88.5	1	40
R287	**0.5**	**1**	93	1	20
S027	0.029	0.098	89	**5.9**	2360
S176	0.1	0.3	100	0.1	5
S638	0.4	1	76	**3**	10
S874	0.1	0.3	110	0.2	5
S913	0.05	0.1	62.1	0.1	4.5
V176	0.02	0.2	98.6	0.2	10
W015	0.1	0.3	105	1	10
W065	0.1	0.2	99	0.1	10
W098	0.06	0.13	93	0.21	27.3

n.r.: not reported
* Participant reported instrument problems

Questionnaire Table – CHR NRLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
B489	0.0013	0.41	103.3	0.06	10
D559	0.1	0.5	90	0.5	20
D566	n.r.	n.r.	n.r.	n.r.	n.r.
D718	0.07	0.2	90	0.2	10
F980	0.1	0.3	90	0.3	20
G065	0.2	0.3	101.5	0.2	20
G943	0.03	0.09	96	0.09	20
H099	0.2	0.4	118	0.5	25
H489	0.04	0.04	66	0.005	10
H716	0.3	0.8	88	1	13
H943	0.01	0.03	72	0.5	5
J945	0.1	0.3	94	0.4	17
K099	0.1	0.5	82	1.2	20
K150	n.r.	n.r.	n.r.	n.r.	n.r.
K408	0.07	0.24	100	0.1	10
K644	0.25	0.83	101.2	1	20
L259	0.3	**1**	118	0.5	20
L874	0.1	0.5	103	0.1	50
R559	0.08	0.25	84	0.25	75.3
R562	0.025	0.05	102	0	20
S177	0.16	0.32	83.9	0.32	25
S406	0.04	0.12	93	0.8	50
T408	0.3	0.9	107	0.9	8
V218	0.01	0.03	78	0.1	40
V320	0.014	0.028	83	0.028	30
W099	0.1	0.3	71	0.1	40

n.r.: not reported

Questionnaire Table – CHR OCLs

Lab code	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Linear working range lower limit [µg/kg]	Linear working range higher limit [µg/kg]
C259	0.1	0.1	92	0.1	10
D023	0.3	0.9	90	1	20
D255	**0.51**	0.84	83	0.2	20
E255	0.2	0.5	95	**5**	500
F710	**<0.5**	**<1**	88.9	1	40
H252	**0.9**	0.3	92	0.9	50
H338	<0.01	0.1	53	n.r.	n.r.
J065	0.07	0.2	85	0.2	200
J713	0.03	0.1	77.2	0.1	5
L177	**0.5**	**<=1**	93.7	0.8	60
L980	**0.5**	**1**	n.r.	n.r.	n.r.
M637	**300***	**400***	n.r.	**300***	2000
M947	0.02	0.1	88	0.1	10
P718	**0.33**	**1**	144	1	40
R287	**0.5**	**1**	86	1	20
S027	0.029	0.098	93	**5.83**	2332
S176	0.1	0.3	100	0.1	5
S638	0.2	0.5	76	**3**	10
S874	**0.4**	**1.4**	103	0.2	5
S913	0.05	0.1	75.7	0.1	4.5
V176	0.02	0.2	101	0.2	10
W015	0.1	0.3	100	1	10
W065	0.1	0.2	99	0.1	10
W098	0.06	0.13	95	0.18	22.6

n.r.: not reported
* Participant reported instrument problems

QUESTIONNAIRE:

On the organisation of the PT

- Did you find the instructions distributed for this PT adequate?
- If NO, please report about possible lacking information (for NRLs no matching case)
- Did you experience any specific problem related to the organisation of this PT?
- If YES, please describe here the main problems you were confronted with (e.g. registration, reporting of results, questionnaire, content of the parcel, material quantity/stability/packaging, instructions concerning the samples, etc)
- In the following field you may add any further information about this PT and the analysis of the samples

NRLs

LabID	Instructions adequate	Organisation problems	Organisation problems description	Additional comments
B489	YES	NO		
D559	YES	NO		
D566				
D718	YES	NO		
F980	YES	NO		
G065	YES	NO		
G943	YES	NO		
H099	YES	YES	Too close to the other PT	
H489	YES	NO		
H716	YES	NO		
H943	YES	NO		
J945	YES	YES	For three replicate analyses we had to ask more olive oil material	
K099	YES	NO		
K150				
K408	YES	NO		
K644	YES	NO		
L259	YES	YES	Too small amount of the sample (we need at least 30 grams)	
L874	YES	NO		maybe blank sample of same matrice
R559	YES	NO		
R562	YES	NO		
S177	YES	NO		
S406	YES	NO		
T408	YES	NO		A standard addition quantification method was performed
V218	YES	NO		
V320	YES	NO		
W099	YES	NO		

OCLs

LabID	Instructions adequate	Lacking information	Organisation problems	Organisation problems description	Additional comments
C259	YES		YES	oil sample bulb broken on receipt, but new sample received one week later	
D023	YES		NO		a indication of the range of analyte
D255	YES		NO		
E255	YES		YES	first, I haven't received my PASSWORD key	
F710	YES		NO		not enough sample material (usually we need 10g for one analysis)
H252	YES		NO		
H338	YES		NO		
J065	YES		NO		
J713	YES		NO		
L177	YES		NO		/
L980	YES		NO		
M637	YES		NO		
M947	YES		NO		
P718	YES		NO		
R287	YES		NO		
S027	YES		NO		
S176	NO	More complicate	NO		
S638	YES		NO		
S874	YES		NO		
S913	YES		NO		The reported values are corrected for recovery!
V176	YES		NO		
W015	YES		NO		
W065	YES		NO		
W098	YES		NO		

On participants profile

- Did your laboratory quantify PAHs in EDIBLE OIL before?
- If YES, for how long? (expressed in years) - If OTHER, please specify
- If YES, how many samples per year does your laboratory analyse for THIS FOOD CATEGORY? - If OTHER, please specify
- Is your laboratory accredited for the determination of PAHs in food?
- If YES, please specify the food matrix included in the accreditation scope - If OTHER, please specify - If you chose "the following of the matrices listed above", please report the corresponding codes
- If YES, please specify the PAHs included in the accreditation scope - If OTHER, please specify

NRLs

LabID	Analysis of PAHs in Edible oil	For how long (years)	Samples / year	Accredited	Matrices in accreditation scope	Analytes in accreditation scope
B489	YES	8-15		YES	All matrices included in legislation	15+1 EU priority PAHs
D559	YES	4-8	< 10	YES	Oils and fats (6.1.1)	4 marker PAHs
D566						
D718	YES	8-15	< 10	NO		
F980	YES	1-4	< 10	NO		
G065	YES	4-8	10-50	YES	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8, plus tea, coffee, food supplements	15+1 EU priority PAH excluding BCL
G943	YES	>15	50-100	YES	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8 plus water	15+1 EU priority PAHs
H099	YES	1-4	< 10	YES	Oils (only oils – 6.1.1) and dietary supplements	15+1 EU priority PAHs
H489	YES	8-15	> 100	YES	All matrices included in legislation	27 PAHs including 15+1 EU priority PAHs
H716	YES	1-4	< 10	YES	6.1.1 and 6.1.3	4 marker PAHs
H943	YES	1-4	10-50	YES	All matrices included in legislation	15+1 EU priority PAHs
J945	YES	4-8	10-50	YES	6.1.1, 6.1.2	BaP
K099	YES	1-4	10-50	YES	6.1.1.; 6.1.2.; 6.1.3.; 6.1.4; 6.1.7; 6.1.8;	15+1 EU priority PAHs
K150						
K408	YES	4-8	10-50	YES	Smoked meats and smoked meat products (6.1.2)	4 marker PAHs
K644	YES	4-8	10-50	NO		
L259	YES	4-8	50-100	YES	Oils and fats (6.1.1)	15+1 EU priority PAHs
L874	YES	4-8	< 10	YES	6.1.1, 6.1.2, 6.1.3, 6.1.7, 6.1.8	15+1 EU priority PAHs
R559	NO			NO		
R562	YES	4-8	50-100	YES	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8, 6.1.9	15+1 EU priority PAHs
S177	YES	>15	10-50	YES	All matrices included in legislation	15+1 EU priority PAHs

LabID	Analysis of PAHs in Edible oil	For how long (years)	Samples / year	Accredited	Matrices in accreditation scope	Analytes in accreditation scope
S406	YES	4-8	> 100	YES	All matrices included in legislation	15+1 EU priority PAHs
T408	YES	8-15	50-100	YES	All matrices included in legislation	15+1 EU priority PAHs
V218	YES	4-8	< 10	YES	All matrices included in legislation	15+1 EU priority PAHs
V320	YES	8-15	10-50	YES	Oils and fats (6.1.1)	15+1 EU priority PAHs
W099	YES	4-8	10-50	YES	All matrices included in legislation	15 EU priority PAHs (not BCL), plus phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, perylene, benz(e)pyrene, anthanthrene, coronene

Food categories as listed in Regulation (EC) No 1881/2006:
Oils and fats (6.1.1)
Smoked meats and smoked meat products (6.1.2)
Muscle meat of smoked fish and smoked fishery products (6.1.3)
Muscle meat of fish (6.1.4)
Crustaceans, cephalopods, other than smoked (6.1.5)
Bivalve molluscs (6.1.6)
Processed cereal-based foods and baby foods for infants and young (6.1.7)
Infant formulae and follow-on formulae (6.1.8)
Dietary foods for special medical purposes (6.1.9)

OCLs

LabID	PAHs in Edible oil	For how long (years)	Samples / year	Accredited	Matrices in accreditation scope	Analytes in accreditation scope
C259	YES	1-4	< 10	YES	6.1.1; 6.1.2; 6.1.3; 6.1.4; 6.1.5; 6.1.6	16 EPA PAH + DLP, DEP, DIP, and DHP
D023	NO			NO		
D255	YES	>15	10-50	NO		
E255	YES	8-15	50-100	YES	All matrices included in legislation	16 EPA PAHs
F710	YES	1-4	10-50	NO		
H252	YES	1-4	10-50	YES	6.1.1, 6.1.2, 6.1.3	BaP
H338	NO			YES		
J065	YES	4-8	< 10	NO		
J713	NO			YES	6.1.3; 6.1.4; 6.1.5, 6.1.6	16 EPA PAHs
L177	YES	4-8	10-50	YES	Muscle meat of fish (6.1.4)	15+1 EU priority PAHs + 16 EPA PAHs excluding anthracene, naphthalene and fluorene
L980	YES	4-8	< 10	YES	6.1.1; 6.1.2; 6.1.3; 6.1.4	BaP
M637	NO			NO		
M947	YES	1-4	10-50	NO		
P718	YES	1-4	< 10	YES	Muscle meat of smoked fish and smoked fishery products (6.1.3)	15+1 EU priority PAHs
R287	YES	4-8	> 100	YES		BaP
S027	YES	<1	< 10	NO		
S176	YES	8-15	10-50	YES	Oils and fats (6.1.1)	BaA, BbF, BkF, BeP, BaP, DHA, BGP, ICP
S638	YES	>15	10-50	YES	6.1.1; 6.1.2; 6.1.3	4 marker PAHs
S874	NO			NO		
S913	YES	8-15	10-50	YES	Oils and fats (6.1.1)	15 + 1 EU priority PAHs (excluding BCL and CPP)
V176	YES	1-4	10-50	NO		
W015	YES	1-4	> 100	YES	Oils and fats (6.1.1)	15+1 EU priority PAHs
W065	YES	1-4	50-100	YES	Oils and fats (6.1.1)	4 marker PAHs
W098	YES	1-4	< 10	YES	All matrices included in legislation	16 EPA PAHs

Food categories as listed in Regulation (EC) No 1881/2006:
Oils and fats (6.1.1)
Smoked meats and smoked meat products (6.1.2)
Muscle meat of smoked fish and smoked fishery products (6.1.3)
Muscle meat of fish (6.1.4)
Crustaceans, cephalopods, other than smoked (6.1.5)
Bivalve molluscs (6.1.6)
Processed cereal-based foods and baby foods for infants and young (6.1.7)
Infant formulae and follow-on formulae (6.1.8)
Dietary foods for special medical purposes (6.1.9)

On the method applied

- How did you prepare the sample?
- Which extraction method did you use?
- Which was the MAIN purification step of your method?
- Which was the instrumental detection method you applied?
- Please describe the analytical column used
- Did you encounter any problems during the analysis of the sample?

NRLs

LabID	Preparation	Extraction	Purification	Detection	Column	Problems
B489	Dilution	No extraction	SEC	HPLC-FLD	C18, 5 µm, 4.6 x 250 mm	
D559	Dilution	No extraction	SPE	HPLC-FLD	RESTEK PinneaclePAH 5µm x 125 mm x 4.6mm	
D566						
D718	Dilution	Liquid/liquid Extraction	SPE	GC-MS	Agilent Technologies DB-17 (50%-Phenyl)-metylpolysiloxane; 30 m; 0.25 i.d.; 0.15 um	
F980	No preparation	Other	SEC	UHPLC-MS/MS	zorbax eclipse PAH 2.1x50 mm 1.8 µm	
G065	No preparation	Saponification	Solvent partitioning	GC-MS	5% phenyl 95% methyl, 60 x 0.25 x 0.25	
G943	Dilution	No extraction	SEC	HPLC-FLD	PAH C18 5um; 4,6x250mm, 5 µm (Waters P/N 186001265)	
H099	No preparation	No extraction	DACC	HPLC-FLD-UV	Pursuit 3 PAH 3µm 100x4.4	Problems with HPLC and column
H489	No preparation	Saponification	Solvent partitioning	GC-MS	(5%phenyl)-methylpolysiloxane 60m 0.25i.d 0.25um	
H716	Dilution	No extraction	SPE	GC-MS/MS	50%-Phenyl-50%-Dimethylpolysiloxane, 30m x 0.25 mm x 0.25 µm	
H943	Dilution	Liquid/liquid-partition	SEC	GC-MS	35% Phenyl, 30 m, 0.25 mm i.d., 0.25 µm film; 5m retention gap	
J945	saponification, solvent partitioning, silicagel column	Saponification	Solvent partitioning	HPLC-FLD-UV	LiChroCART 250-4 LiChrospher PAH (5 µm)	BAA peak was double

LabID	Preparation	Extraction	Purification	Detection	Column	Problems
K099	Dilution	No extraction	SEC	GC-MS	DB-EUPAH, 20 m × 0.18 mm × 0.14 micrometer	The olive oil contains squalene which interferes with BAA and CHR when we use our routine method. We have an additional cleaning step for oils, but this time it didn't work, so we used your MVS method.
K150						
K408	Dilution	liquid/liquid partitioning	SPE	GC-MS	Capillary GC Column Zebron ZB-50 (30m×0,25mm×0,25µm)	
K644	No preparation	LIQUID LIQUID EXTRACTION	SPE	HPLC-FLD-UV	Grace Vydac, C18 250x4.6 mm, 5µm	
L259	No preparation	liquid extraction	GPC	GC-MS	DB EU PAH 20mx0.18mmx0.14um	
L874	Dilution	No extraction	SEC	GC-MS	HP17MS 30m,0,25 mm, 0,25 um	
R559	No preparation	Saponification	Solvent partitioning	HPLC-FLD-UV	Waters PAH C18, S-5 µm, 250x3.0 mm	
R562	Dilution	oil samples just dissolved in chloroform	GPC	HPLC-FLD	Waters PAH C18 5um 2.1x250mm	
S177	No preparation	liquid-liquid extraction	SPE	HPLC-FLD	Varian Pursuit PAH (C18), 250 x 4,6 mm, particle size 5 um	
S406	Dilution	No extraction	SEC	HPLC-FLD	Vydac 201 TP 54, 5 µ, 250mm, 4,6 mm	
T408	No preparation	LIQUID EXTRACTION (LIQUID - LIQUID PARTITION)	SPE	HPLC-FLD-UV	C18, 5um , 250mm , 4.6 (VYDAC 21TP54)	
V218	Dilution	No extraction	SPE	GC-MS/MS	Varian Select PAH, 30m x 0.25 x 0.15	
V320	Dilution	No extraction	SEC	GC-HRMS	Varian PAH-select, 30m x 0.25 mm x 0.15 µm	Interference on deuterated BAA in GC-HRMS measurement
W099	Saponification	cyclohexane extraction	SPE	GC-MS	DB 35ms, 30m, i.d. 0.25 mm, 0.15 µm	

OCLs

LabID	Preparation	Extraction	Purification	Detection	Column	Problems
C259	No preparation	No extraction	SPE	GC-MS/MS	VF17MS 30 m 0.25µm, 0.25 mm	
D023	Dilution	No extraction	SEC	GC-MS		problems with purification step
D255	Dilution	Saponification	SPE	HPLC-FLD-UV	C18, 250x4.6 mm, 5µm	
E255	lyophilisation	Pressurized liquid extraction	SPE	GC-MS/MS	VF 17MS (60m * 0.25 mm * 0,25 µm)	
F710	Dilution	Dilution with ethylacetate/cyclohexan 50/50 v/v	Solvent partitioning	GC-MS	DB-EUPAH, 20m, 0.180mm, 0.14µm	
H252	Dilution	No extraction	SEC	HPLC-FLD	SunFire C18, 5um, 250mm, 4.6mm	
H338	Dilution	Saponification	Solvent partitioning	UHPLC-FLD		
J065	No preparation	Soxhlet extraction	SPE	GC-MS/MS	Column: ZB50 - lenght: 30 mètres - id :0.25 mm - Film thickness : 0.25 µm	
J713	Dilution	No extraction	SPE	GC-MS/MS	Zebron ZB 5MS 30M x 0.25mm x 0.25µm; 5% polysilarylene-95%polyMesiloxane	
L177	Dilution	No extraction	SEC	GC-MS	ZB-50; 30 m; 0,25 mm; 0,25 µm	
L980	No preparation	Saponification	Solvent partitioning	HPLC-FLD		
M637	Dilution	Solid Phase Extraction cartridges	SPE	GC-MS	Zebron ZB-5ms (5% Polysilarylene - 95% Polydimethylsiloxane copolymer) 30m x 0.25mm x 0.25um	Instrumentation problems occurred during the analysis which affected our sensitivity and limit of detection. Due to the time limit, we were unable to overcome these problems and for this reason we can only quote below the current limit of detection which is outside the range of the trial.
M947	heat for short time to 40 ~C, so the oil is more homogeneous	Saponification	Solvent partitioning	HPLC-FLD		

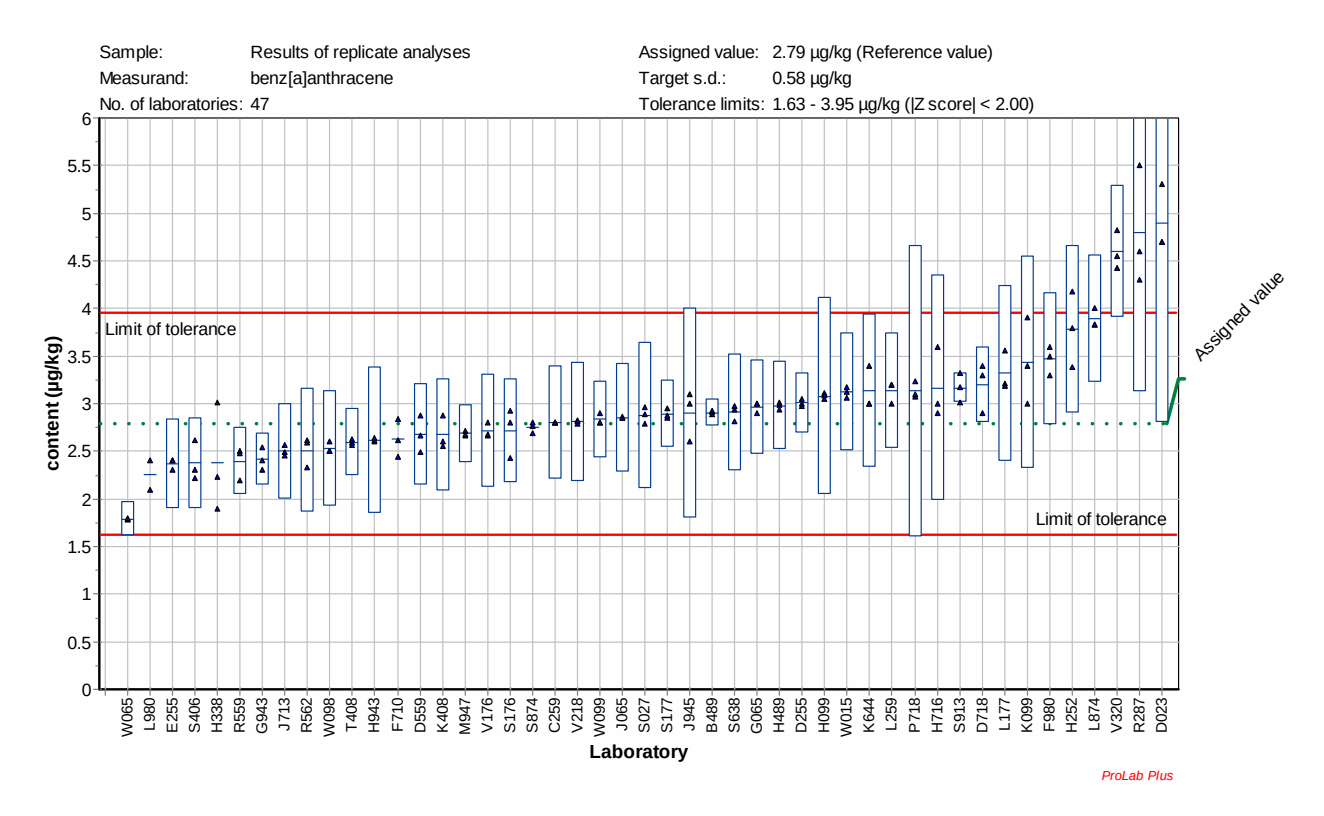
LabID	Preparation	Extraction	Purification	Detection	Column	Problems
P718	No preparation	No extraction	SPE	GC-MS/MS	ZB50 30m-0.25mm-0.25µm	
R287	No preparation	Saponification	clean-up over silica column	GC-MS	HP-5MS 30m x 0.25mm x 0.25µm	
S027	Dilution	extraction liquide liquide	SPE	GC-MS/MS	zebron ZB50 (phenomenex) 30m 0.25mm 0.25µm	
S176	Dilution	extraction with DMSO	Solvent partitioning	GC-MS	VF-5MS 60mx0.25mmx0.25um	
S638	Dilution	Pressurized liquid extraction	GPC	HPLC-FLD	Lichrocart, PAH 5um, 250mm-4mm	
S874	column clean-up	No extraction	SPE	GC-MS	Select PAH 15 m x 0,15 mm x 0,1 µm	
S913	Dilution	liquid-liquid-extraction and complexation with caffeine	SPE	HPLC-FLD	Supelcosil LC-PAH 250mmx4,6 mm, 5 µm with precolumne Supelcosil LC-18 Supelcoguard	
V176	Dilution	No extraction	SEC	GC-MS	DB EUPHA,20 m, 0.18 mm, 0.14 µm	
W015	Dilution	Pressurized liquid extraction	SEC	HPLC-FLD	Reversed Phase C18, 5µm, 150 x 4.6mm	
W065	extraction	KOH; liquid too liquid	SPE	GC-MS	15m Varian Select PAH; 0,15mm; 0,1µm	
W098	No preparation	Saponification	Solvent partitioning	GC-HRMS	V17MS, 60 m, 0.25mm, 0.25 µm	

ANNEX 8: Data reported by participants

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

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

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



Results reported by *NRLs* for the content of benz[*a*]anthracene (BAA) in the olive oil test material. Assigned value is 2.79 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
B489	2.89	2.91	2.92	2.91	0.14
D559	2.67	2.49	2.87	2.68	0.54
D566	n.r.	n.r.	n.r.	3.30	n.r.
D718	3.3	2.9	3.4	3.2	0.4
F980	3.6	3.5	3.3	3.5	0.7
G065	2.9	3	3	3	0.5
G943	2.54	2.41	2.3	2.42	0.27
H099	3.046	3.11	3.085	3.08	1.035
H489	2.99	2.94	3.01	2.99	0.47
H716	2.9	3	3.6	3.2	1.2
H943	2.6	2.62	2.64	2.62	0.77
J945	3.1	3	2.6	2.9	1.1
K099	3.4	3.9	3	3.4	1.1
K408	2.6	2.55	2.88	2.68	0.59
K644	3	3.4	3	3.1	0.8
L259	3.2	3	3.2	3.1	0.6
L874	3.83	3.83	4.01	2.68	0.46
R559	2.51	2.2	2.48	2.4	0.35
R562	2.33	2.59	2.61	2.51	0.65
S177	2.85	2.95	2.88	2.89	0.35
S406	2.22	2.61	2.3	2.4	0.48
T408	2.59	2.63	2.56	2.58	0.35
V218	2.83	2.79	2.81	2.81	0.63
V320	4.82	4.55	4.43	4.6	0.69
W099	2.8	2.8	2.9	2.8	0.4

n.r.: not reported

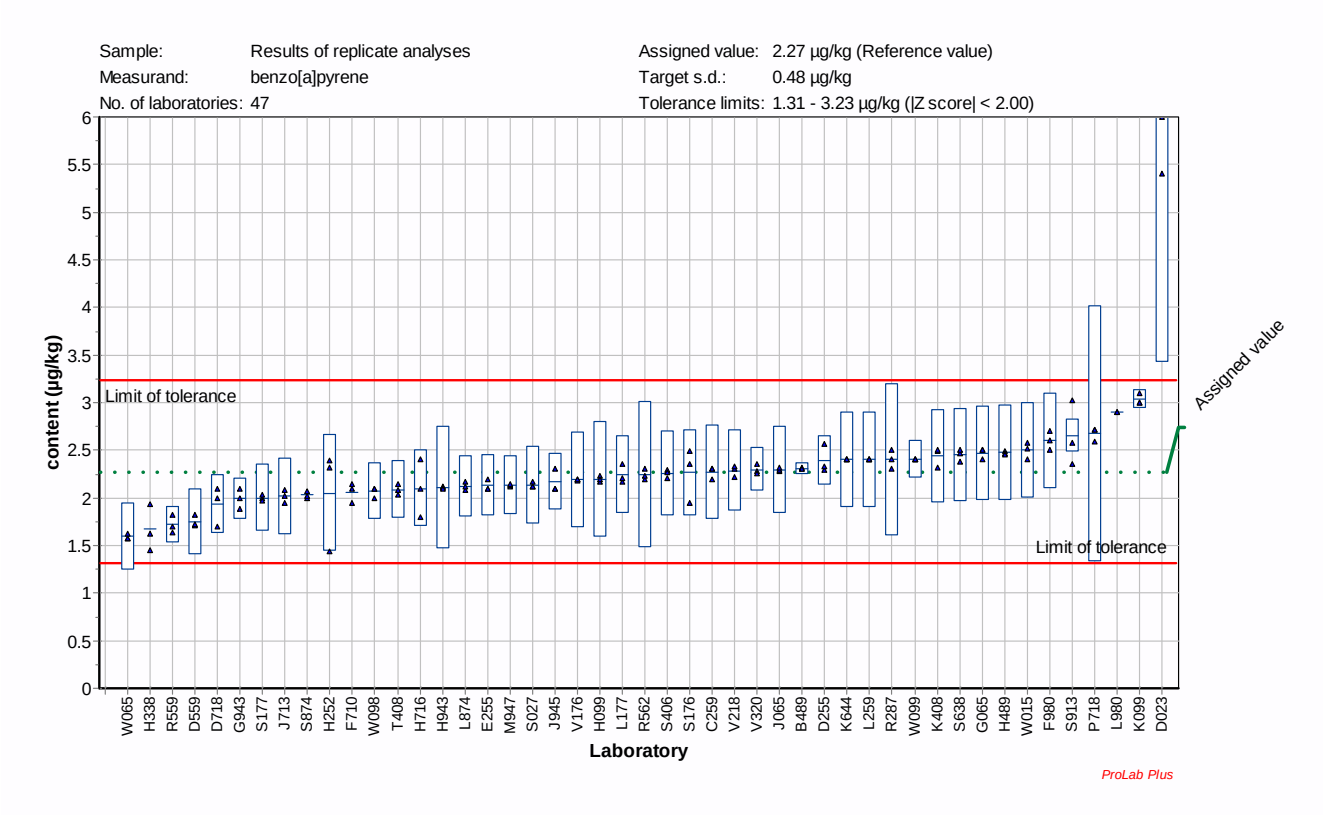
Results reported by *OCLs* for the content of benz[*a*]anthracene (BAA) in the olive oil test material. Assigned value is 2.79 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
C259	2.8	2.8	2.8	2.8	0.6
D023	4.7	5.3	4.7	4.9	**2.1**
D255	3	2.97	3.05	3.01	0.32
E255	2.3	2.4	2.4	2.4	0.48
F710	2.84	2.62	2.44	2.62	n.r.
H252	4.18	3.79	3.38	3.78	**1.76**
H338	3.01	2.23	1.9	2.38	n.r.
J065	2.86	2.85	2.85	2.85	0.57
J713	2.56	2.49	2.45	2.5	0.5
L177	3.56	3.21	3.18	3.21	0.9
L980	n.r.	2.4	2.1	2.3	n.r.
M637	< 300	< 300	< 300	< 300	n.r.
M947	2.71	2.67	2.68	2.71	0.31
P718	3.07	3.1	3.23	3.07	**1.5**
R287	5.5	4.6	4.3	4.3	1.5
S027	2.959	2.787	2.884	2.877	0.77
S176	2.8	2.92	2.43	2.72	0.546
S638	2.98	2.81	2.94	2.91	0.61
S874	2.76	2.69	2.8	2.75	n.r.
S913	3.32	3.01	3.17	3.17	0.16
V176	2.66	2.68	2.8	2.71	0.6
W015	3.178	3.068	3.125	3.124	0.6248
W065	1.78	1.78	1.8	1.79	0.18
W098	2.5	2.6	2.5	2.5	0.6

n.r.: not reported

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

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



Results reported by *NRLs* for the content of benzo[*a*]pyrene (BAP) in the olive oil test material. Assigned value is 2.27 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
B489	2.31	2.32	2.3	2.31	0.06
D559	1.71	1.82	1.72	1.75	0.35
D566	n.r.	n.r.	n.r.	2.31	n.r.
D718	2	1.7	2.1	1.9	0.3
F980	2.5	2.7	2.6	2.6	0.5
G065	2.4	2.5	2.5	2.5	0.5
G943	2.09	1.99	1.89	1.99	0.22
H099	2.17	2.226	2.192	2.196	0.61
H489	2.49	2.47	2.46	2.47	0.5
H716	2.1	2.4	1.8	2.1	0.4
H943	2.12	2.11	2.09	2.11	0.65
J945	2.3	2.1	2.1	2.2	0.3
K099	3	3	3.1	3	0.1
K408	2.32	2.49	2.5	2.44	0.49
K644	2.4	2.4	2.4	2.4	0.5
L259	2.4	2.4	2.4	2.4	0.5
L874	2.17	2.08	2.12	2.12	0.32
R559	1.82	1.64	1.7	1.72	0.19
R562	2.2	2.23	2.31	2.25	0.77
S177	2	1.97	2.03	2	0.35
S406	2.29	2.27	2.21	2.3	0.46
T408	2.15	2.03	2.08	2.06	0.3
V218	2.31	2.33	2.22	2.29	0.43
V320	2.28	2.35	2.26	2.3	0.23
W099	2.4	2.4	2.4	2.4	0.2

n.r.: not reported

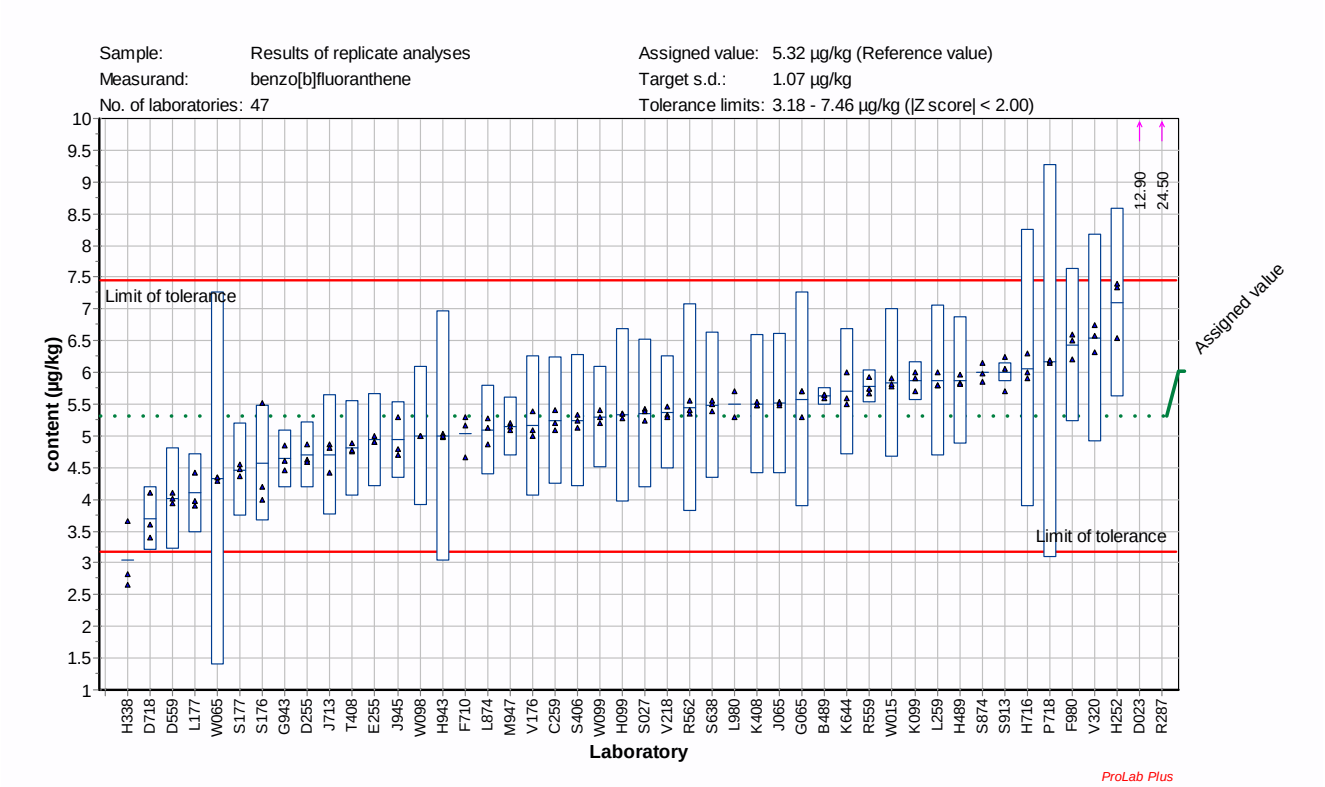
Results reported by *OCLs* for the content of benzo[*a*]pyrene (BAP) in the olive oil test material. Assigned value is 2.27 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
C259	2.3	2.3	2.2	2.3	0.5
D023	5.4	6	6.7	6	**2.6**
D255	2.29	2.33	2.56	2.39	0.26
E255	2.1	2.1	2.2	2.1	0.315
F710	2.14	2.1	1.95	2.1	n.r.
H252	2.39	1.44	2.32	2.05	**1.22**
H338	1.63	1.93	1.45	1.67	n.r.
J065	2.28	2.29	2.32	2.3	0.46
J713	2.08	2.02	1.95	2.02	0.4
L177	2.36	2.17	2.21	2.21	0.4
L980	n.r.	2.9	2.9	2.8	n.r.
M637	< 300	< 300	< 300	< 300	n.r.
M947	2.12	2.13	2.15	2.16	0.31
P718	2.71	2.59	2.72	2.59	**1.3**
R287	2.5	2.4	2.3	2.4	0.8
S027	2.117	2.167	2.126	2.137	0.41
S176	2.35	1.95	2.49	2.26	0.455
S638	2.47	2.5	2.38	2.45	0.49
S874	2	2.07	2.02	2.03	n.r.
S913	2.58	2.35	3.02	2.65	0.172
V176	2.2	2.18	2.19	2.19	0.5
W015	2.409	2.575	2.516	2.5	0.5
W065	1.58	1.62	1.58	1.59	0.35
W098	2.1	2.1	2	2.1	0.3

n.r.: not reported

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

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



Results reported by *NRLs* for the content of benzo[*b*]fluoranthene (BBF) in the olive oil test material. Assigned value is 5.32 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
B489	5.64	5.59	5.64	5.62	0.14
D559	3.93	4.11	4.02	4.02	0.8
D566	n.r.	n.r.	n.r.	5.70	n.r.
D718	3.6	4.1	3.4	3.7	0.5
F980	6.6	6.2	6.5	6.4	1.2
G065	5.7	5.7	5.3	5.6	1.7
G943	4.85	4.45	4.61	4.64	0.46
H099	5.28	5.343	5.352	5.325	1.374
H489	5.83	5.97	5.81	5.97	1.02
H716	6	6.3	5.9	6.1	2.2
H943	4.98	5.04	4.99	5	1.97
J945	5.3	4.7	4.8	4.9	0.6
K099	5.7	5.9	6	5.8	0.3
K408	5.49	5.48	5.54	5.5	1.1
K644	5.5	5.6	6	5.7	1
L259	5.8	5.8	6	5.9	1.2
L874	5.13	5.27	4.86	5.09	0.71
R559	5.93	5.67	5.75	5.78	0.26
R562	5.35	5.41	5.56	5.44	1.63
S177	4.48	4.36	4.56	4.47	0.74
S406	5.13	5.34	5.24	5.2	1.04
T408	4.89	4.75	4.77	4.78	0.75
V218	5.47	5.33	5.3	5.37	0.89
V320	6.57	6.75	6.32	6.55	1.64
W099	5.3	5.4	5.2	5.3	0.8

n.r.: not reported

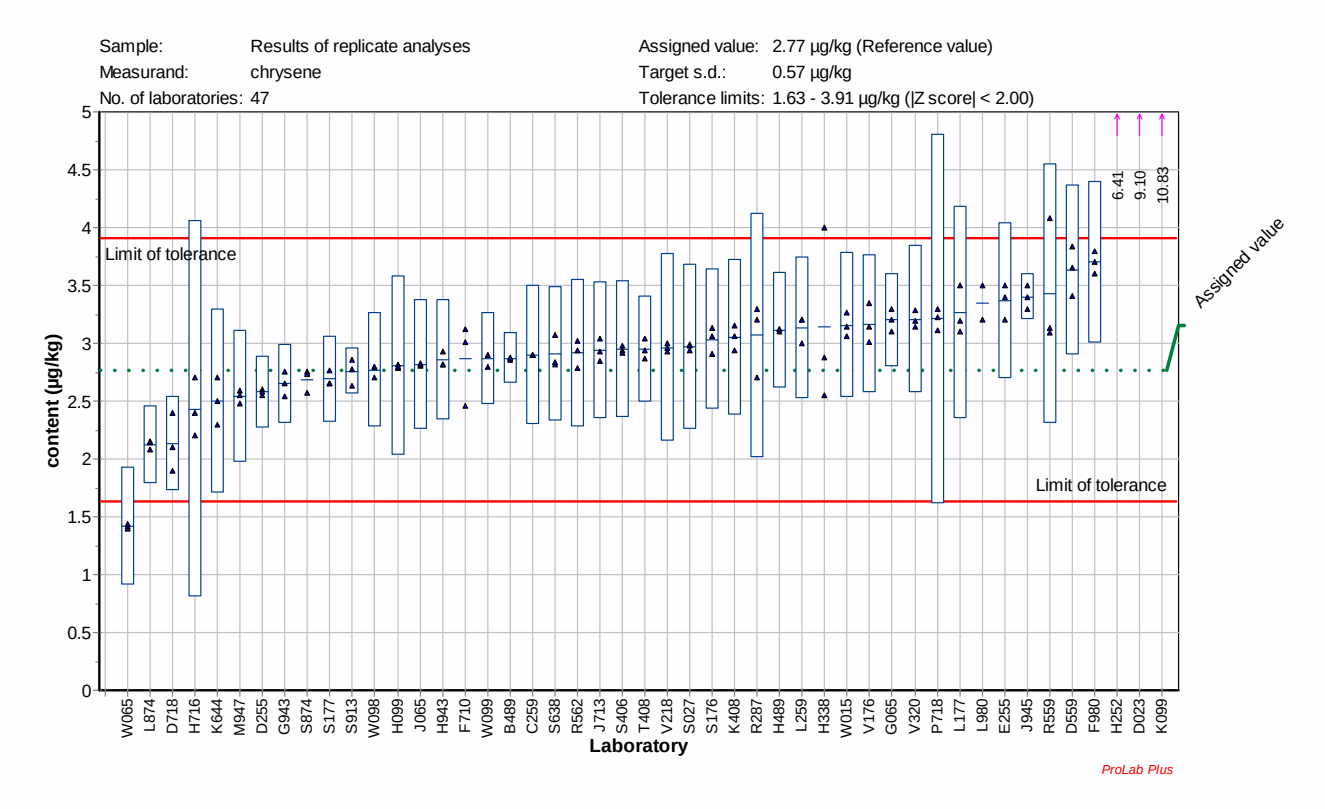
Results reported by *OCLs* for the content of benzo[*b*]fluoranthene (BBF) in the olive oil test material. Assigned value is 5.32 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
C259	5.4	5.1	5.2	5.2	1
D023	12.7	12.7	13.3	12.9	**5.7**
D255	4.63	4.58	4.87	4.69	0.52
E255	4.9	5	4.9	4.9	0.735
F710	5.29	5.16	4.66	5.16	n.r.
H252	7.35	7.4	6.54	7.1	**2.98**
H338	2.83	3.66	2.66	3.01	n.r.
J065	5.48	5.54	5.52	5.51	1.1
J713	4.86	4.81	4.43	4.7	0.94
L177	4.43	3.9	3.97	3.97	0.6
L980	n.r.	5.3	5.7	5.5	n.r.
M637	< 300	< 300	< 300	< 300	n.r.
M947	5.2	5.1	5.14	5.19	0.47
P718	6.15	6.19	6.19	6.19	**3.1**
R287	26.7	27.1	19.7	26.7	9.3
S027	5.429	5.388	5.242	5.353	1.17
S176	4.2	5.52	4	4.57	0.916
S638	5.5	5.39	5.55	5.48	1.15
S874	6.15	5.98	5.85	5.99	n.r.
S913	6.25	6.05	5.71	6	0.148
V176	5.39	4.99	5.09	5.16	1.1
W015	5.91	5.788	5.81	5.836	1.1672
W065	4.3	4.35	4.35	4.33	**2.94**
W098	5	5	5	5	1.1

n.r.: not reported

Distribution of individual results of replicate determinations of chrysene (CHR) in the olive oil test sample.

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



Results reported by *NRLs* for the content of chrysene (CHR) in the olive oil test material. Assigned value is 2.77 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
B489	2.86	2.87	2.88	2.87	0.22
D559	3.84	3.65	3.41	3.63	0.73
D566	n.r.	n.r.	n.r.	3.35	n.r.
D718	1.9	2.1	2.4	2.1	0.4
F980	3.7	3.8	3.6	3.7	0.7
G065	3.1	3.2	3.3	3.2	0.4
G943	2.76	2.65	2.54	2.65	0.34
H099	2.788	2.821	2.799	2.803	0.776
H489	3.12	3.1	3.12	3.1	0.5
H716	2.7	2.4	2.2	2.4	**1.6**
H943	2.82	2.82	2.93	2.86	0.52
J945	3.3	3.4	3.5	3.4	0.2
K099	13.2	8.4	10.9	10.8	**5.9**
K408	2.94	3.06	3.15	3.05	0.67
K644	2.3	2.7	2.5	2.5	0.8
L259	3.2	3.2	3	3.1	0.6
L874	2.08	2.15	2.14	2.12	0.34
R559	3.13	3.09	4.08	3.43	1.12
R562	2.94	2.79	3.02	2.92	0.64
S177	2.65	2.77	2.65	2.69	0.37
S406	2.98	2.94	2.92	2.9	0.58
T408	3.04	2.94	2.87	2.91	0.45
V218	2.93	2.96	3	2.96	0.81
V320	3.19	3.29	3.14	3.21	0.64
W099	2.8	2.9	2.9	2.9	0.4

n.r.: not reported

Results reported by *OCLs* for the content of chrysene (CHR) in the olive oil test material. Assigned value is 2.77 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [%]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
C259	2.9	2.9	2.9	2.9	0.6
D023	9	9	9.3	9.1	**4**
D255	2.55	2.6	2.58	2.58	0.31
E255	3.5	3.2	3.4	3.4	0.68
F710	3.12	2.46	3.01	3.01	n.r.
H252	5.75	7.22	6.25	6.41	**2.72**
H338	2.88	4	2.55	3.15	n.r.
J065	2.81	2.82	2.83	2.82	0.56
J713	2.93	3.04	2.85	2.94	0.59
L177	3.19	3.1	3.5	3.19	0.9
L980	n.r.	3.5	3.2	3.4	n.r.
M637	< 300	< 300	< 300	< 300	n.r.
M947	2.59	2.55	2.48	2.59	0.58
P718	3.3	3.22	3.11	3.22	**1.6**
R287	2.7	3.2	3.3	3.2	1.1
S027	2.935	2.989	2.981	2.968	0.72
S176	3.13	2.91	3.06	3.03	0.608
S638	2.82	3.07	2.84	2.91	0.58
S874	2.75	2.73	2.57	2.68	n.r.
S913	2.86	2.63	2.78	2.76	0.198
V176	3.01	3.14	3.35	3.17	0.6
W015	3.266	3.146	3.06	3.157	0.6314
W065	1.4	1.42	1.44	1.42	0.51
W098	2.8	2.8	2.7	2.8	0.5

n.r.: not reported

Results reported by *NRLs* for the sum of the four marker PAHs (SUM) in the olive oil test material. Assigned value is 13.2 µg/kg

Lab code	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
B489	13.71	**1.34**
D559	12.08	**2.41**
D566	14.7	n.r.
D718	10.9	**1.7**
F980	16.2	**3.2**
G065	14.2	**3.1**
G943	11.69	**1.75**
H099	13.404	**3.796**
H489	14.53	**2.51**
H716	13.7	3
H943	12.59	**7.6**
J945	13.4	**1.6**
K099	**23**	6
K408	13.67	**5.74**
K644	13.7	1.6
L259	14.5	1.6
L874	12.01	**1.83**
R559	13.33	**0.98**
R562	13.11	**3.67**
S177	12.05	**3.63**
S406	12.8	1.36
T408	12.33	0.99
V218	13.43	**2.7**
V320	16.65	**4.16**
W099	13.4	1

n.r.: not reported

Results reported by *OCLs* for the sum of the four marker PAHs (SUM) in the olive oil test material. Assigned value is 13.2 µg/kg

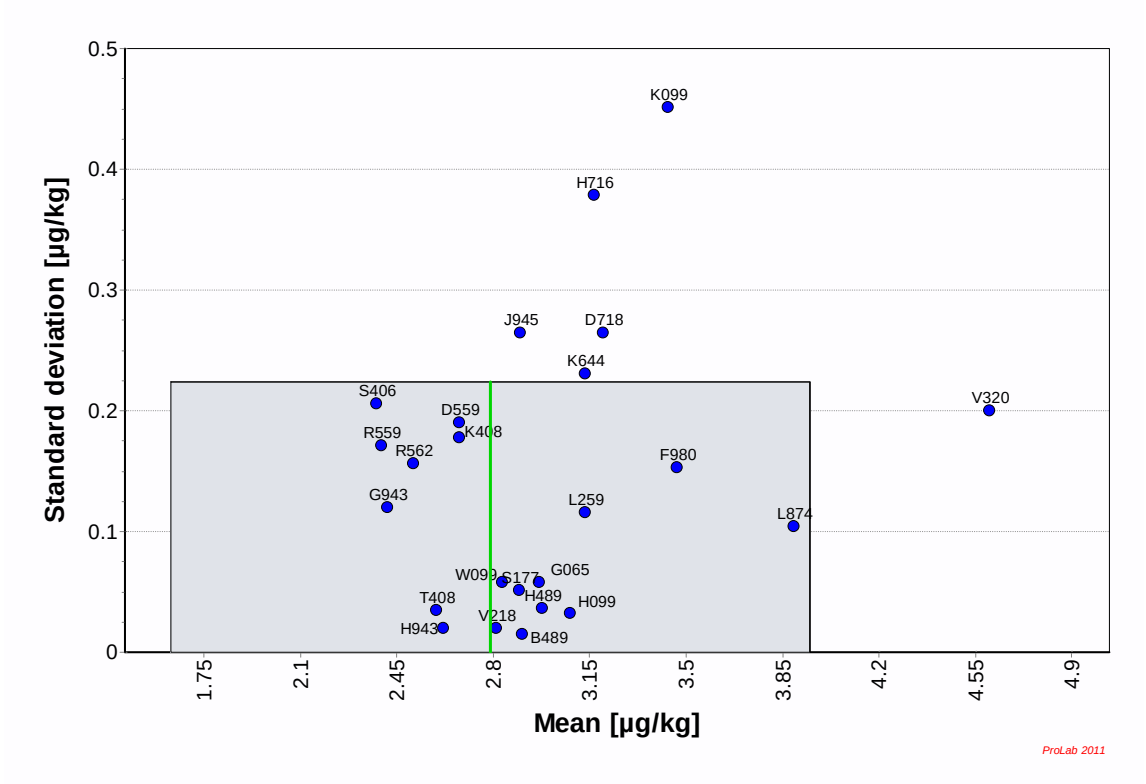
Lab code	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
C259	13.2	**5.3**
D023	**33**	**14**
D255	12.67	**1.41**
E255	12.8	**2.56**
F710	12.89	n.r.
H252	19.3	2.28
H338	10.21	n.r.
J065	13.48	**2.696**
J713	12.15	**2.43**
L177	12.58	**2.5**
L980	**14**	n.r.
M637	**< 300**	n.r.
M947	12.64	**1.63**
P718	15.07	**7.5**
R287	36.6	**12.8**
S027	13.335	**6.19**
S176	12.6	1.31
S638	13.75	1.5
S874	13.46	n.r.
S913	14.58	**0.678**
V176	13.23	1.48
W015	14.617	**2.9234**
W065	9.13	**1**
W098	12.4	**4.9**

n.r.: not reported

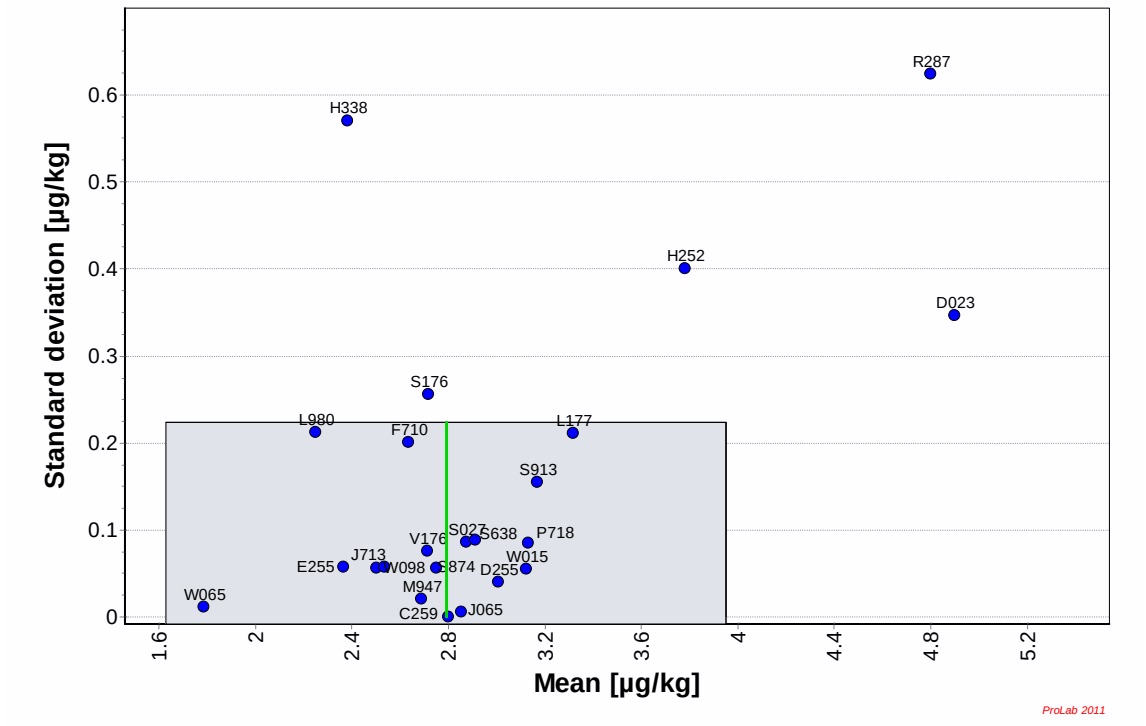
ANNEX 9: Laboratory means and repeatability standard deviation

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

NRLs

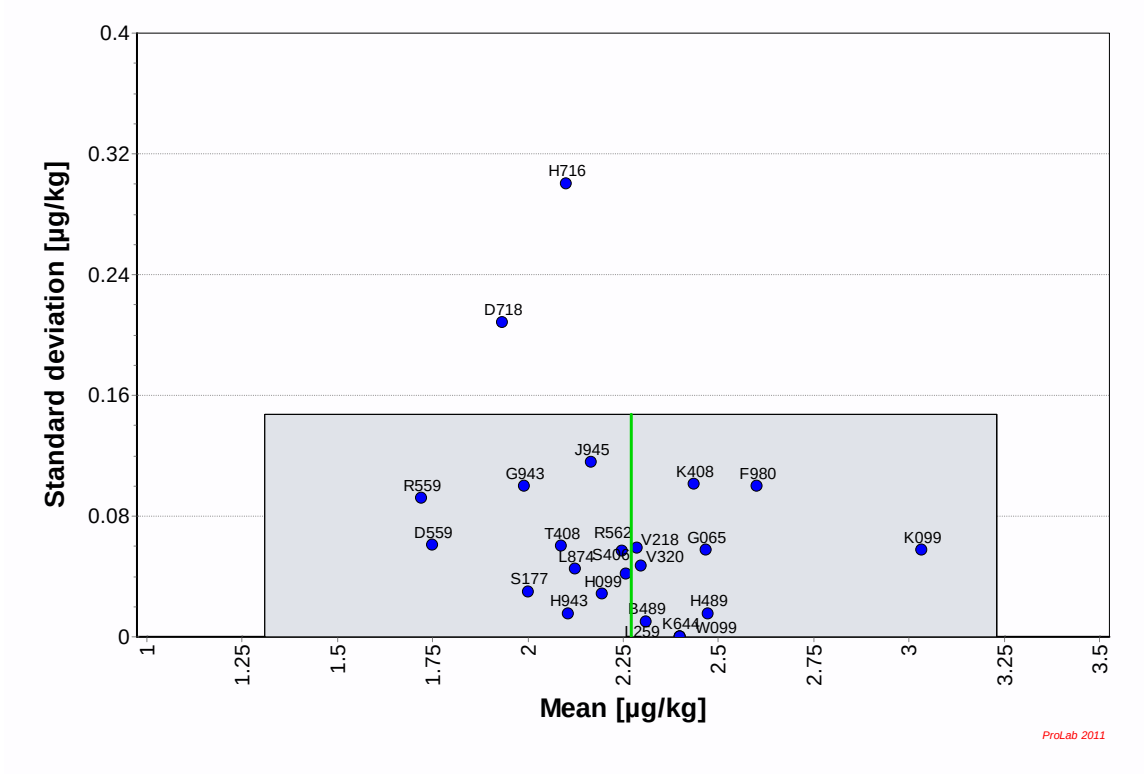


OCLs



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

NRLs



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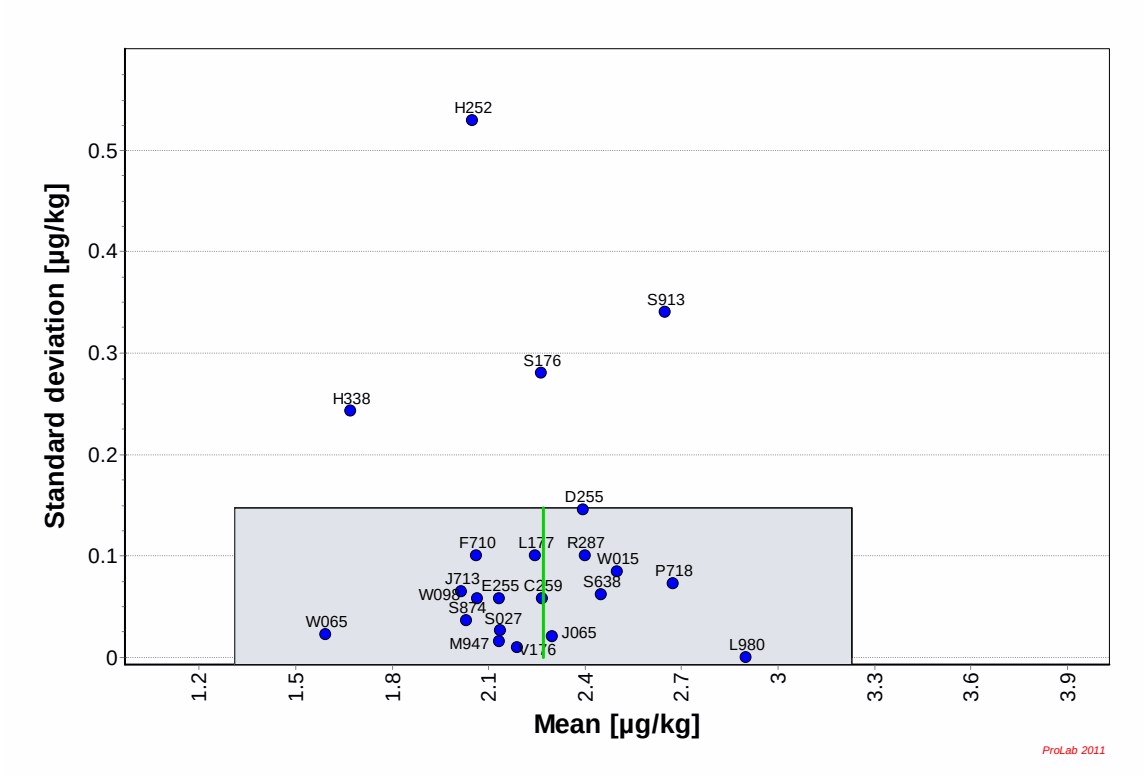
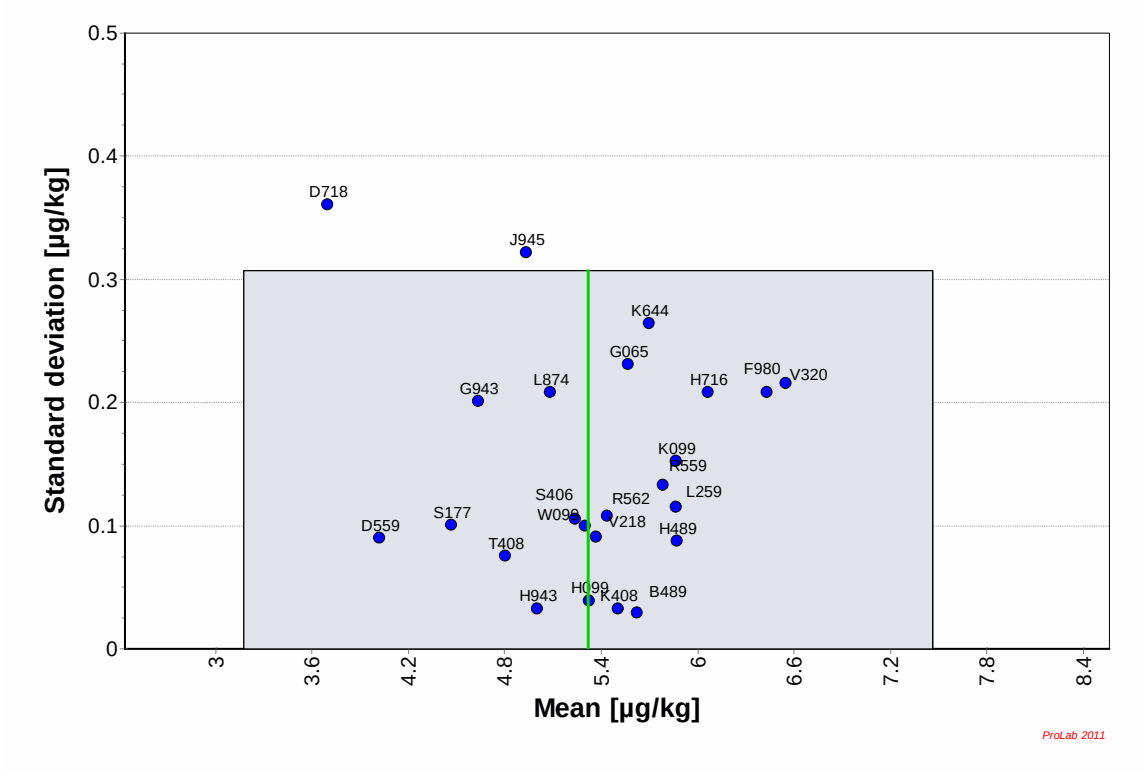


Lab means and repeatability standard deviation for the determination of BBF in the olive oil test material

NRLs



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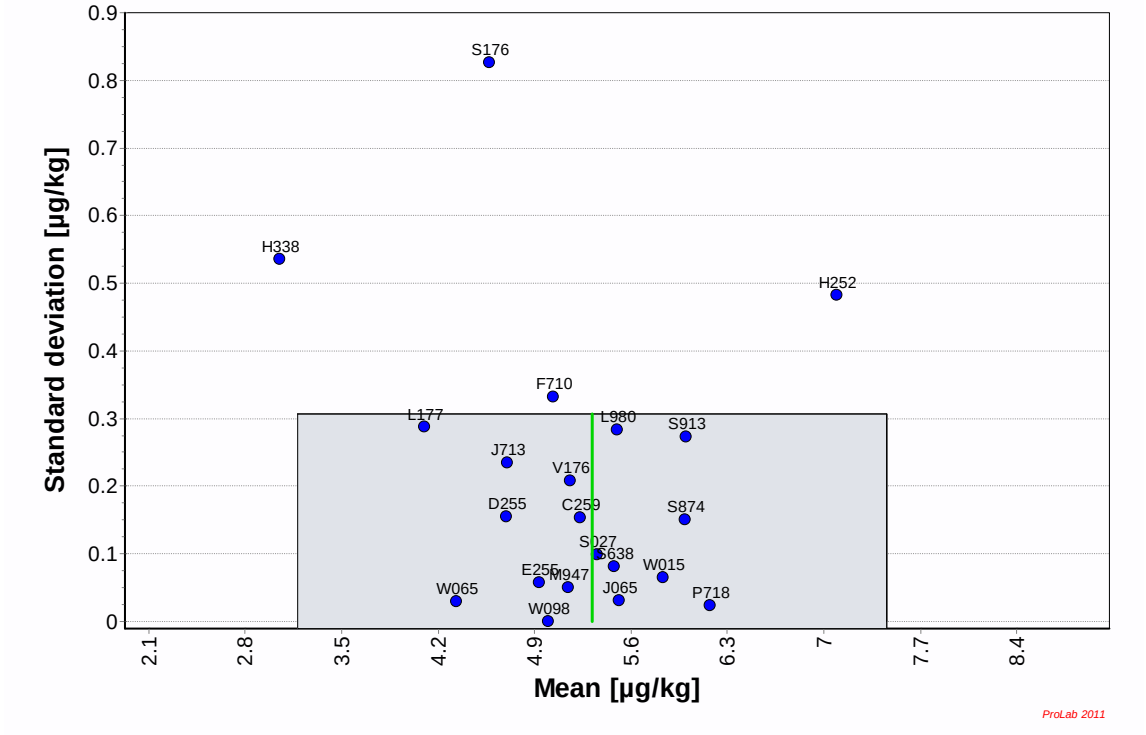
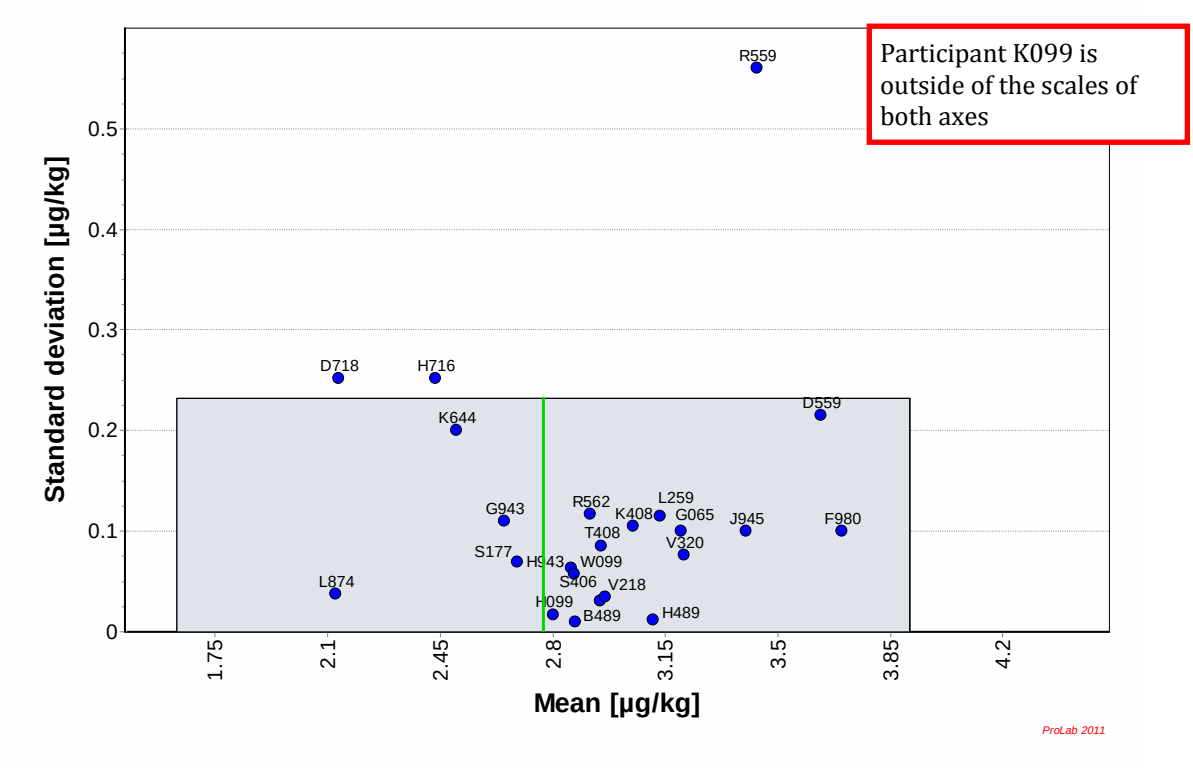
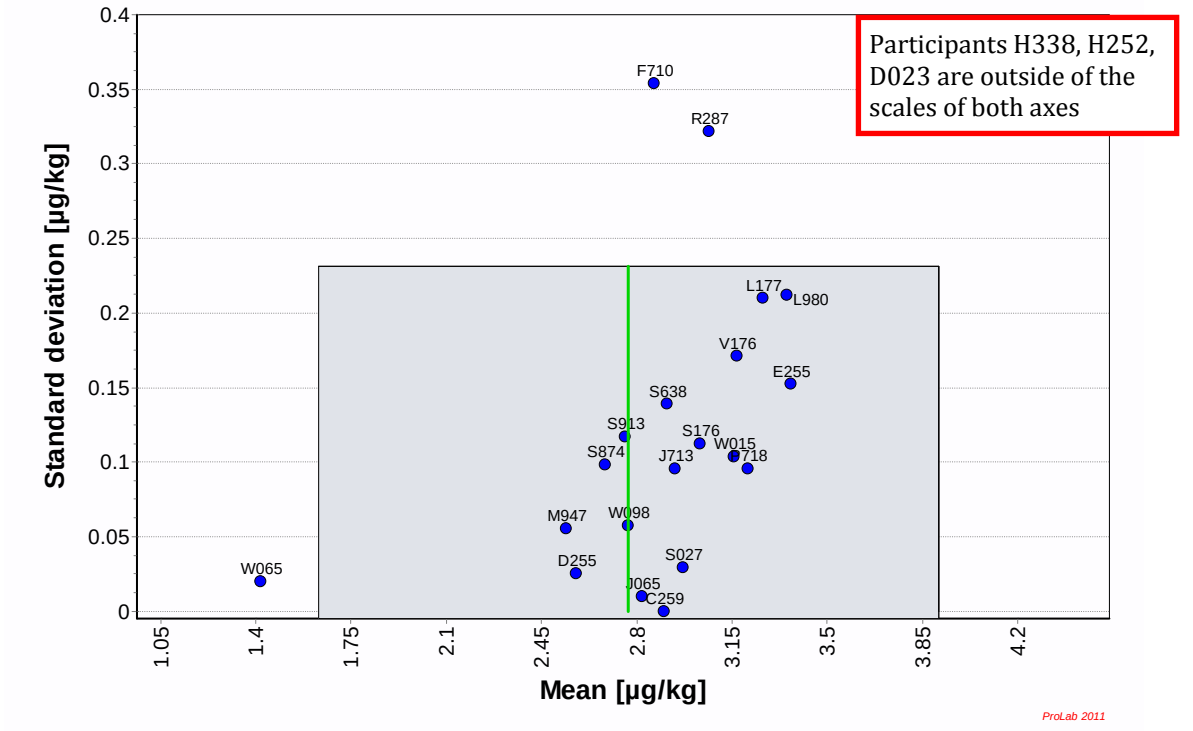


Lab means and repeatability standard deviation for the determination of CHR in the olive oil test material

NRLs



OCLs



European Commission
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Title: **Report on the 9th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons – Four marker PAHs in spiked olive oil**

Authors: Donata Lerda, Philippe Verlinde, Thomas Wenzl

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Abstract

The proficiency test here reported concerned the determination of the four marker polycyclic aromatic hydrocarbons (PAHs) in an olive oil test sample: benz[a]anthacene, benzo[a]pyrene, benzo[b]fluoranthene, and chrysene. Participants to these PT were National Reference Laboratories for PAHs (NRLs-PAHs) and EU official food control laboratories. The number of participants was 50.
The PT was organised according to ISO Standard 17043:2010.
The test material used was olive oil spiked with the target PAHs. Participants also received a solution of the PAHs either in an organic solvent for checking their instrument calibration.
The results from participants were rated with z-scores and zeta-scores. About 96 % and 88 % of the results reported by NRLs and OCLs respectively were attributed with z-scores with an absolute value of below two, which is the threshold for satisfactory performance. The zeta-score ratings were worse, which indicates problems in the estimation of reliable measurement uncertainty values.

LA-NA-25300-EN-N

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