European Commission

JRC SCIENCE AND POLICY REPORTS

Report on the 15th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in smoked meat

Stefanka Bratinova,
Zuzana Zelinkova,
Thomas Wenzl

2014

European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Stefanka Bratinova
Address: Joint Research Centre, Retieseweg 111, B-2440 Geel, Belgium
E-mail: jrc-irmm-eurl-pah@ec.europa.eu
Tel.: +32 14 571 320
Fax: +32 14 571 783

https://ec.europa.eu/jrc

JRC91933

EUR 26850 EN

ISBN 978-92-79-41238-7 (PDF)

ISSN 1831-9424 (online)

doi:10.2787/99057

Luxembourg: Publications Office of the European Union, 2014

Abstract

This report presents the results of the fifteenth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAH) on the determination of the four EU marker PAHs, benz[a]anthracene (BAA), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF) and chrysene (CHR) in smoked meat. It was conducted under ISO 17043 accreditation. Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States were admitted as participants.
In agreement with National Reference Laboratories, the test material used in this exercise was smoked sausage. 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.
The participants were free to choose the method of analysis. Reference values were used to benchmark the results reported by participants. The performance of the participating laboratories in the determination of the target PAHs in smoked meat was expressed by z-scores. Satisfactory performance with regard to z-scores was assigned to about 93% of the reported results.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Report on the 15th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in smoked meat

Stefanka Bratinova, Zuzana Zelinkova and Thomas Wenzl

EC-JRC-IRMM

(September 2014)

Table of Contents

1 Executive summary

This report presents the results of the fifteenth inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAHs) to benchmark the proficiency of National Reference Laboratories (NRLs) and several official control laboratories (OCLs) in the determination of the four EU marker PAHs, benz[*a*]anthracene (BAA), benzo[*a*]pyrene (BAP), benzo[*b*]fluoranthene (BBF) and chrysene (CHR) in smoked meat.

The test material used in this exercise was commercial smoked sausage obtained from an artisanal butcher. The sausage was additionally hot smoked at the EURL PAH in order to increase the PAH content. Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with disclosed PAH content for the verification of their instrument calibration.

Both NRLs and (OCLs) of the EU Member States participated. Twenty-six NRLs and 14 OCLs subscribed for participation.

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

Participants were free to choose the method of analysis. The performance of the participating laboratories in the determination of the target PAHs in the test materials was expressed by z-scores and zeta-scores, which describe the agreement of a participants result with the assigned property values. Additionally, the compliance of reported method performance characteristics was checked against specifications given in legislation.

This proficiency test (PT) demonstrated the competence of the participating laboratories in the analysis of regulated PAHs in smoked meat. More than 93 % of the reported test results were graded with z-scores that were below an absolute value of 2, indicating acceptable agreement with the assigned reference values of the test material.

Additionally, the EURL PAH asked participants to assess the compliance of the sample according to the legislative limits.

2 Introduction

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

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

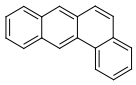
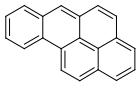
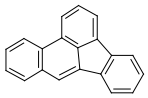
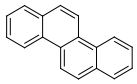
In 2002 the European Commission's Scientific Committee on Food identified 15 individual PAHs as being of major concern for human health. These 15 EU priority PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene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

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

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

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

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

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

3 Scope

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

This ILC aimed to evaluate the comparability of results reported by NRLs and EU official food control laboratories (OCLs) for the four EU marker PAHs in smoked sausages. 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.

JRC-IRMM is an ISO Standard 17043:2010 [9] accredited provider of PTs. .

4 Participating Laboratories

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

Table 2: List of participating National Reference Laboratories

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

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

From the 26 NRLs registered for participation, two NRLs did not report results; one NRL did not register for the PT.

Table 3: List of participating Official Food Control Laboratories

Institute	***Country***
MA 38 - Lebensmitteluntersuchungsanstalt der Stadt Wien	Austria
Institut für Umwelt und Lebensmittelsicherheit des Landes Vorarlberg	Austria
Amt der Kärntner LR, LUA Kärnten (ILV Kärnten)	Austria
Institut Dr. Wagner Lebensmittel Analytik GmbH	Austria
ANALYTEC® Labor für Lebensmitteluntersuchung und Umweltanalytik DI Helmut Frühwirth & DI Claus Frühwirth ZT-GmbH	Austria
Federal Laboratory for the Safety of the Food Chain	Belgium
Laboratorium ECCA NV	Belgium
Laboratoire de l'environnement et de l'alimentation de la Vendée	FRANCE
SCL MASSY	FRANCE
INOVALYS	FRANCE
LABOCEA	FRANCE
LABORATOIRE DEPARTEMENTAL D'ANALYSES DU MORBIHAN	FRANCE
CVUA MEL	Germany
GV. CONSELLERIA DE SANIDAD. CENTRO DE SALUD PÚBLICA	SPAIN

All fourteen OCLs, registered for participation, reported results.

5 Time frame

The ILC was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on 25 April 2014 (see ANNEX 2) with deadline for (see ANNEX 3) until 12 May 2014 Test samples were dispatched (see ANNEX 4) on 21 May 2014 and the deadline for reporting of results was set to 25 June 2014. The documents sent to the participants are presented in ANNEX 5.

6 Confidentiality

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

7 Test materials

7.1 Preparation

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

The smoked meat test item was prepared at the EURL PAH starting from three kilos of sausage, purchased from an artisanal butcher. As the contents of all 4 markers PAHs were lower then 0.3 µg/kg, the sausages were additionally hot-smoked using a commercial charcoal smoker. Afterwards the material was ground and homogenized, giving a sausage meat paste. Aliquots of about 20 g were packed in amber glass screw cap vials and stored in the freezer.

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

7.2 Homogeneity and stability

The smoked sausage paste was tested for significant inhomogeneity, according to the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [16], and for sufficient homogeneity according to ISO 13528 [10]. Homogeneity experiments consisted of sample extraction by pressurized liquid extraction, size-exclusion chromatography followed by solid phase extraction clean-up and gas-chromatography with mass-spectrometric detection. The method precision complied with the requirements laid down in ISO 13528.

Homogeneity experiments included duplicate analysis of 10 samples randomly selected among the amber glass vials prepared for dispatch along the filling sequence. The duplicate analyses were performed in random order. The test material was rated sufficiently homogenous and no trend was observed. Details of the homogeneity tests are given in ANNEX 7. For BAP and CHR the relative heterogeneity standard deviation was significantly different from zero at a

significance level of 5%. However, for the purpose of the PT at a target standard deviations of around 20% (see table 4) both tests requirements of IUPAC protocol and the ISO standard proved sufficient homogeneity for all the measurands, as the relative heterogeneity standard deviation was less than 30% of the target standard deviation, meaning that the residual inhomogeneity does not significantly influence the performance statement (z-score) of a particular laboratory.

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

The first set of 3 samples was stored refrigerated (~5 °C); the second set of 3 samples was stored at -80 °C (reference temperature) where no change of the material was expected. The third set of 3 samples was stored at -5 °C for the half of the period and then put at reference temperature until the end of the stability study. At the end of the test period, all 9 samples were analysed in duplicate under repeatability conditions.

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

7.3 Assigned value and standard deviation for proficiency assessment

The assigned values were determined at the EURL PAH applying a method based on isotope dilution mass spectrometry] [11]. This included the preparation of standard solutions from totally independent sources - NIST SRM 2260a and neat certified reference materials BCR® from IRMM. The analytical method was fully validated by collaborative trial and is accredited according to ISO 17025. This method will become a European standard in short time. The respective associated uncertainties of the assigned values were calculated based on the GUM approach [17].

The assigned value for the sum of PAH 4 (SUM4PAH) was calculated from the individual assigned values, and its corresponding uncertainty was calculated from the uncertainties of the individual assigned values according to error propagation considering covariances.

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

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

where U_f relates to the maximum tolerated standard measurement uncertainty, LOD to the limit of detection, α to a numeric factor depending on the concentration C as given in Commission Regulation (EC) No 333/2007, amended by Regulation (EC) 836/2011 [7].

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

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

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	**6.44**	**0.41**	1.30	20.1
Chysene	CHR	**6.70**	**0.52**	1.35	20.1
Benzo[*b*]fluoranthene	BBF	**4.93**	**0.42**	1.00	20.2
Benzo[*a*]pyrene	BAP	**8.54**	**0.49**	1.71	20.1
Sum of the four marker PAHs	SUM4PAH	**26.61**	**1.21**	2.73	10.2

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

8 Design of the proficiency test

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

Participants were asked to report besides analysis results also details of the performance of the applied analysis method (see ANNEX 9). Additionally, the participants were asked to assess the compliance of the sample according to the current legislative limits.

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

9 Evaluation of Laboratories

9.1 General

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the test materials, which was expressed by z-scores [10]. zeta-Scores were calculated in addition considering the uncertainty of the test results as estimated by each participant.

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

The results as reported by participants are listed in ANNEX 10. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed.

9.2 Evaluation criteria

z-Scores

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

Equation 3 $$z = \frac{\left(x_{lab} - X_{assigned}\right)}{\sigma_P}$$ [10]

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

zeta-Scores

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

Equation 4 $$zeta = \frac{x_{lab} - X_{assigned}}{\sqrt{u_{lab}^2 + u_{assigned}^2}}$$ [10]

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

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

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

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [**Error! Bookmark not defined.**]. The following scheme was applied for the interpretation of z-scores:

|score| ≤ 2.0 = satisfactory performance
2.0<|score| < 3.0 = questionable performance
|score| ≥ 3.0 = unsatisfactory performance

9.3 Evaluation of results

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

Each laboratory had to report a total of 17 results; therefore the expected number of results of the 40 reporting participants was 680. Two NRLs did not report results due to technical problems. In total 646 results were submitted, which equals to 95 % of the maximum number of results. The results reported by participants are presented in ANNEX 10.

Statistical evaluation of the results was performed using PROLab software [12]. Robust mean values and robust standard deviations were calculated according to Algorithm A+S of ISO 13528:2005 [10].

It should be noted that the robust means calculated from the participants' results (ANNEX 10) fall inside the confidence interval for the assigned values for all parameters (Robust standard deviations for the 4 markers PAHs in smoked sausage were lower than the target standard deviations.

93.2 % of the results reported by the participants were rated as satisfactory (z-scores < = +/- 2). Only 0.5 % of the results (one result) fell in the unsatisfactory field of z-scores > +/- 3 (Figure 1).

Only four participants had less than 80% satisfactory z-scores and two participants did not report results. In general the overall performance of the participants could be summarised as satisfactory.

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

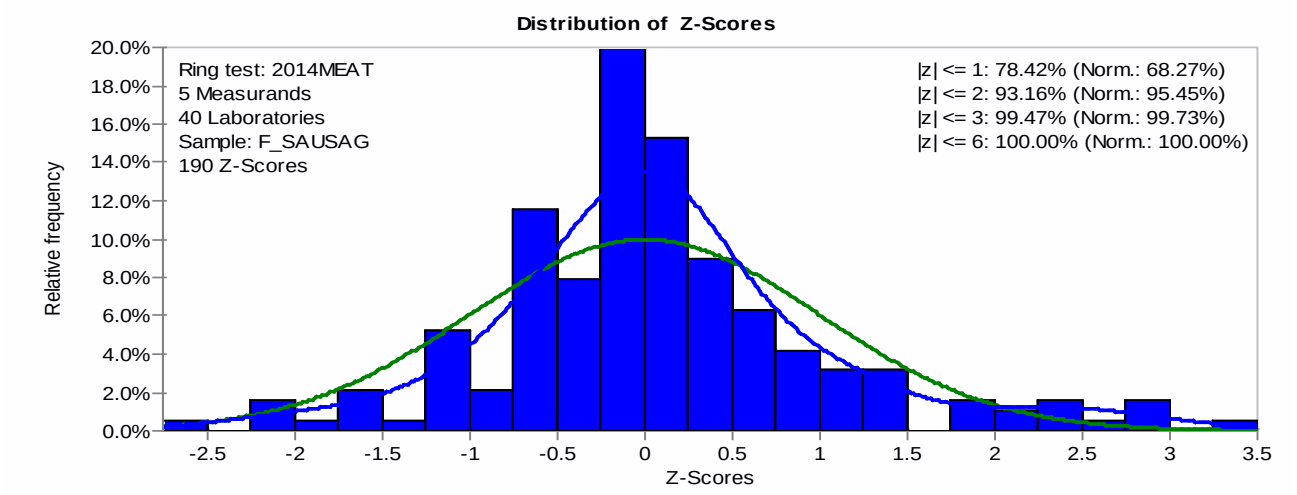


Figure 2 and Figure 3 provide overviews of the individual z-scores assigned to the results for smoked sausage test material for NRLs and OCLs respectively. The larger the triangles, the larger were the differences to the assigned values. Yellow triangles represent z-scores in the questionable and red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

The numerical values of the calculated z-scores are compiled in Table 6. All z-scores with an absolute value of ≥ 2 are highlighted in yellow on a yellow background.

Table 7 present the respective zeta-scores. Data outside the satisfactory performance range are highlighted in red. The assessment of the performance of the participants based on the reported measurement uncertainty gave a less favourable picture. Only 75% of the zeta-scores assigned for the four individual analytes and for the SUM4PAH were within the satisfactory performance range. It has to be noted that the absolute values of the zeta-scores were for many participants much higher than the z-scores attributed to the same results.

Consequently the laboratories perform according to internationally agreed standards, which form the basis for the z-scores, but seem to have difficulties in estimating realistic measurement uncertainty values.

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

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

Estimating realistic measurement uncertainty values still causes major problem for a number of participants. The compliance of the reported uncertainty with the maximum thresholds given by the "fitness-for-purpose" function U_f was assessed and non-complying uncertainties are highlighted in yellow. However, attention should be paid to the unrealistic low uncertainties reported by some participants. Comparing the precision estimated from the results of the three replicate analyses with the uncertainty reported with the final values, it becomes obvious that some laboratories based their uncertainty estimates purely on the standard deviation of the three replicate analyses. The relative expanded uncertainty reported by the participants for all the parameters and samples varied widely - between 1% and 60% with the two extremes of 13 values less than 5 % and 15 values above 40% [Figure 4].

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

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

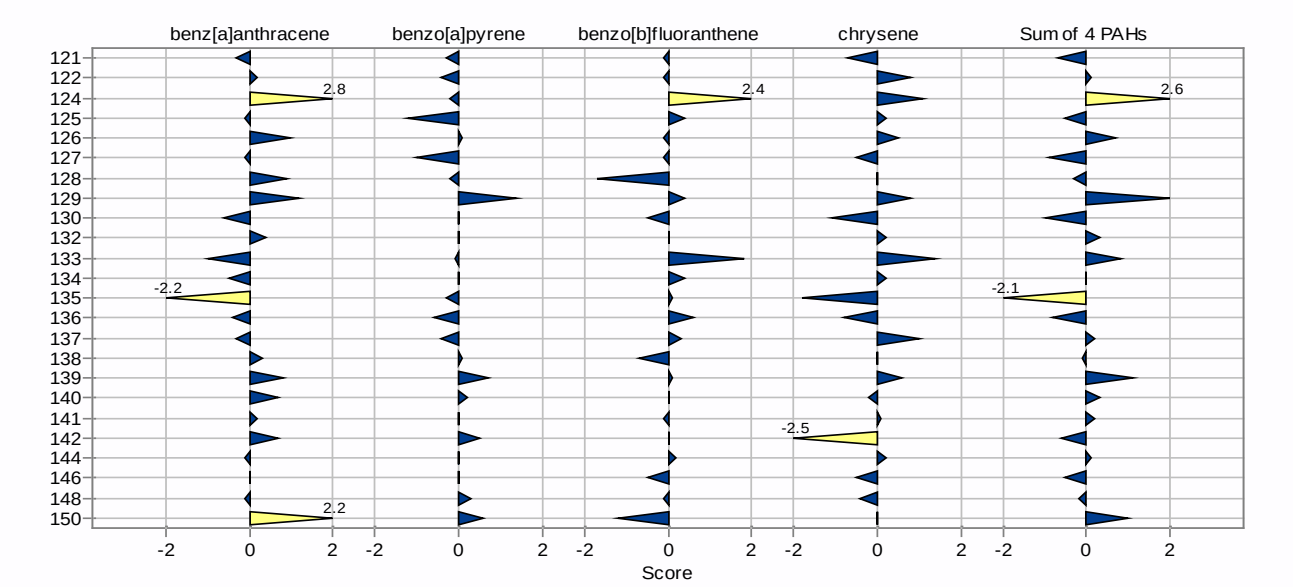


Figure 3: Graphical presentation of **z-scores** corresponding to the "final values for proficiency assessment" reported by the OCLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the smoked meat.

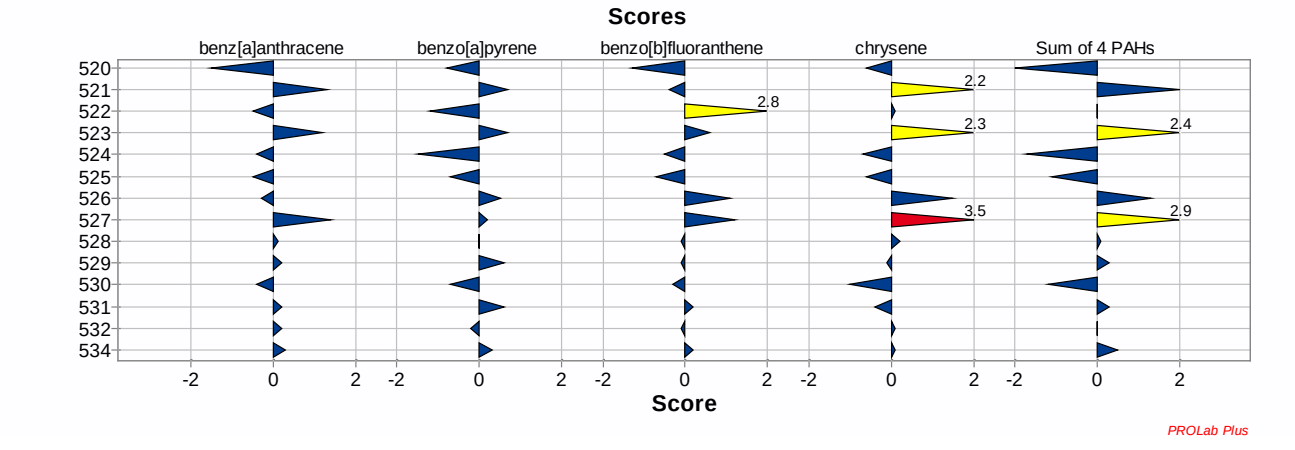


Table 6: Compilation of z-scores calculated from the "final values" reported by the participants for test material**:**

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

	Sample/Measurand				
Lab Code	BAA	BAP	BBF	CHR	SUM4PAH
	NATIONAL CONTROL LABORATORIES (NRLs)				
121	-0.3	-0.3	-0.1	-0.7	-0.7
122	0.2	-0.4	-0.1	0.8	0.1
123					
124	2.8	-0.2	2.4	1.1	2.6
125	-0.1	-1.2	0.4	0.2	-0.5
126	1.0	0.1	-0.1	0.5	0.7
127	-0.1	-1.0	-0.1	-0.5	-0.9
128	0.9	-0.2	-1.7	0.0	-0.3
129	1.2	1.4	0.4	0.8	2.0
130	-0.6	0.0	-0.5	-1.1	-1.0
131					
132	0.4	0.0	0.0	0.2	0.3
133	-1.0	-0.1	1.8	1.4	0.8
134	-0.5	0.0	0.4	0.2	0.0
135	-2.2	-0.3	0.1	-1.8	-2.1
136	-0.4	-0.6	0.6	-0.8	-0.8
137	-0.3	-0.4	0.3	1.0	0.2
138	0.3	0.1	-0.7	0.0	-0.1
139	0.8	0.7	0.1	0.6	1.1
140	0.7	0.2	0.0	-0.2	0.3
141	0.2	0.0	-0.1	0.1	0.2
142	0.7	0.5	0.0	-2.5	-0.6
144	-0.1	0.0	0.2	0.2	0.1
146	0.0	0.0	-0.5	-0.5	-0.5
148	-0.1	0.3	-0.1	-0.4	-0.2
150	2.2	0.6	-1.2	0.0	1.0
	OFFICIAL CONTROL LABORATORIES (OCLs)				
520	-1.5	-0.8	-1.3	-0.6	-2.0
521	1.3	0.7	-0.4	2.2	2.0
522	-0.5	-1.2	2.8	0.1	0.0
523	1.2	0.7	0.6	2.3	2.4
524	-0.4	-1.5	-0.5	-0.7	-1.7
525	-0.5	-0.7	-0.7	-0.6	-1.1
526	-0.3	0.5	1.1	1.5	1.3
527	1.4	0.2	1.2	3.5	2.9
528	0.1	0.0	-0.1	0.2	0.1
529	0.2	0.6	-0.1	-0.1	0.3
530	-0.4	-0.7	-0.3	-1.0	-1.2
531	0.2	0.6	0.2	-0.4	0.3
532	0.2	-0.2	-0.1	0.1	0.0
534	0.3	0.3	0.2	0.1	0.5

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

zeta-scores outside the satisfactory range (|zeta| > 2) are highlighted in red. Yellow highlighted cells indicate measurement uncertainty values that did not comply with the thresholds given by the "fitness-for-purpose" function U_f (BAA, BAP, BBF, and CHR)

	BAA			BAP			BBF			CHR			SUM		
Assigned value +/- U, µg/kg	6.44 ± 0.41			8.54 ± 0.49			4.93 ± 0.42			6.7 ± 0.52			26.61 ± 1.21		
	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score	Result	MU	zeta-score
Lab code	µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%		µg/kg	%	
	National Reference Laboratories (NRLs)														
121	6.07	3	-1.6	8.06	4	-1.6	4.84	5	-0.4	5.73	5	-3.3	24.7		-3.2
122	6.7	30	0.3	7.8	30	-0.6	4.8	30	-0.2	7.8	30	0.9	27	15	0.2
123															
124	10.031	67	1.1	8.175	46	-0.2	7.327	35	1.8	8.166	47	0.8	33.7	49	0.9
125	6.28	20	-0.2	6.56	21	-2.7	5.37	16	0.9	7	22	0.4	25.21	22	-0.5
126	7.7	28	1.2	8.7	23	0.2	4.8	23	-0.2	7.4	32	0.6	28.6	14	1.0
127	6.32	3	-1	6.9	12	-3	4.8	6	-1	6.05	7	-1.9	24.07	4	-3.3
128	7.58	26	1.1	8.18	34	-0.3	3.24	30	-3.2	6.67	22	0.0	25.67	15	-0.5
129	8.02	22	1.7	10.9	10	4.0	5.34	19	0.7	7.73	22	1.2	31.99	39	0.9
130	5.71	14	-1.6	8.54	13	0.0	4.44	40	-0.5	5.2	26	-2.1	23.9	40	-0.6
131															
132	6.93	22	0.6	8.61	19	0.1	4.89	17	-0.1	6.94	27	0.2	27.36	20	0.3
133	5.12	64	-0.8	8.38	58	-0.1	6.69	54	1.0	8.52	58	0.7	28.7	30	0.5
134	5.84	20	-1.0	8.61	20	0.1	5.33	20	0.7	6.91	20	0.3	26.69	10	0.1
135	3.59	50	-3.1	8.08	50	-0.2	5.04	50	0.1	4.22	50	-2.3	20.94	50	-1.1
136	5.87	20	-0.9	7.55	20	-1.2	5.53	20	1.0	5.58	20	-1.8	24.5	20	-0.8
137	6.108	20	-0.5	7.904	20	-0.8	5.194	20	0.5	8.009	20	1.6	27.216	20	0.2
138	6.8	4	1.5	8.7	3	0.6	4.2	7	-2.9	6.7	5	0.0	26.4	10	-0.1
139	7.47	20	1.3	10	20.0	1.2	5.04	20	0.2	7.48	20	1.0	29.7	20	1.0
140	7.4	23	1.1	8.9	20	0.4	4.9	30	0.0	6.4	20	-0.4	27.5	11	0.5
141	6.73	16	0.5	8.62	17	0.1	4.84	18	-0.2	6.86	16	0.3	27.05	9	0.3
142	7.4	30	0.9	9.4	30	0.6	4.9	30	0.0	3.4	30	-5.8	25	15	-0.8
144	6.26	18	-0.3	8.5	14	-0.1	5.15	14	0.5	7.02	18	0.5	26.93	28	0.1
146	6.39	15	-0.1	8.49	10	-0.1	4.39	15	-1.4	6.01	13	-1.5	25.3	7	-1.2
148	6.3	3	-0.6	9	4	1.6	4.8	2	-0.6	6.1	3	-2.2	26.2	11	-0.3
150	9.32	17	3.5	9.59	18	1.2	3.7	20	-2.9	6.69	20	0.0	29.3	38	0.5
	Official Control Laboratories (OCLs)														
520	4.46			7.15			3.62			5.85			21.08		
521	8.1	27	1.5	9.8	19	1.3	4.5	22	-0.8	9.7	22	2.7	32	27	1.2
522	5.73	20	-1.2	6.44	20	-3.0	7.71	20	3.5	6.85	20	0.2	26.73	20	0.0
523	8	27	1.4	9.7	20	1.2	5.5	16	1.2	9.8	29	2.1	33	21	1.8
524	5.86	20	-0.9	6.03	20	-3.9	4.41	20	-1.1	5.69	20	-1.6	21.98	20	-2.0
525	5.84	20	-1.0	7.42	20	-1.4	4.26	20	-1.4	5.94	20	-1.2	23.5	20	-1.3
526	6.06	25	-0.5	9.33	25	0.7	6.06	25	1.4	8.68	25	1.8	30.13	25	0.9
527	8.3	39	1.1	8.8	44	0.1	6.1	34	1.1	11.4	41	2.0	34.6	40	1.2
528	6.56	20	0.2	8.62	20	0.1	4.86	20	-0.1	6.96	20	0.3	27.01	20	0.1
529	6.7	20	0.4	9.5	15	1.3	4.8	25	-0.2	6.5	20	-0.3	27.5		
530	5.90	30	-0.6	7.32	30	-1.1	4.66	30	-0.4	5.376	30	-1.6	23.26	22	-1.3
531	6.7	40	0.2	9.5	40	0.5	5.1	40	0.2	6.2	40	-0.4	27.5	23	0.3
532	6.65	20	0.3	8.26	20	-0.3	4.86	20	-0.1	6.88	20	0.2	26.65	24	0.0
534	6.85	25	0.5	9.1	21	0.6	5.17	14	0.6	6.81	12	0.2	27.93	25	0.4

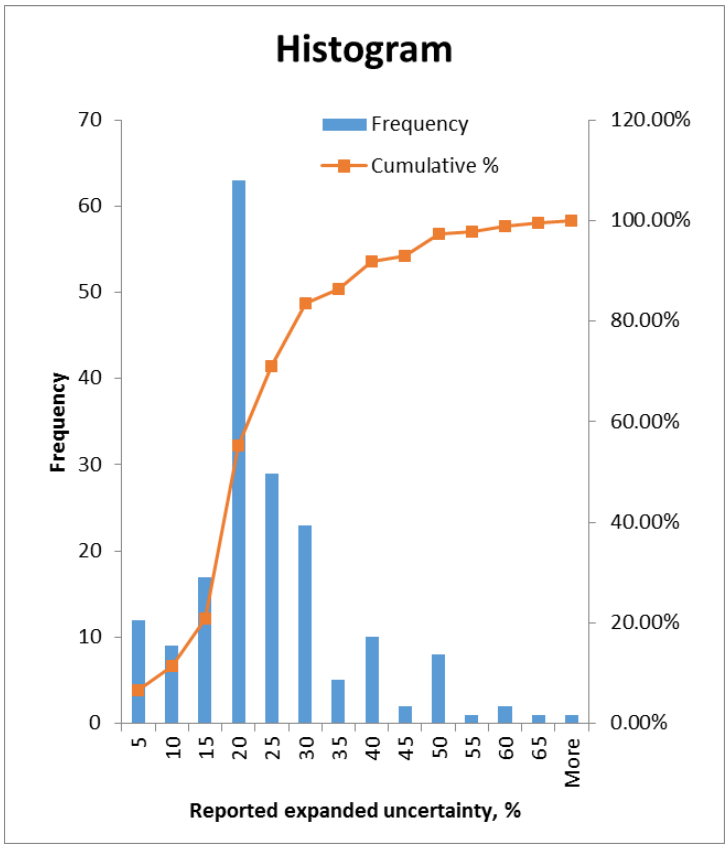


Figure 4 Histogram of the relative expanded uncertainties allocated to the reported test results for the 4 markers PAHs in smoked meat.

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

As could be seen from the Kernel density plots (ANNEX 10) the distributions of results are close to the Gaussian distribution. The major modes are close to the assigned (reference) value and the robust mean calculated from the results of the participants. This supports the conclusion that the measurement of PAHs in smoked sausage samples is well under control.

The figures in ANNEX 11 are an aid to allow laboratories to compare the performance of their method with that of other participants with respect to bias (closeness to the assigned value, plotted on the x-axis) and precision (the standard deviation for repeatability, plotted on the y-axis). A vertical solid bold line depicts the assigned value; laboratories are represented by blue dots (mean value of the replicates and the associated standard deviation of the replicates). The light blue area indicates the satisfactory performance area, which is defined by the assigned value $\pm 2\sigma_P$ along the x-axis and by the average repeatability standard deviation of the results reported by the participants along the y-axis. The latter was obtained by analysis-of-variance of the data set received for each analyte. Participants whose data are outside the satisfactory performance area should perform root cause analysis and report reasons for the deviation to the EURL PAH.

9.4 Additional information extracted from the questionnaire

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

Most of the participants have already a lot of experience with the determination of PAHs in smoked meat, as smoked meat is a regulated food matrix. Only two participants (1 NRL and 1 OCL) do not analyse this matrix in routine, while 6 (4 NRLs and 2 OCLs) participants are not accredited for this type of analysis.

More than half of the participants (22) used GC with different types of mass spectrometric detectors and 14 laboratories used HPLC-FLD for determination of PAHs. The analysis of all data revealed that laboratory performance was not linked to any analytical technique or sample preparation method used.

The survey on the instrument calibration revealed that 8 participants did not use internal standards. However, those are mainly laboratories applying HPLC/FLD as measurement technique. One laboratory used GC-MS/MS in combination with matrix matched calibration, and three participants reported the application of standard addition technique.

Most participants (except 7) reported results corrected for recovery (on purpose, or implicitly corrected by internal standards). Concerning uncertainty, most of the participants report it always next to the test results, 3 participants provided it only when the results exceed ML, another 3 participants only on request by the customer and another 3 participants do not state it at all.

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

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

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

Comments of the participants regarding this inter-laboratory comparison are summarised in ANNEX 9.

9.5 Compliance assessment

As important as the correct analysis of the test sample is the interpretation of results. The assigned analyte contents of the smoked meat test material exceeded the maximum level specified for BAP in Commission Regulation (EU) No 835/2011, but complied with the maximum level specified for the sum of four PAHs. The respective maximum levels (ML) for BAP and for the sum of the four PAHs are 5.0 µg/kg and 30.0 µg/kg.

The EURL asked the participants in this study to assess, based on their analysis results, the compliance of the sample with the current legislative limits (valid until 31.08.2014). Figure 6 presents the reported results with associated uncertainties for BaP and the sum of four PAHs in relation to the maximum levels defined in legislation (indicated by red lines).

The decision criterion for non-compliance is specified in Commission Regulation (EC) No 333/2007 [ ]. A lot or sublot shall be rejected if the content value of this lot or sublot is beyond reasonable doubt above the respective maximum level given in legislation, taking into account the expanded measurement uncertainty and correction for recovery. This translates in a content value that is derived from the measured and recovery corrected content value by subtraction of the expanded uncertainty. This situation is provided in Figure 6 if the lower end of the error bar (representing the expanded measurement uncertainty) associated with the reported result(black dot) is above the red line.

Twenty four laboratories out of 32 laboratories providing a compliance statement classified the test sample correctly as non-compliant. However, the compliance assessment cannot be retraced for participants 532 and 534, as they did not report uncertainty values.

Eight participants (25 %) assessed the non-compliant test sample as compliant. Only one of them (participant 524) applied the decision rule correctly; however, the zeta-scores for this laboratory (-3.9 for BaP) indicate that the laboratory had the analytical method not fully under control. Two other laboratories (124, and 133) declared the sample also as "compliant" but

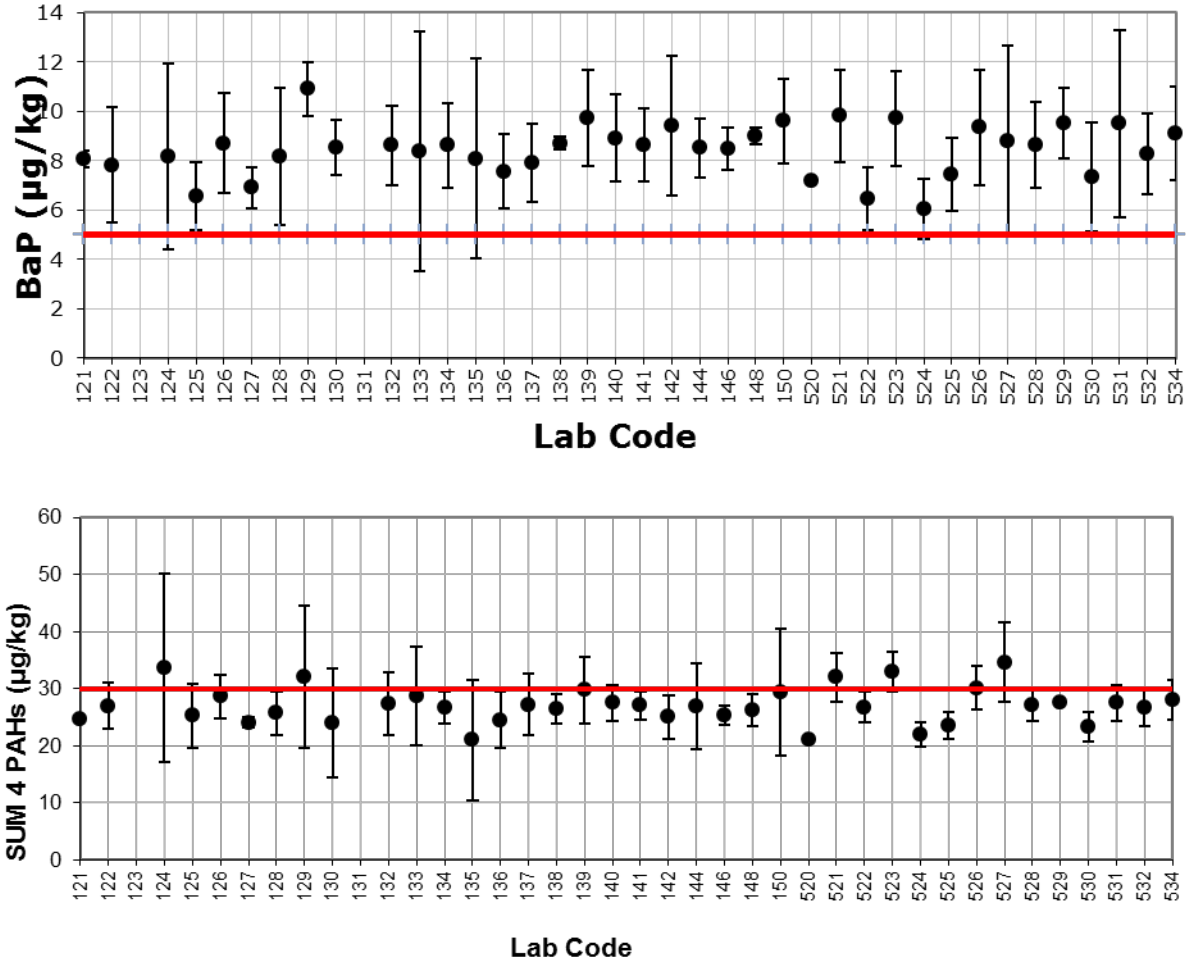


Figure 6. Distribution of the results reported by the participants and the associated expanded measurement uncertainties for BaP and the SUM PAHs in relation to the MLs.

Red lines represent the maximum levels (MLs) defined in Commission Regulation (EC) No 835/2011, 5.0 g/kg for BAP and 30.0 µg/kg for the sum of four PAHs respectively. The sample has to be declared as non-compliant if the concentration value provided by the measurement result minus the expanded measurement uncertainty is larger than the ML.

used for the assessment uncertainty values that were above the maximum uncertainty tolerated by legislation. Three laboratories (125, 148, 523, 530, 531) made false compliant decisions, as their reported result for BAP, reduced by the associated expanded measurement uncertainty provides a content value, which still exceeds the ML.

The (correct) non-compliance decision of laboratory 135 is not supported by its data. Based on its own measurements, it should have come to the conclusion that the BAP content of the test sample is not beyond reasonable doubt above the maximum level – resulting in a "compliant" statement. However, also this laboratory has to improve its analysis method in order to lower the measurement uncertainty below the maximum tolerated uncertainty threshold.

This study revealed that the interpretation of results provided problems to the participants. They are therefore requested to familiarise with the rules for interpretation of analysis results provided in the "Report on the relationship between analytical results, measurement uncertainty, recovery factors and the provisions of EU food and feed legislation, with particular reference to Community legislation concerning contaminants in food" [13] They might also

wish to consult the EURACHEM/CITAC Guide "Use of uncertainty information in compliance assessment" [14].

10 Follow-up actions for underperforming laboratories

All laboratories that got "questionable" or "non-satisfactory" performance ratings (z-scores) are urged to perform root cause analysis, and to implement corrective actions.

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

11 Conclusions

Thirty eight participants reported analysis results. The performance of most participants was satisfactory. More than 93% of the results reported by NRLs and OCLs obtained satisfactory performance ratings.

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

The great majority of participants in this PT applied analytical methods which, with regards to performance characteristics, were compliant with EU legislation. However, some participants are urged to improve in this respect.

Some laboratories need to improve in the interpretation of analysis results and assessing compliance of the test item with maximum levels laid down in legislation.

12 Acknowledgements

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

13 References

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

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

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

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

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

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

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

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

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

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

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

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

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

13 EU, Report on the relationship between analytical results, measurement uncertainty, recovery factors and the provisions of EU food and feed legislation, with particular reference to Community legislation concerning contaminants in food, Available from: http://ec.europa.eu/food/food/chemicalsafety/contaminants/report-sampling_analysis_2004_en.pdf

14 EURACHEM/CITAC Guide: Use of uncertainty information in compliance assessment, First edition 2007, Ed: S.L.R Ellison, A. Williams. Available from: http://www.eurachem.org/images/stories/Guides/pdf/Interpretation_with_expanded_uncertainty_2007_v1.pdf

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

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

14 ANNEXES

ANNEX 1 – Announcement of the PT on the IRMM webpage

ANNEX 2 – Announcement via e-mail and invitation

ANNEX 3 – Registration form

ANNEX 4 - Announcement of material dispatch

ANNEX 5 – Documents sent to participants

ANNEX 6 – Technical specifications of the calibration solutions

ANNEX 7 – Homogeneity of the test material

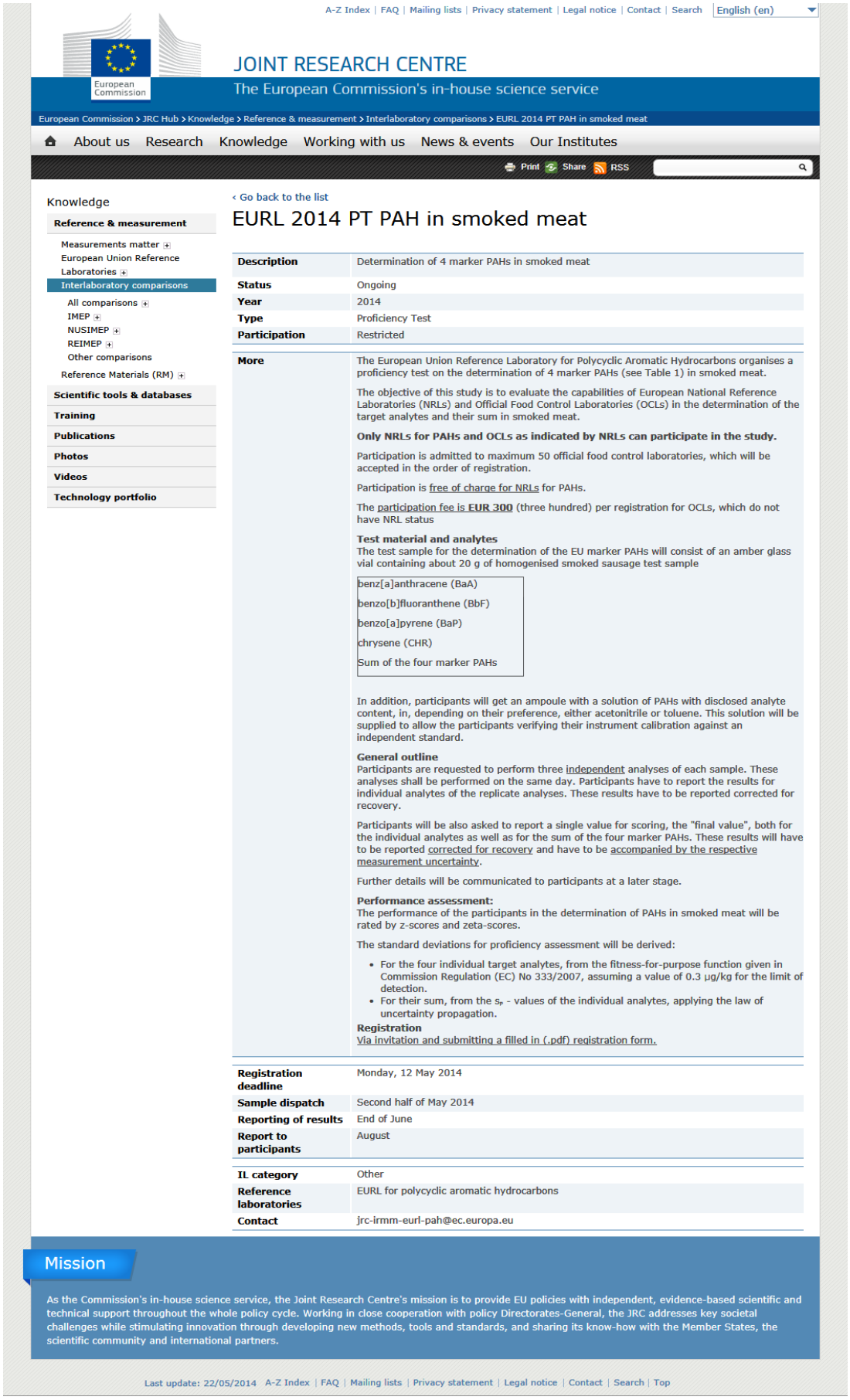
ANNEX 8 - Stability test of the test material

ANNEX 9 – Questionnaire and method performance data

ANNEX 10 – Data reported by participants

ANNEX 11 - Laboratory means and repeatability standard deviation

ANNEX 1: Announcement of the PT on the IRMM webpage



A-Z Index | FAQ | Mailing lists | Privacy statement | Legal notice | Contact | Search | English (en)

European Commission

JOINT RESEARCH CENTRE

The European Commission's in-house science service

European Commission > JRC Hub > Knowledge > Reference & measurement > Interlaboratory comparisons > EURL 2014 PT PAH in smoked meat

About us | Research | Knowledge | Working with us | News & events | Our Institutes

Print | Share | RSS

Knowledge

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

‹ Go back to the list

EURL 2014 PT PAH in smoked meat

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

More

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

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

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

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

Participation is free of charge for NRLs for PAHs.

The participation fee is **EUR 300** (three hundred) per registration for OCLs, which do not have NRL status

Test material and analytes
The test sample for the determination of the EU marker PAHs will consist of an amber glass vial containing about 20 g of homogenised smoked sausage test sample

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

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

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

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

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

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

The standard deviations for proficiency assessment will be derived:

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

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

Registration deadline	Monday, 12 May 2014
Sample dispatch	Second half of May 2014
Reporting of results	End of June
Report to participants	August
IL category	Other
Reference laboratories	EURL for polycyclic aromatic hydrocarbons
Contact	jrc-irmm-eurl-pah@ec.europa.eu

Mission

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

Last update: 22/05/2014 A-Z Index | FAQ | Mailing lists | Privacy statement | Legal notice | Contact | Search | Top

ANNEX 2: Announcement of the PT via e-mail

Ref. Ares(2014)1299566 - 25/04/2014

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 25/04/2014
Ref. Ares(2014) – 25/04/2014

Interlaboratory comparison on the determination of four EU marker PAHs in smoked meat

Dear Madame/Sir,

Registration for participation in the interlaboratory comparison study organised by the EURL PAH on the determination of the 4 marker PAHs in smoked meat is **open until 12 May 2014.**

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

In support to the NRLs, and to facilitate fulfilling their tasks as defined in Regulation (EC) No 882/2004, EU Official Food Control Laboratories (OCLs) falling under the responsibility of the NRLs may participate in the study. **The participation fee for official food control laboratories is 300 Euro per participation.**

The target analytes are listed in the following Table.

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

Results have to be reported corrected for recovery and accompanied by the respective measurement uncertainty for both the individual PAHs and the sum of the four marker PAHs. **Additionally participants will be asked to perform compliance assessment according to the corresponding legislative limits**

Each participant will be provided with an amber glass vial containing about 20 g of smoked sausage test sample

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

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

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

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

Detailed information will 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: 12 May 2014**
- Dispatch of samples: **second half of May.** A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser
- Deadline for reporting of results: **4 weeks after the dispatch of the samples**.

Registration procedure:

This year EURL PAHs is planning to use ProLab software not only for statistical evaluation of reported results but also as platform for reporting of results. Therefore, the registration to the PT will be done via a PDF Registration Form which you will receive via mail.

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

Participants are requested to indicate the preferred solvent type of the standard solution (either toluene or acetonitrile) in the attached Registration Form.

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

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

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

performance data of the respective official food control laboratories will be disclosed to the NRL.

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

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

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

With kind regards,

Stefanka Bratinova

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

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

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

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

ANNEX 3: Registration form

EUROPEAN COMMISSION
DIRECTORATE-GENERAL - JOINT RESEARCH CENTRE

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

REGISTRATION FORM

2014 PT- PAHs in SMOKED MEAT

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

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

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

Participants are requested to choose either toluene or acetonitrile as solvent for the solution of PAHs in solvent. This interlaboratory comparison is organised under accreditation to ISO 17043.

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

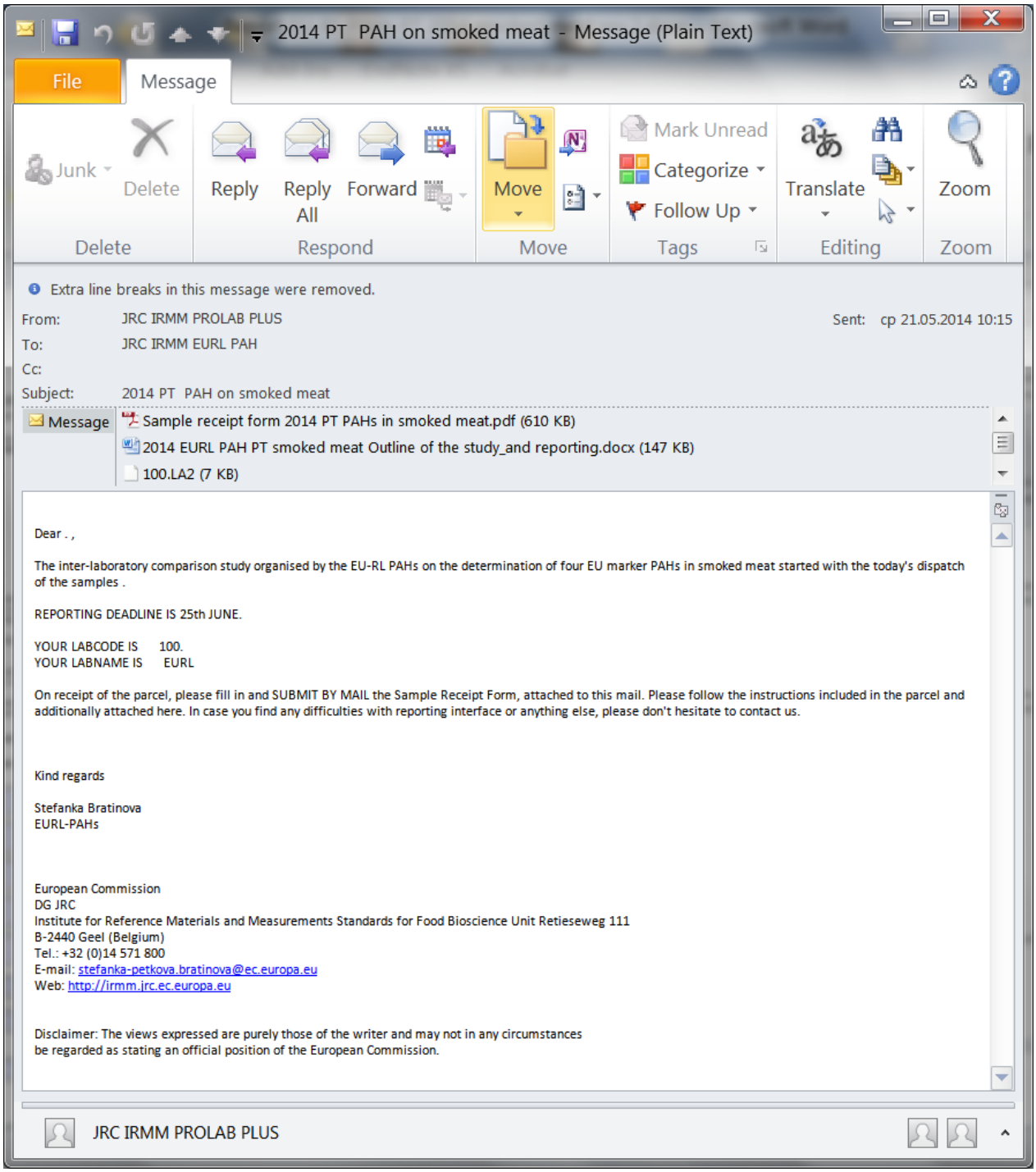
The PARTICIPATION FEE is 300 Euro for Official Food Control Laboratories per participation

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

Submit by Email

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

ANNEX 4: Announcement of material dispatch



2014 PT PAH on smoked meat - Message (Plain Text)

File | Message

Junk | Delete | Reply | Reply All | Forward | Move | Mark Unread | Categorize | Follow Up | Translate | Zoom

Delete | Respond | Move | Tags | Editing | Zoom

Extra line breaks in this message were removed.

From: JRC IRMM PROLAB PLUS
Sent: cp 21.05.2014 10:15
To: JRC IRMM EURL PAH
Cc:
Subject: 2014 PT PAH on smoked meat

Message
Sample receipt form 2014 PT PAHs in smoked meat.pdf (610 KB)
2014 EURL PAH PT smoked meat Outline of the study_and reporting.docx (147 KB)
100.LA2 (7 KB)

Dear . ,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of four EU marker PAHs in smoked meat started with the today's dispatch of the samples .

REPORTING DEADLINE IS 25th JUNE.

YOUR LABCODE IS 100.
YOUR LABNAME IS EURL

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

Kind regards

Stefanka Bratinova
EURL-PAHs

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

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

JRC IRMM PROLAB PLUS

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

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 20 May 2014

2014 PT- PAHs in smoked meat

Dear Madame/Sir,

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

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

Each participant is provided with crimp cap amber vials containing a portion of smoked sausages, naturally contaminated with PAHs and a known standard solution in either toluene or acetonitrile for checking of the instrument calibration against an external reference.

Outline of the study.

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

The laboratories shall report the results by **25th June 2014 at the latest** following the instructions provided further on in this document.

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

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

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

Test material and analytes

1. One crimp cap amber vial, labelled as "EU-RL PAHs PT 2014 Interlaboratory comparison 424, 4 EU PAHs in smoked meats, containing about 20 g of a *naturally contaminated homogenised smoked sausage*. The concentration of the individual analytes is in the range of about 0.5 µg/kg to 10 µg/kg. The analyte content shall be determined in triplicate. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value". The homogeneity is proven at the level of 2.5 g test portion

Store the smoked meat sample in the refrigerator below 6°C, protected of light.

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

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

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

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

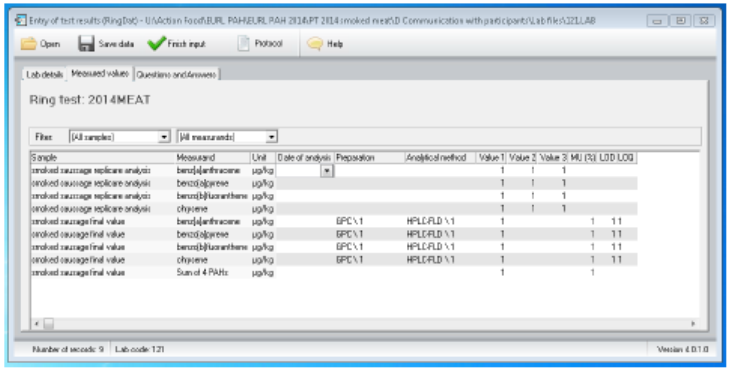
Reporting the results

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

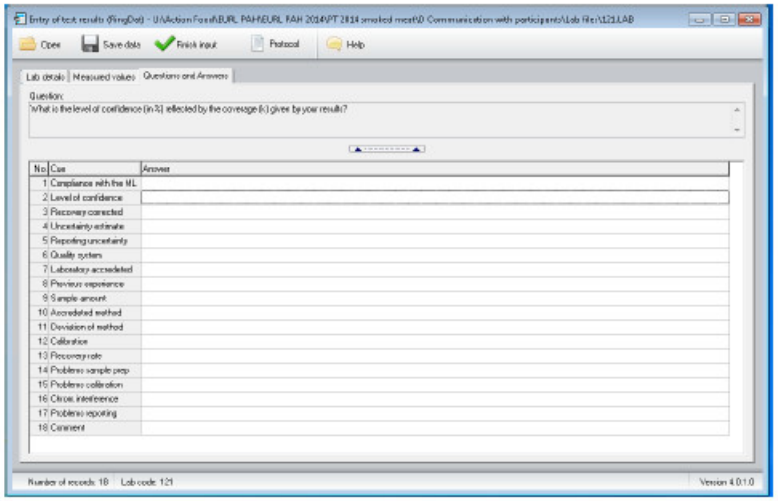
1. Download a simple data entry program RingDat free from the QuoData web page using following link: http://quodata.de/ringdat_en.php
User: *ringdat*
Password: *prolabdata*

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

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



- Third tab contains a general questionnaire.



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

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

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

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

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

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

With kind regards,

Stefanka Bratinova
EURL-PAHs

SAMPLE RECEIPT

EUROPEAN COMMISSION
DIRECTORATE-GENERAL - JOINT RESEARCH CENTRE

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

Confirmation of the receipt of the samples: RECEIPT FORM

2014 PT- PAHs in smoked meat

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

Content of the parcel

a) One amber glass vial containing about 20 g of smoked sausage

b) One brown glass ampoule with 1 ml standard solution of PAHs in solvent (known concentrations)

c) A specification sheet for the item b) content (standard solution), e-mailed as well

d) Material safety data sheets for acetonitrile / toluene

d) One inter-laboratory comparison sample receipt form (= this form), which is e-mailed as well to be filed and send electronically

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

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

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

Date of the receipt of the test sample		
All items have been received undamaged	○ Yes	○ No
If NO, please list damaged items		
All items listed have been received	○ Yes	○ No
If NO, please list missing items		
Serial number of the smoked meat sample you received		

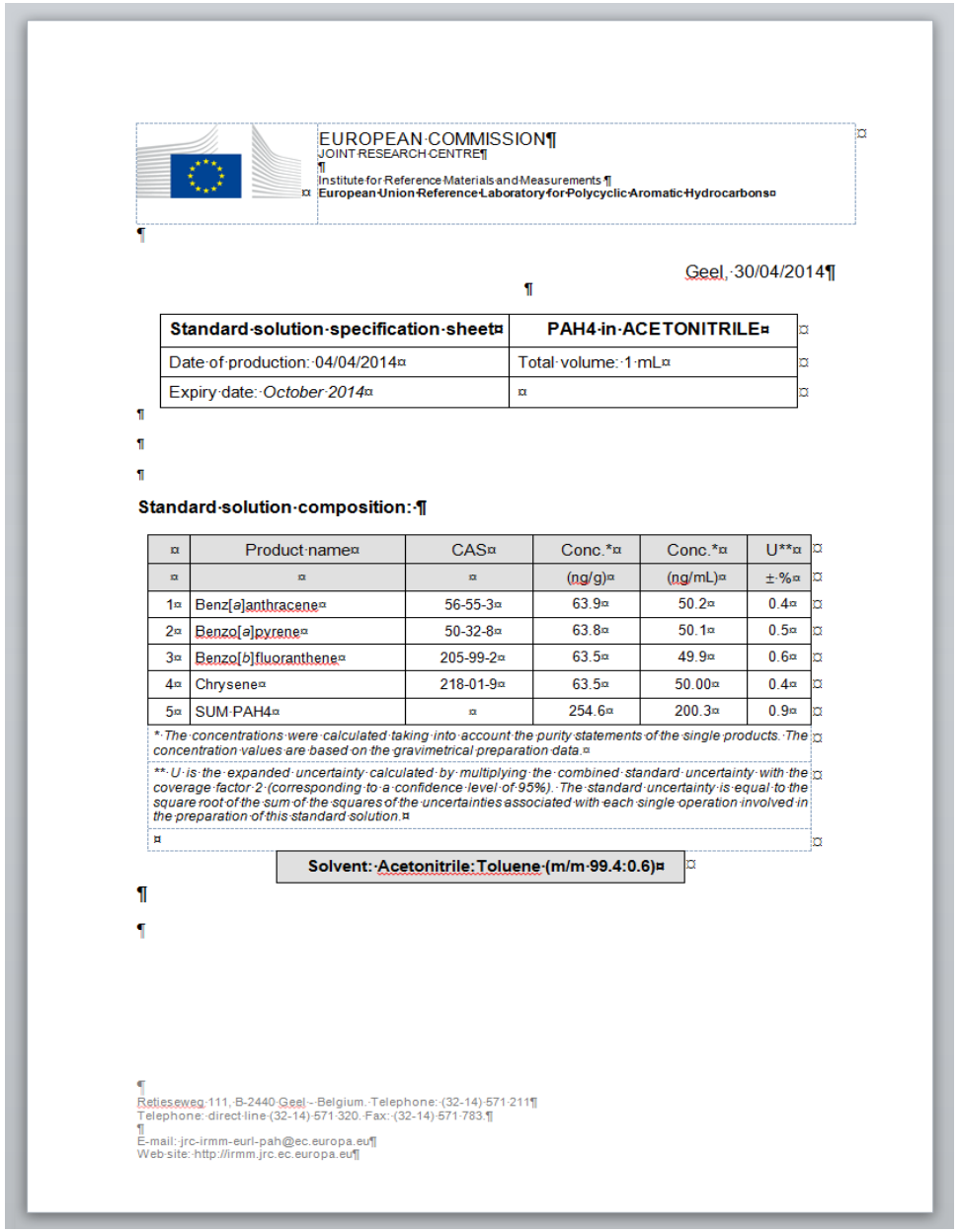
Date Field

Submit by Email

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

ANNEX 6: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION



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

Geel, 30/04/2014

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

Standard solution composition:

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

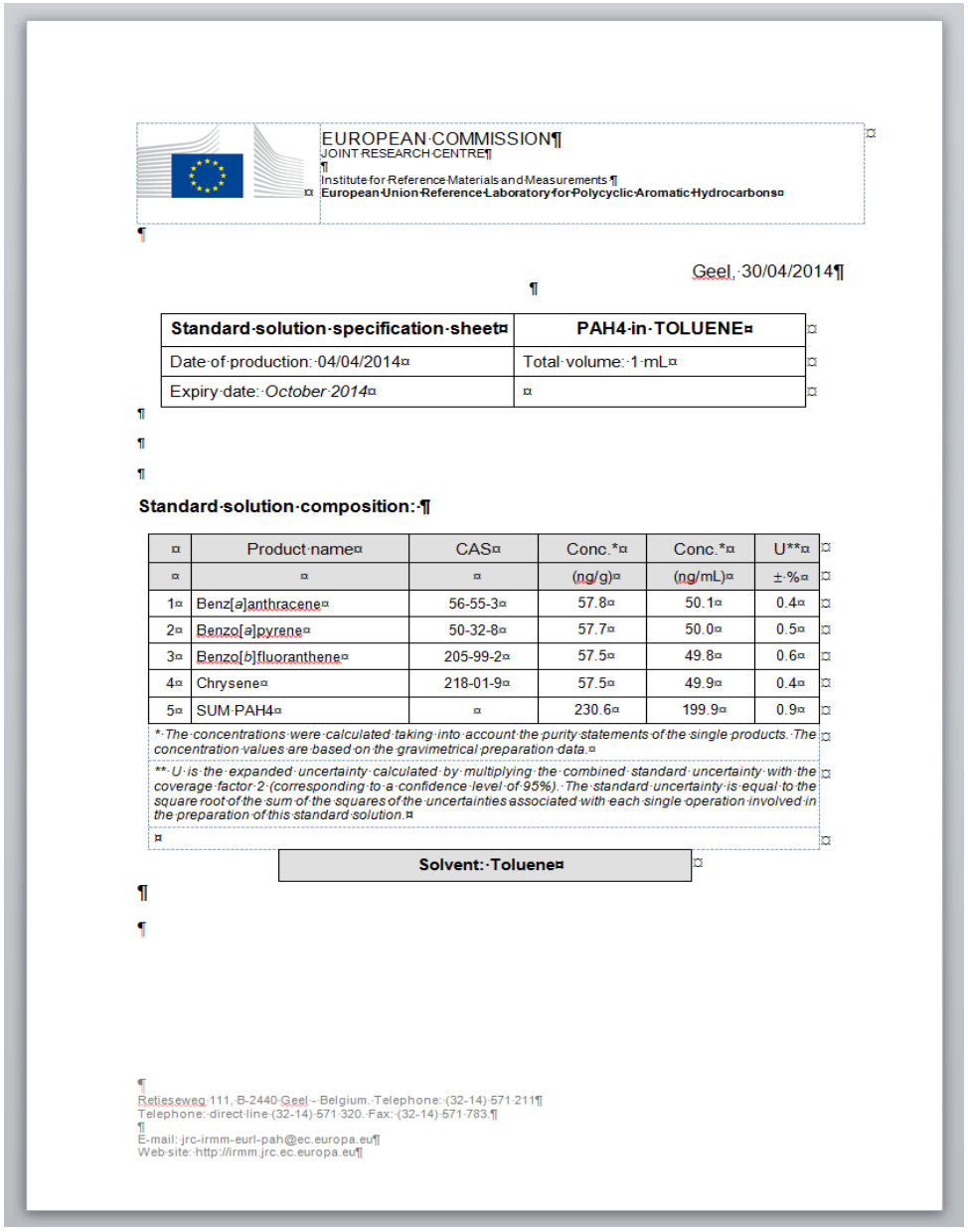
** The concentrations were calculated taking into account the purity statements of the single products. The concentration values are based on the gravimetrical preparation data.*

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

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

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

TOLUENE SOLUTION



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

Geel, 30/04/2014

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

Standard solution composition:

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

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

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

Solvent: Toluene

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

ANNEX 7: Homogeneity of the smoked meat test material

Analyte: **BAA**

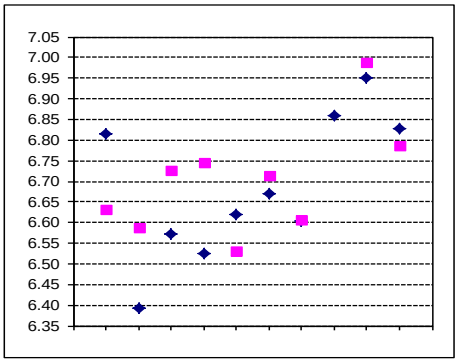
	n =	10		
	mean =	6.7009	22%	= **σ-trg(%)**
0.020634332	s_x =	0.1436	1.4742	= **σ-trg**
√MSW =	s_w =	0.0884		
	s_s =	0.1293	0.4423	= **0,3*s**

ISO-13528	passed		
F =	5.27664248	3.02038295	= Fcrit
	failed		

IUPAC			
(MSB-MSW)/2	0.0167	0.3756	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	6.81	6.63	0.18	13.45	6.72
Ampoule 22	6.39	6.59	-0.20	12.98	6.49
Ampoule 37	6.57	6.73	-0.15	13.30	6.65
Ampoule 48	6.53	6.75	-0.22	13.27	6.64
Ampoule 61	6.62	6.53	0.09	13.15	6.57
Ampoule 70	6.67	6.71	-0.04	13.39	6.69
Ampoule 83	6.61	6.61	0.00	13.21	6.61
Ampoule 95	6.86		0.00	13.72	6.86
Ampoule 103	6.95	6.99	-0.04	13.94	6.97
Ampoule 111	6.83	6.79	0.04	13.62	6.81

∑(diff)^2 =	0.15642016	
var(sum)/2 =	0.04127	=MSB



Analyte: **BAP**

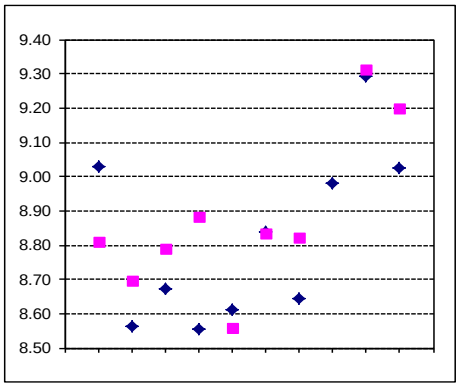
	n =	10		
	mean =	8.8546	22%	= **σ-trg(%)**
0.051085823	s_x =	0.2260	1.9480	= **σ-trg**
√MSW =	s_w =	0.1126		
	s_s =	0.2115	0.5844	= **0,3*s**

ISO-13528	passed		
F =	8.05410387	3.02038295	= Fcrit
	failed		

IUPAC			
(MSB-MSW)/2	0.0447	0.6549	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	9.03	8.81	0.22	17.84	8.92
Ampoule 22	8.56	8.70	-0.13	17.26	8.63
Ampoule 37	8.67	8.79	-0.12	17.46	8.73
Ampoule 48	8.55	8.88	-0.33	17.44	8.72
Ampoule 61	8.61	8.56	0.05	17.17	8.58
Ampoule 70	8.84	8.84	0.00	17.67	8.84
Ampoule 83	8.64	8.82	-0.18	17.47	8.73
Ampoule 95	8.98		0.00	17.96	8.98
Ampoule 103	9.29	9.31	-0.02	18.60	9.30
Ampoule 111	9.03	9.20	-0.17	18.22	9.11

∑(diff)^2 =	0.25371326	
var(sum)/2 =	0.10217	=MSB

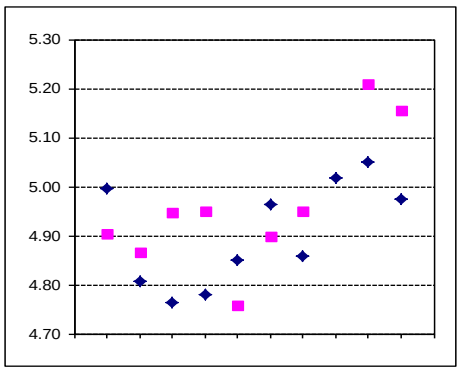


Analyte: **BBF**

	n =	10		
	mean =	4.9358	22%	= **σ-trg(%)**
0.011276063	s_x =	0.1062	1.0859	= **σ-trg**
√MSW =	s_w =	0.0879		
	s_s =	0.0861	0.3258	= **0,3*s**

ISO-13528	passed		
F =	2.91866417	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	0.0074	0.2073	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	5.00	4.90	0.09	9.90	4.95
Ampoule 22	4.81	4.87	-0.06	9.67	4.84
Ampoule 37	4.76	4.95	-0.18	9.71	4.85
Ampoule 48	4.78	4.95	-0.17	9.73	4.86
Ampoule 61	4.85	4.76	0.09	9.61	4.80
Ampoule 70	4.96	4.90	0.06	9.86	4.93
Ampoule 83	4.86	4.95	-0.09	9.81	4.90
Ampoule 95	5.02		0.00	10.04	5.02
Ampoule 103	5.05	5.21	-0.16	10.26	5.13
Ampoule 111	4.97	5.16	-0.18	10.13	5.07



$\sum$**(diff)^2** = 0.15453731

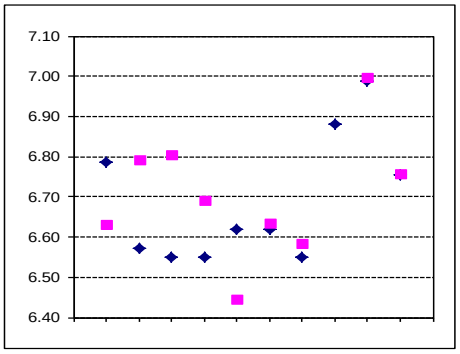
var(sum)/2 = 0.02255 =MSB

Analyte: **CHR**

	n =	10		
	mean =	6.7048	22%	= **σ-trg(%)**
0.019998614	s_x =	0.1414	1.4750	= **σ-trg**
√MSW =	s_w =	0.0976		
	s_s =	0.1234	0.4425	= **0,3*s**

ISO-13528	passed		
F =	4.19641509	3.02038295	= Fcrit
	failed		
IUPAC			
(MSB-MSW)/2	0.0152	0.3778	= F1*(0,3*s)^2+F2*MSW
	passed		

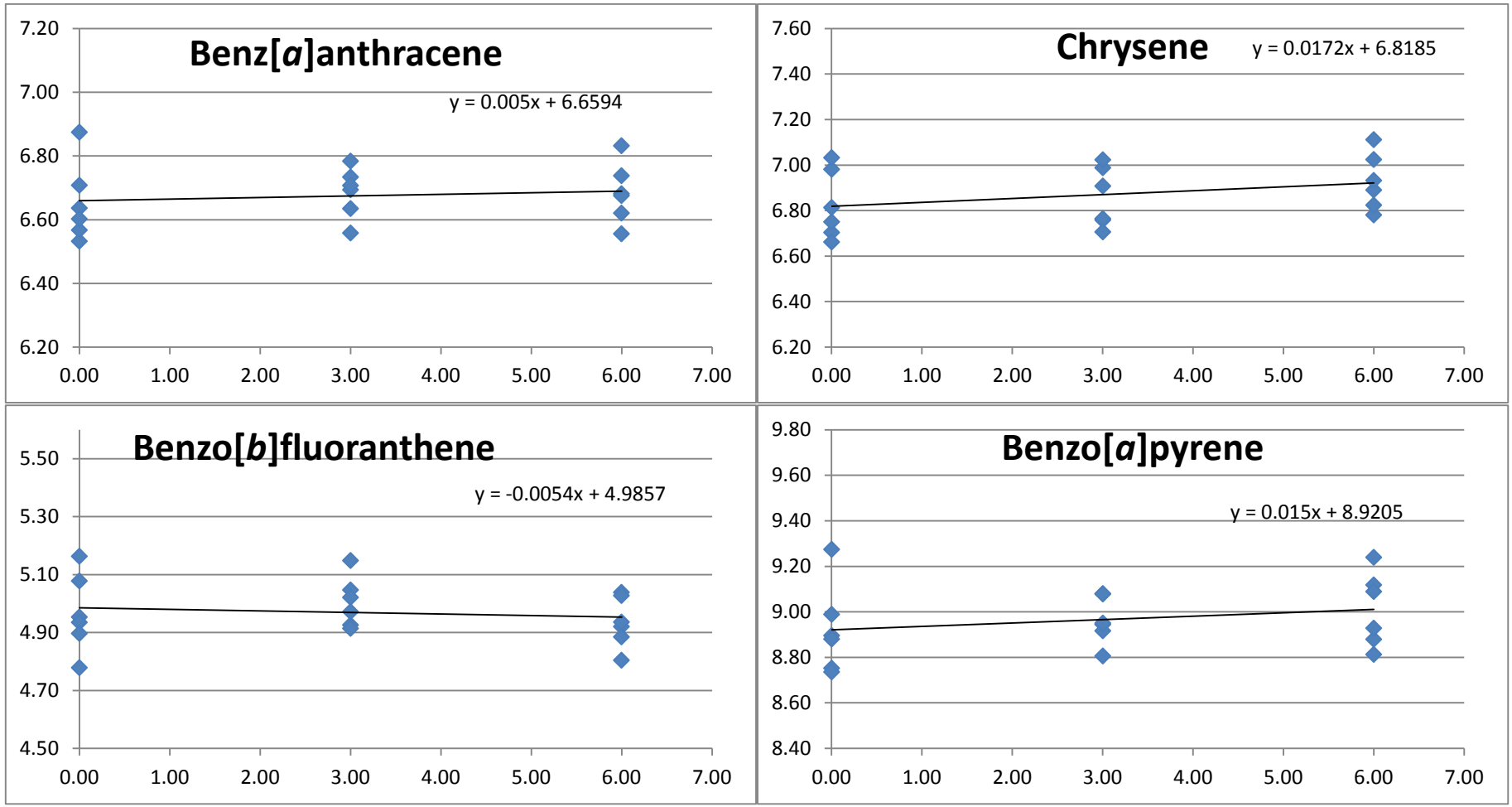
Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	6.79	6.63	0.16	13.42	6.71
Ampoule 22	6.57	6.79	-0.22	13.36	6.68
Ampoule 37	6.55	6.80	-0.26	13.35	6.68
Ampoule 48	6.55	6.69	-0.14	13.24	6.62
Ampoule 61	6.62	6.45	0.17	13.07	6.53
Ampoule 70	6.62	6.63	-0.01	13.25	6.63
Ampoule 83	6.55	6.58	-0.04	13.13	6.57
Ampoule 95	6.88		0.00	13.76	6.88
Ampoule 103	6.99	7.00	-0.01	13.99	6.99
Ampoule 111	6.76	6.76	0.00	13.51	6.76



$\sum$**(diff)^2** = 0.1906257

var(sum)/2 = 0.04000 =MSB

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



ANNEX 9. Questionnaire and method performance characteristics

RV_Nr	Frage_kurz	Frage_lang	Antworten	SortIndex
2014MEAT	Compliance with the ML	Is the test sample compliant with the CURRENT legislative maximum levels (MLs)?	32	1
2014MEAT	Level of confidence	What is the level of confidence (in %) reflected by the coverage (k) given by your results?	31	2
2014MEAT	Recovery corrected	Are your results recovery corrected and how?	33	3
2014MEAT	Uncertainty estimate	What is the basis of your unceratinty estimate?	32	4
2014MEAT	Reporting uncertainty	Do you usually provide an uncertainty statment to your customers for this type of analysis?	32	5
2014MEAT	Quality system	Does your laboratory have a quality system in place (ISO 17025, ISO 9000 series, other)?	32	6
2014MEAT	Laboratory accredeted	Is your laboratory accredeted for analysis of PAHs in smoked meat?	33	7
2014MEAT	Previous experience	How many samples/year do you analyse usually?	33	8
2014MEAT	Sample amount	What is the sample amount you take per analysis?	33	9
2014MEAT	Accredeted method	Have you analysed the samples following the procedure of an accredeted method for determination of PAHs?	33	10
2014MEAT	Deviation of method	Did you deviate from the accredeted method in one or several steps and what are the deviations	33	11
2014MEAT	Calibration	What type of calibration did you use - external calibration, internal calibration, standard addition	33	12
2014MEAT	Recovery rate	What is the range of your recovery rates (apparent recovery, real recovery) ?	33	13
2014MEAT	Problems sample prep	Did you experience problem during sample preparation?	33	14
2014MEAT	Problems calibration	Did you experience problems during calibration?	33	15
2014MEAT	Chrom.interference	Did you experience chromatographic interferences?	33	16
2014MEAT	Problems reporting	Did you experience problem during reporting	32	17
2014MEAT	Comment	Do you have any comments? Please let us know ...	16	18

Participants with Lab Codes 123, 129, 526, 527, 528 did not reply to the questionnaire

Lab Code	Compliance with the ML	Level of confidence	Recovery corrected
121	B(a)p: 2MU= 0,66ug/kg(7,39-8,72ug/kg) it means the resluts exceed ML(5ug/kg)	B(a)A: 6,8%, B(a)p:8,2%, B(b)f:9,0%, Chr:9,2%	B(a)A:97%, B(b)f: 106%, B(a)p:100%, chr:100%
122	no	2	no
124	YES, YES	k=2	Yes, the recoveries come from 2 control samples (performed the same day)
125	yes	95	no
126	No	95%	Yes, using spiked samples
127	Result for BaP does not comply and result for the Sum of 4 PAH complies with the current ML, respectively	95% (k = 2)	Yes, recoveries have been estimated from spiking results
128	no (BaP level exceeds ML 5ug/kg)		yes, spike to test sample
130	no	95	yes (via internal standard)
131		95	
132	NO	95%, k=2	YES - Corrected using mass labelled internal standards
133	Yes	95%, k=2	according internal standard
134	No concerning the BaP amount. Yes concerning the sum of the 4 PAH	60	Yes
135	no	95%	no, but not necessary as we do standard addition
136	exceeds the ML	95	no
137	No		Yes (Isotopically labeled ISTD)
138	The sample is not compliant.	95%	Yes, we use deuterised internal standards.
139	non-compliant for Benzo(a)pyrene	Confidence 95%, coverage factor 2.	yes, isotope dilution
140	No. Taking MU into account sample contains not less than 7.1 µg/kg BaP. Based on current BaP limit of 5.0 µg/kg.	95% 2k	Yes. Results are corrected with a validated correction factor.
141	No	95%	Yes - Stable isotope dilution
142	SumPAH4 <ML Benzo(a)pyrene > ML	k=2, 95%	No
144	NO	95	YES
146	Not for Benzo(a)pyrene	95%, k=2	no
148	Yes	95%	Yes
150	No	2	Yes. Using of Reference material
520			No
521	no	95%	yes (x 100/ recovery from validation)
522	no	2	yes, ISTD
523	yes	95%	yes
524	YES	10%	YES internal Standard
525	BAP: no	95 % avec K= 2	yes
529		95% (k=2)	
530	yes	?	no
531	yes, the sample test is compliant with the current legislative ML	95%	yes, by internal standard
532	No	95% (k=2)	Yes - The IS are added to the beginning of sample handling
534	no		Yes, corrected by the addition of isotopic labelled IS C13

Lab Code	Uncertainty estimate	Reporting uncertainty	Quality system
121	Internal reproducibility	yes	ISO17025
122	validation, EU Vo 401/2006	yes	ISO 17025
124	2*RSD of the "matrix with extraction" control chart	No	ISO 17025
125	calculated from validation data	yes	ISO 17025
126	Expanded uncertainty calculated by ISO-GUM	Yes	Yes
127	We have taken into account both contributions: internal reproducibility and recovery	Yes	Yes, ISO 17025
128	2x RSD	yes	yes
130	validation data (in-house reproducibility), uncertainty of standard solutions	yes	yes (ISO 17025)
132	Sum of individual source of uncertainty	YES	We are accreditated based on ISO 17025
133	method validation data, intenal QC measures	Yes	Yes
134	Expanded uncertainty type B	Yes	Yes
135	Horwitz-equation	only if the result is above the maximum level	yes, ISO 17025
136	0,2	0,2	ISO 17025
137	Control Charts	Yes	Yes
138	Validation and calculation with InterVal software	yes, in '± xx µg/kg' form	ISO 17025
139	based on validation study	yes	ISO 17025:2005
140	Eurochem Guide 3rd edition 2012.	Yes. Relative expanded uncertainty in µg/kg.	ISO 17025
141	Expanded measurement uncertainty based on validation data and everyday ongoing QC	On request	ISO 17025
142	Uncertainity is based on validation data	No	Yes
144	RSD and CRM, rcovery	YES	ISO17025
146	certified ref material and inhouse ref material	yes	ISO 17025
148	reproducibility	Yes	Yes, ISO 17025
150	statistic	Yes	Yes, ISO 17025
520			
521	from validation	no	ISO17025
522	standard deviation	yes	yes, ISO 17025
523	validation and control charts	in case of non-compliant result yes, in other cases measurement uncertainty is provided if requested by the client	yes
524	Replicate analyses of reference materials.	YES	ISO 17025
525	validation parameter	yes	yes, ISO 17025
529			
530	statistic evaluation	yes	yes iso 17025
531	calculated with horwitz	no	yes iso 17025
532	Guide ANGVHAP (LABERCA)	Yes	ISO 17025
534	the uncertainty is basis on the quality control tests realised at each batch of analysis in the year	yes only for benzo (a)pyrène and the sum of 4 PAH	ISO17025

Lab Code	Laboratory accredited	Previous experience	Sample amount
121	yes	200	3-5g
122	yes	100	2,3 g
124	No	1 experience (your PT)	0
125	yes	10	1 g
126	No	50 samples per year	10g
127	Yes	About 100 samples/year	3 g
128	yes	about 50	2.5g
130	accredited on flexible scope	different matrcies > 250 s /year	3.0 g
132	YES	100	1g
133	Yes	40 - 80	15g
134	Yes	30-40 samples per year of smoked and grilled meat and meat products	2,5-5 g depending on the contamination level
135	yes	yes	70 gr
136	yes	8 year	1 g
137	Yes	500 a year	2.5 g
138	Yes, the laboratory is accredited for analysis of PAH in food.	about 60 smoked meat samples in a year. The total sample for PAH analysis is about 200.	2 g
139	yes	yes	10 gram
140	Yes	100 - 120	5g
141	Yes	>100	2.5g (based on what homge-neity was proven at). For routine samples we take between 5g and 12g depending on information supplied.
142	No	No	0.5g
144	YES	This year 150	2 g
146	yes	40	10 g
148	No	20	5g
150	Yes	250	1 gram
520	Yes	Yes	5g
521	yes	650 of which estimated 20% meat	1g
522	yes	50-100	2 g
523	no	500 (40 meat)	20 g
524	YES	100	3 g
525	yes	yes	2 g
529			
530	yes	50	1 g
531	no	100	1g
532	Yes	20	2 g
534	yes	80	1g

Lab Code	Accredited method	Deviation of method	Calibration
121	yes	No	internal calibration
122	yes	no	external calibration
124	Yes	No	calibration with internal standard in solvent
125	yes	no	external calibration
126	No	No	External calibration
127	Yes	The sample and the solvent amount were different than in the accredeted method	external calibration
128	yes	yes, sample weight 2.5g instead of 5g	external calibration
130	method is validated, accreditation is on flexible scope	no	external calibration
132	YES	NO	Internal calibration
133	No for this matrix, accredited Oils and smoked fish products	No	internal calibration
134	Yes	No	Standard addition
135	yes	yes, less amount as usual due to provided amount of sample	standard addition
136	yes	no	ESTD
137	Yes	No	Internal calibration
138	Yes	No	We use standards in solvents (not in matrix) for calibration. We add deuterised internal standards to the samples and to the calibration solutions as well.
139	yes	no	internal, relative response factor
140	Yes	No	Internal calibration with isotopically labelled IS.
141	Yes	No	internal calibration
142	Yes	No	Internal
144	YES	NO	External calibration, internal standard BbC only for extraction yield estimation
146	yes	no	internal calibration
148	The method is not accredeted	The method used is an in-house method	Internal calibration
150	Yes	No	external
520	No	No	Yes, with internal standard used
521	yes	no	internal calibration
522	yes	no	external calibration, standard addition
523	yes	no	internal calibration
524	YES	NO	External, corrected by one internal standard.
525	yes	no	internal calibration
529			
530	yes	no	internal calibration
531	no	/	internal calibration
532	Yes	No	Internal calibration with stable isotope labelled analogues
534	yes	no	internal calibration with isotope standards

Lab Code	Recovery rate	Problems sample prep	Problems calibration
121	real recovery	No	No
122	90 - 100 %	no	no
124	real recovery : 88% (excepted BaA: 71%)	No	No
125	92-97%	no	no
126	70-85%	No	No
127	91,8 - 95,0%	no	no
128	84-100%	no	no
130	100-107% (analysis of reference material)	no	no
132	40-70%	NO	NO
133	88-99% apparent recovery	No	No
134	85,9-100,0%	No	No
135	real recovery: 53 - 71 %	no	no
136	90-105 %	no	no
137	50%	No	No
138	94-106	No	No
139	46% on average	no	no
140	Validated recovery correction factors (apparent recovery against isotopically labelled IS) are between 95 - 100%. Yield of labelled IS typically 75 - 90%. Result not corrected by yield.	No	No
141	71-77%	No	No
142	80-120	No	No
144	real recovery	NO	NO
146	60-70%	no	no
148	98% - 104%	No	No
150	70-110 % apparent	No	No
520	87-99%	No	No
521	88-109	no	no
522	90-100%	no	no
523	50%-120%	no	no
524	approxymately 70 - 80%	NO	NO
525	70 % -110 %, recovery Standard fpr the internal standard, calculated in each sample	no	no
529			
530	30% - 140 %	no	no
531	50-120%	/	/
532	Real recovery	No	No
534	50-120	no	no

Lab Code	Chromatographic interferences	Problems reporting	Comment
121	No	No	No
122	no	no	
124	Yes, for BaA	No	No
125	minor	no	no
126	No	No	
127	no	no	
128	yes, for BaA	no	
130	interference in the peak of CHR	no	
132	NO	NO	
133	No	No	1. The form is not sufficient to describe sample prep. Sample prep: Saponification, LLE, Silica clean-up.
134	No	No	
135	no	no	
136	Not known	no	no
137	No	No	
138	No	Yes, the RingDat application "froze" several times after I pushed the 'Save Data' button.	Please note that I have corrected the lab details.
139	Interference on chrysene, however peaks were seperated with a chromatographic resolution of 0.25	no	no
140	No	No	
141	No	No	
142	No	No	
144	benz(a)nthracene	NO	---
146	no	no	The sample amounte recieved was too small. We require at least 30 g if we have to determine the analyte content in triplicate.
148	No	No	No
150	benzo(a)anthracene	No	No
520	No		
521	no	no	no
522	no	no	
523	no	no	
524	Sometimes, according to the matrix.	My firewall blocked your software.	
525	no		
529		no	
530	no	no	no
531	/	/	/
532	No	No	No
534	no	no	no

METHOD PERFORMANCE LOD and LOQ

With reference to Commission Regulation (EC) No 333/2007 as amended by Commission Regulation (EU) No 836/2011, non-compliant method performance characteristics are marked in the tables in bold red font. Threshold values for the evaluation were LOD≤ 0.30 µg/kg, LOQ ≤ 0.90 µg/kg..

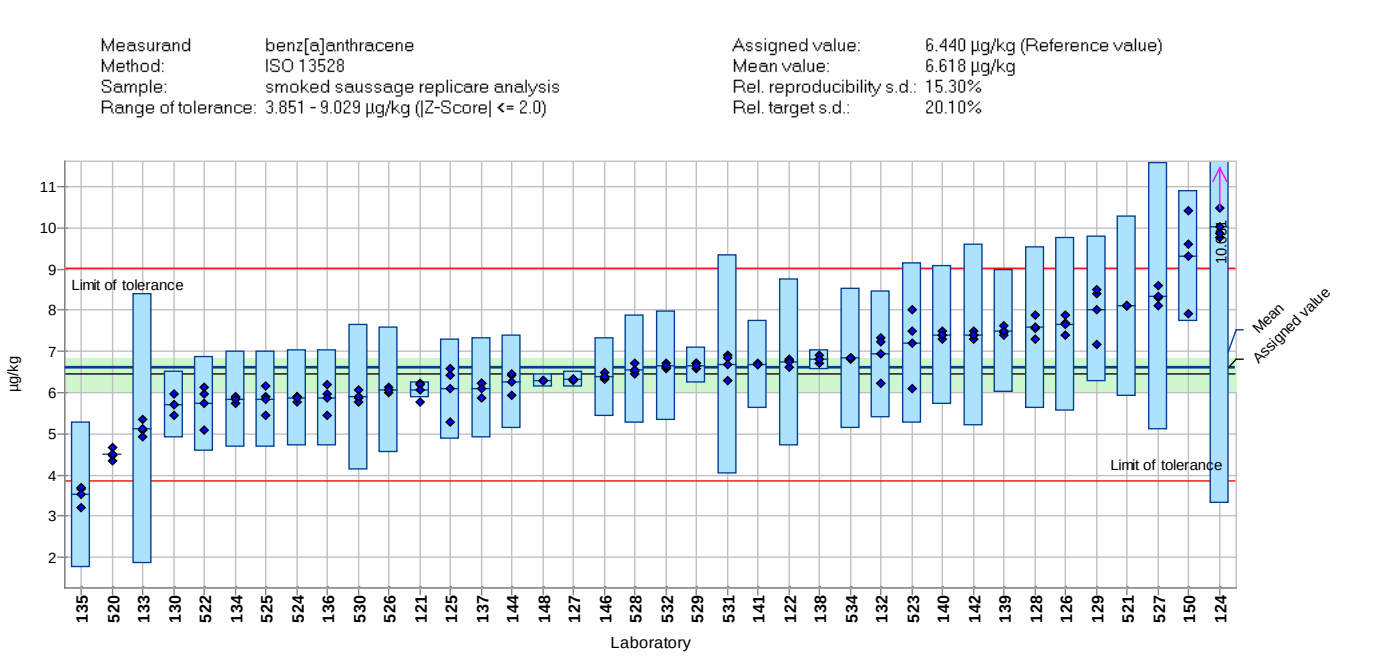
Lab Code	BaA		BaP		BbF		CHR	
	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]
121	0.1	0.2	0.1	0.3	0.1	0.3	0.1	0.3
122	0.01	0.03	0.01	0.03	0.015	0.045	0.004	0.012
123								
124	0.2	0.4	0.2	0.4	0.2	0.4	0.2	0.4
125	0.2	0.5	0.1	0.5	0.1	0.5	0.1	0.5
126	0.17	0.56	0.15	0.48	0.15	0.48	0.16	0.52
127	0.012	0.4	0.005	0.4	0.034	0.4	0.01	0.4
128	0.025	0.05	0.025	0.05	0.05	0.1	0.025	0.05
129								
130	0.05	0.18	0.07	0.24	0.06	0.21	0.03	0.12
131								
132	0.01	0.03	0.01	0.03	0.01	0.03	0.01	0.03
133	0.06	0.2	0.06	0.2	0.06	0.2	0.2	0.5
134	0.2	0.6	0.1	0.3	0.3	0.9	0.3	0.9
135	0.02	0.23	0.01	0.06	0.01	0.04	0.02	0.15
136	0.1	0.5	0.04	0.2	0.04	0.2	0.1	0.5
137	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
138	0.2	0.8	0.2	0.6	0.2	0.7	0.26	0.88
139	0.003	0.005	0.003	0.006	0.001	0.003	0.003	0.005
140	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
141	0.02	0.02	0.15	0.15	0.11	0.11	0.11	0.11
142	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
144	0.3	0.6	0.16	0.32	0.16	0.32	0.3	0.6
146	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
148	**0.5**	**1**	**0.5**	**1**	**0.5**	**1**	**0.5**	**1**
150	0.12	0.36	0.08	0.24	0.11	0.3	0.03	0.09
520		0.5		0.5		0.5		0.5
521	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5
522	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5
523	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9
524	0.17	0.33	0.17	0.33	0.17	0.33	0.17	0.33
525	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.1
526	0.15	0.5	0.15	0.5	0.15	0.5	0.15	0.5
527	0.2	0.7	0.2	0.7	0.2	0.7	0.2	0.7
528	0.2	0.5	0.23	0.5	0.35	0.8	0.15	0.25
529	0.2		0.2		0.2		0.2	
530	0.022	0.022	0.052	0.052	0.032	0.032	0.036	0.036
531	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1
532	0.1	0.3	0.1	0.3	0.1	0.3	0.1	0.3
534	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07

ANNEX 10: Data reported by participants

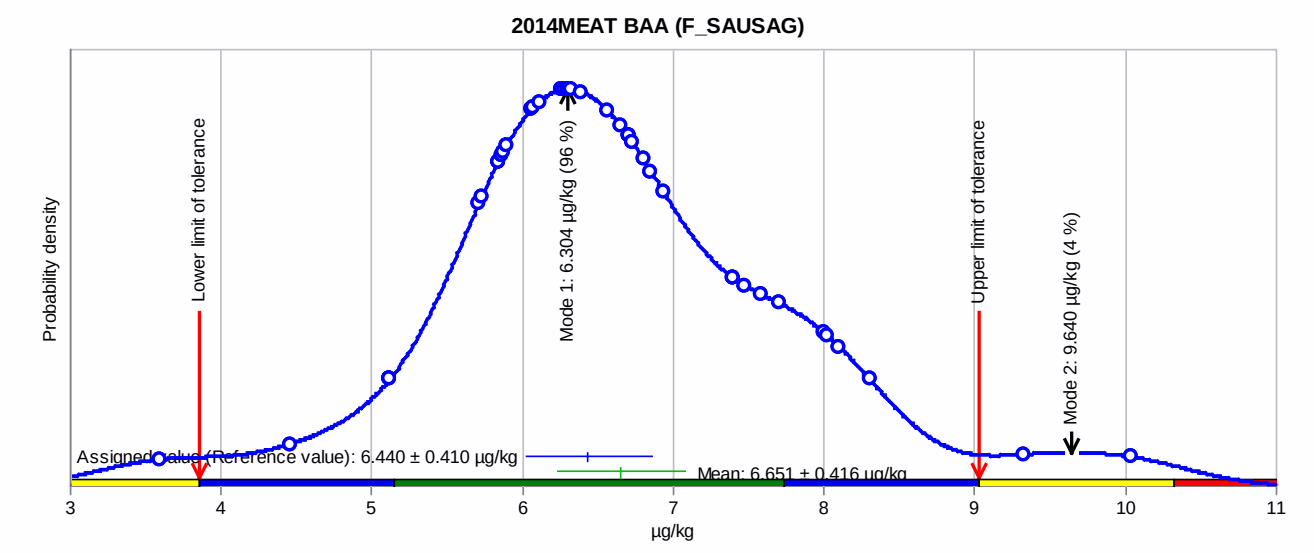
The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores.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

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

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



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



Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA) of the smoked meat test sample.

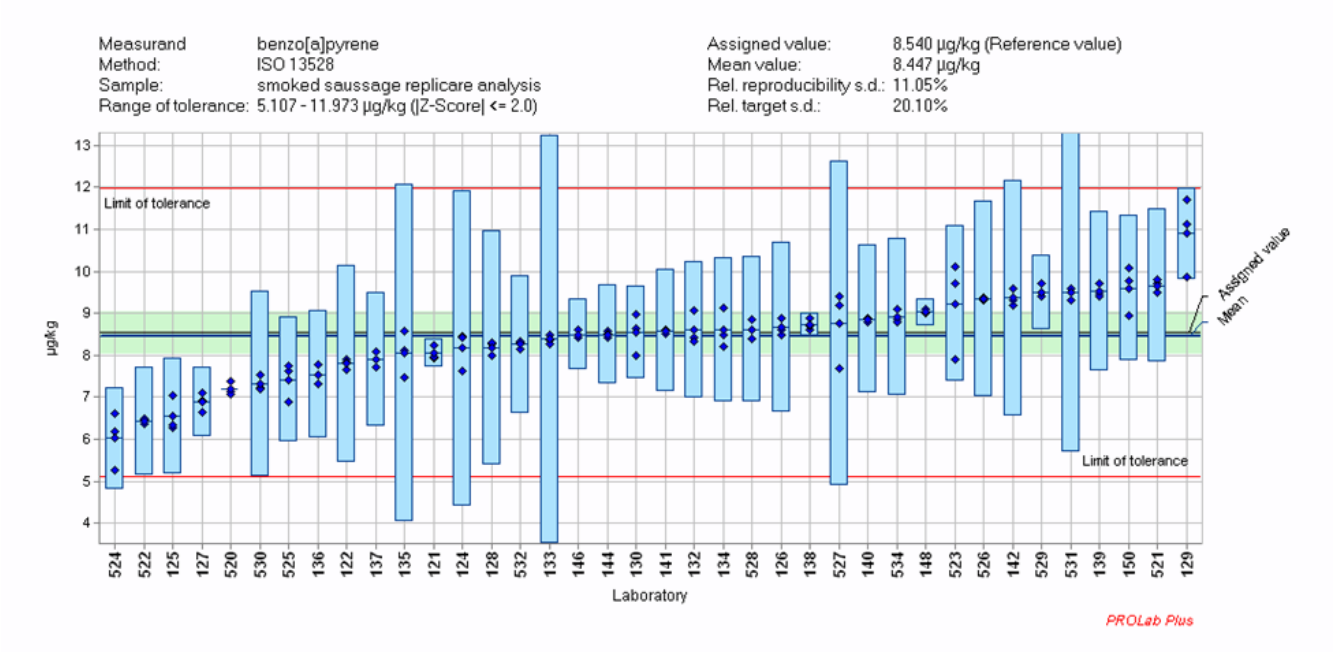
Assigned value is 6.44 µg/kg**.** The uncertainty refers to the "final value for proficiency assessment".

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
121	BaA	6.23	6.21	5.77	6.07	3.4	GC-MS
122	BaA	6.63	6.77	6.80	6.7	30	HPLC-FLD
123	BaA	n.r.	n.r	n.r	n.r	n.r	n.r
124	BaA	10.48	9.754	9.860	10.031	67	HPLC-FLD
125	BaA	5.28	6.43	6.58	6.28	20	GC-MS
126	BaA	7.7	7.4	7.9	7.7	27.6	HPLC-FLD
127	BaA	6.31	6.33	6.33	6.32	3.20	HPLC-FLD
128	BaA	7.55	7.30	7.88	7.58	26	HPLC-FLD
129	BaA	7.18	8.39	8.49	8.02	22	n.r
130	BaA	5.44	5.72	5.98	5.71	14	GC-MS
131	BaA	n.r	n.r	n.r	n.r	n.r	n.r
132	BaA	7.33	6.22	7.24	6.93	22.3	GC-MS/MS
133	BaA	5.35	4.93	5.08	5.12	64	HPLC-FLD
134	BaA	5.86	5.91	5.74	5.84	20.1	HPLC-FLD
135	BaA	3.214	3.652	3.698	3.59	50	GC-MS/MS
136	BaA	5.96	5.44	6.20	5.87	20	HPLC-FLD
137	BaA	6.226	5.885	6.214	6.108	20	GC-MS/MS
138	BaA	6.8	6.9	6.7	6.8	3.5	GC-MS/MS
139	BaA	7.47	7.41	7.63	7.47	20	GC-HRMS
140	BaA	7.3	7.4	7.5	7.4	22.89	GC-MS
141	BaA	6.68	6.68	6.73	6.73	16	GC-MS
142	BaA	7.3	7.4	7.5	7.4	30	GC-MS/MS
144	BaA	6.41	6.44	5.94	6.26	18	HPLC-FLD
146	BaA	6.33	6.35	6.49	6.39	15	GC-MS
148	BaA	6.3	6.3	6.3	6.3	2.5	GC-MS
150	BaA	7.93	9.62	10.42	9.32	17	HPLC-FLD
520	BaA	4.34	4.46	4.68	4.46	n.r.	n.r
521	BaA	8.1	8.1	8.1	8.1	27	GC-MS
522	BaA	5.10	6.13	5.96	5.73	20	HPLC-FLD
523	BaA	8.0	7.5	6.1	8.0	27	GC-MS
524	BaA	5.90	5.92	5.76	5.86	20	HPLC-FLD
525	BaA	6.16	5.46	5.89	5.84	20	GC-MS/MS
526	BaA	5.99	6.08	6.12	6.06	25	HPLC-FLD
527	BaA	8.1	8.6	8.3	8.3	39	GC-MS
528	BaA	6.52	6.71	6.46	6.56	20	HPLC-FLD
529	BaA	6.6	6.7	6.7	6.7	6.7	n.r
530	BaA	6.064	5.862	5.767	5.898	30	GC-MS/MS
531	BaA	6.9	6.85	6.30	6.7	40	GC-MS/MS
532	BaA	6.60	6.62	6.72	6.65	20	GC-MS/MS
534	BaA	6.85	6.82	6.84	6.85	25	GC-MS/MS

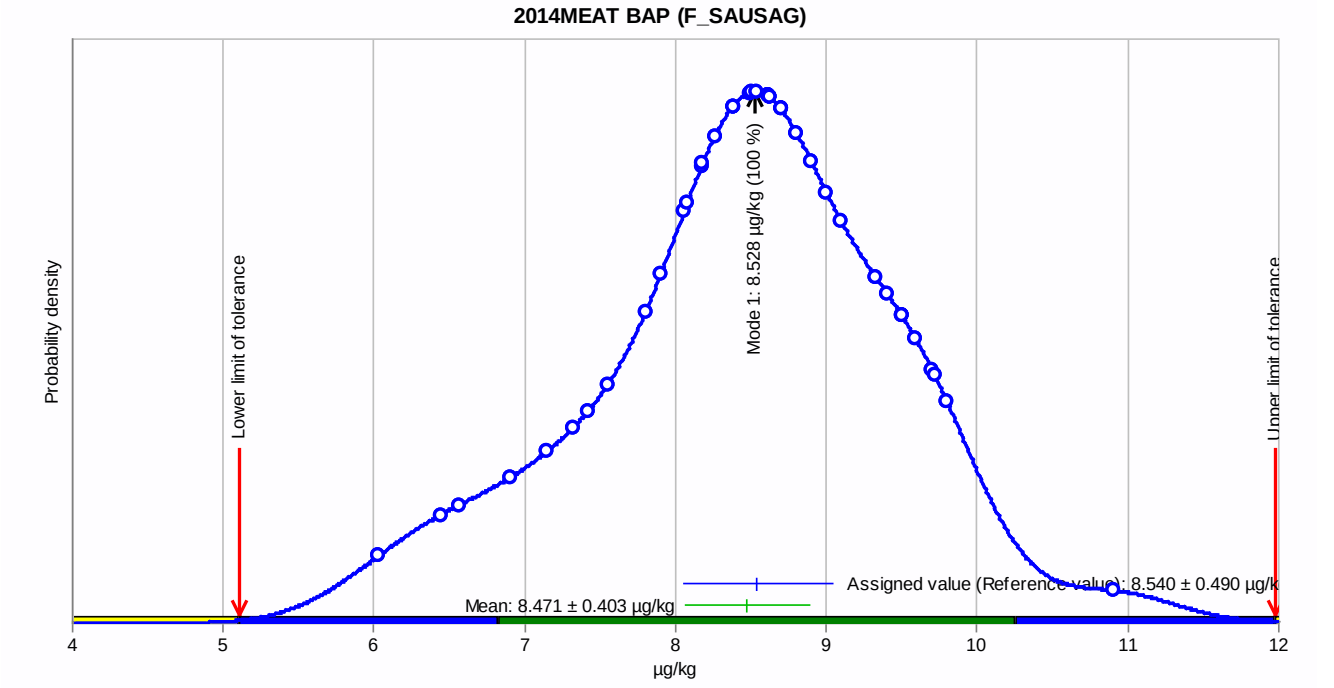
n.r.: not reported

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

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



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



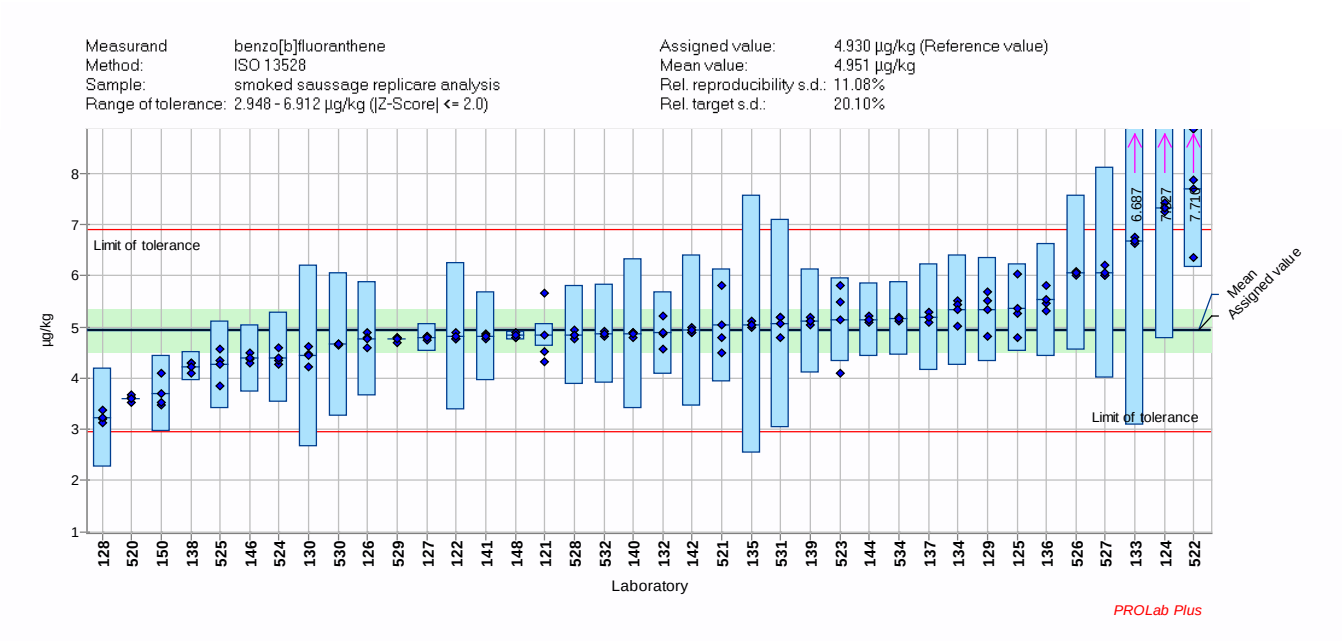
Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP) of the smoked meat test sample.
Assigned value is 8.54 µg/kg**.** The uncertainty refers to the final value.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
121	BaP	7.94	8.24	7.98	8.06	4.1	GC-MS
122	BaP	7.91	7.83	7.67	7.8	30	HPLC-FLD
123	BaP	n.r	n.r	n.r	n.r	n.r	n.r
124	BaP	8.469	8.430	7.626	8.175	46	HPLC-FLD
125	BaP	6.28	7.06	6.35	6.56	21	GC-MS
126	BaP	8.5	8.9	8.6	8.7	23.4	HPLC-FLD
127	BaP	6.64	7.12	6.93	6.90	12.05	HPLC-FLD
128	BaP	8.26	8.00	8.29	8.18	34	HPLC-FLD
129	BaP	9.87	11.12	11.7	10.9	9.9	n.r
130	BaP	8.01	8.64	8.98	8.54	13	GC-MS
131	BaP	n.r	n.r	n.r	n.r	n.r	n.r
132	BaP	9.06	8.43	8.34	8.61	18.8	GC-MS/MS
133	BaP	8.37	8.49	8.28	8.38	58	HPLC-FLD
134	BaP	9.13	8.48	8.22	8.61	20.0	HPLC-FLD
135	BaP	8.568	7.487	8.104	8.08	50	GC-MS/MS
136	BaP	7.31	7.54	7.79	7.55	20	HPLC-FLD
137	BaP	7.909	7.730	8.074	7.904	20	GC-MS/MS
138	BaP	8.9	8.6	8.7	8.7	3.2	GC-MS/MS
139	BaP	9.72	9.47	9.41	9.72	20	GC-HRMS
140	BaP	8.9	8.9	8.8	8.9	19.85	GC-MS
141	BaP	8.53	8.60	8.62	8.62	17	GC-MS
142	BaP	9.2	9.3	9.6	9.4	30	GC-MS/MS
144	BaP	8.57	8.51	8.42	8.50	14	HPLC-FLD
146	BaP	8.43	8.43	8.62	8.49	10	GC-MS
148	BaP	9.0	9.0	9.1	9.0	3.6	GC-MS
150	BaP	8.96	9.76	10.07	9.59	18	HPLC-FLD
520	BaP	7.15	7.39	7.08	7.15	n.r	GC-MS
521	BaP	9.7	9.5	9.8	9.8	19	GC-MS
522	BaP	6.37	6.47	6.48	6.44	20	HPLC-FLD
523	BaP	9.7	10.1	7.9	9.7	20	GC-MS
524	BaP	6.19	6.63	5.26	6.03	20	HPLC-FLD
525	BaP	7.62	6.89	7.75	7.42	20	GC-MS/MS
526	BaP	9.31	9.30	9.39	9.33	25	HPLC-FLD
527	BaP	7.7	9.2	9.4	8.8	44	GC-MS
528	BaP	8.38	8.86	8.62	8.62	20	HPLC-FLD
529	BaP	9.4	9.7	9.4	9.5	9.5	n.r
530	BaP	7.531	7.229	7.203	7.321	30	GC-MS/MS
531	BaP	9.6	9.6	9.3	9.5	40	GC-MS/MS
532	BaP	8.14	8.29	8.34	8.26	20	GC-MS/MS
534	BaP	9.10	8.86	8.78	9.10	21	GC-MS/MS

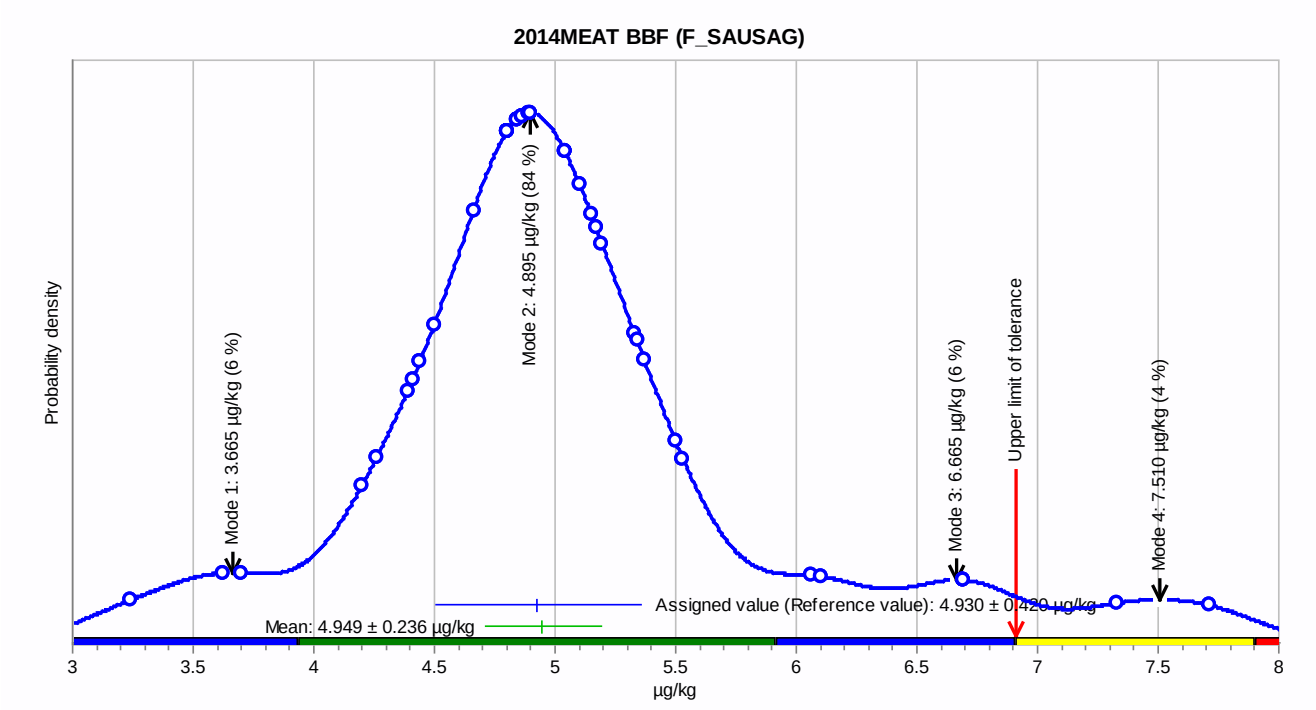
n.r.: not reported

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

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



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



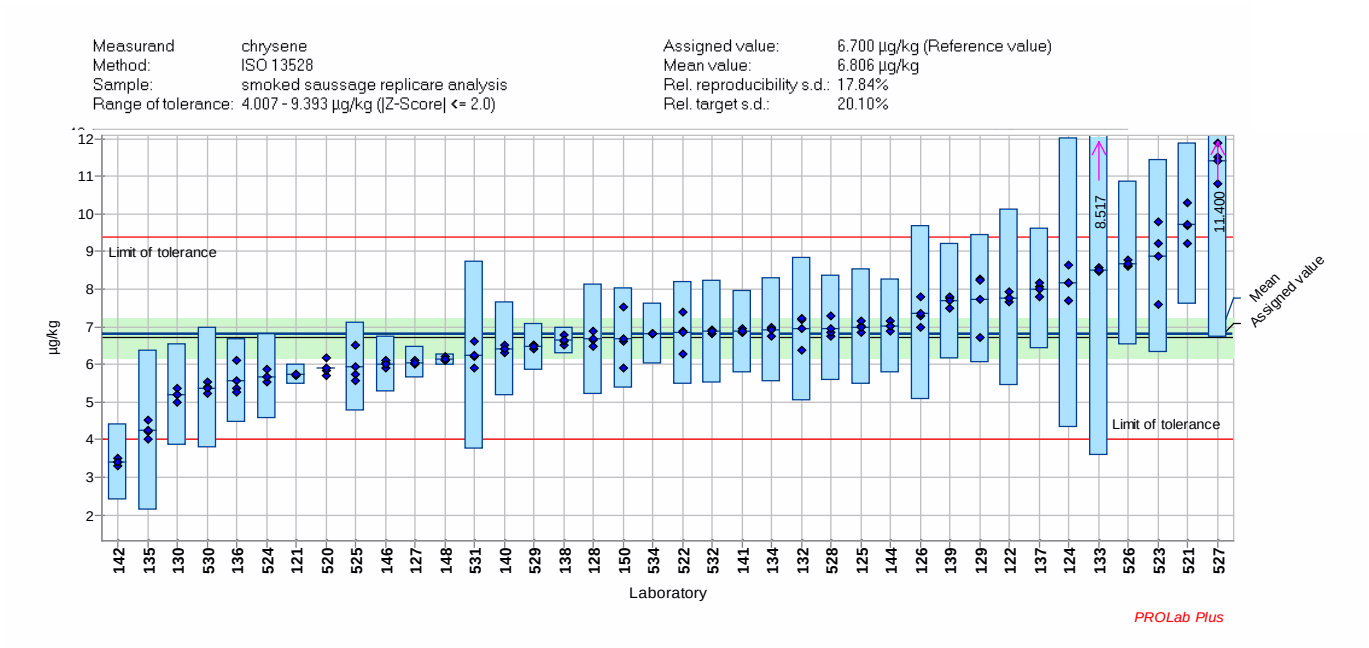
Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF) of the smoked meat test sample.
Assigned value is 4,93 µg/kg. The uncertainty refers to the final value.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
121	BbF	4.33	4.52	5.66	4.84	4.5	GC-MS
122	BbF	4.89	4.77	4.77	4.8	30	HPLC-FLD
123	BbF	n.r	n.r	n.r	n.r	n.r	n.r
124	BbF	7.423	7.243	7.316	7.327	35	HPLC-FLD
125	BbF	6.04	4.80	5.27	5.37	16	GC-MS
126	BbF	4.9	4.6	4.8	4.8	23.4	HPLC-FLD
127	BbF	4.75	4.81	4.83	4.80	5.64	HPLC-FLD
128	BbF	3.21	3.12	3.38	3.24	30	HPLC-FLD
129	BbF	4.82	5.51	5.69	5.34	19	n.r
130	BbF	4.23	4.46	4.62	4.44	40	GC-MS
131	BbF	n.r	n.r	n.r	n.r	n.r	n.r
132	BbF	5.21	4.58	4.87	4.89	16.5	GC-MS/MS
133	BbF	6.68	6.75	6.63	6.69	54	HPLC-FLD
134	BbF	5.52	5.45	5.02	5.33	20.2	HPLC-FLD
135	BbF	4.997	5.105	5.045	5.04	50	GC-MS/MS
136	BbF	5.47	5.31	5.81	5.53	20	HPLC-FLD
137	BbF	5.202	5.092	5.289	5.194	20	GC-MS/MS
138	BbF	4.3	4.1	4.3	4.2	6.9	GC-MS/MS
139	BbF	5.04	5.12	5.20	5.04	20	GC-HRMS
140	BbF	4.9	4.9	4.8	4.9	30.09	GC-MS
141	BbF	4.77	4.87	4.84	4.84	18	GC-MS
142	BbF	4.9	4.9	5.0	4.9	30	GC-MS/MS
144	BbF	5.21	5.14	5.08	5.15	14	HPLC-FLD
146	BbF	4.37	4.29	4.50	4.39	15	GC-MS
148	BbF	4.8	4.8	4.9	4.8	1.9	GC-MS
150	BbF	3.47	4.10	3.52	3.70	20	HPLC-FLD
520	BbF	3.62	3.67	3.53	3.62	n.r	GC-MS
521	BbF	5.8	4.8	4.5	4.5	22	GC-MS
522	BbF	8.88	6.37	7.88	7.71	20	HPLC-FLD
523	BbF	5.5	5.8	4.1	5.5	16	GC-MS
524	BbF	4.28	4.35	4.59	4.41	20	HPLC-FLD
525	BbF	4.58	3.85	4.35	4.26	20	GC-MS/MS
526	BbF	6.01	6.07	6.09	6.06	25	HPLC-FLD
527	BbF	6.2	6.0	6.60	6.1	34	GC-MS
528	BbF	4.85	4.95	4.76	4.86	20	HPLC-FLD
529	BbF	4.8	4.7	4.8	4.8	n.r	n.r
530	BbF	4.654	4.671	4.658	4.661	30	GC-MS/MS
531	BbF	5.2	4.8	5.2	5.1	40	GC-MS/MS
532	BbF	4.81	4.87	4.91	4.86	20	GC-MS/MS
534	BbF	5.17	5.11	5.19	5.17	14	GC-MS/MS

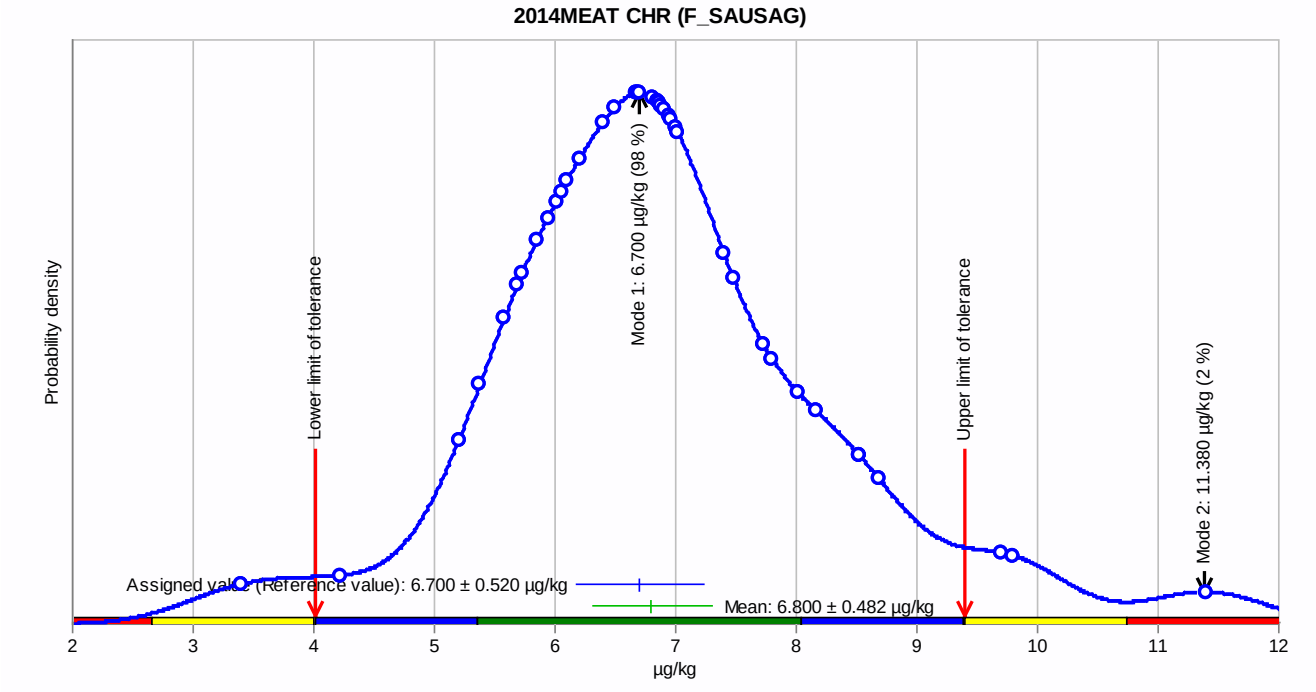
n.r.: not reported

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

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



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



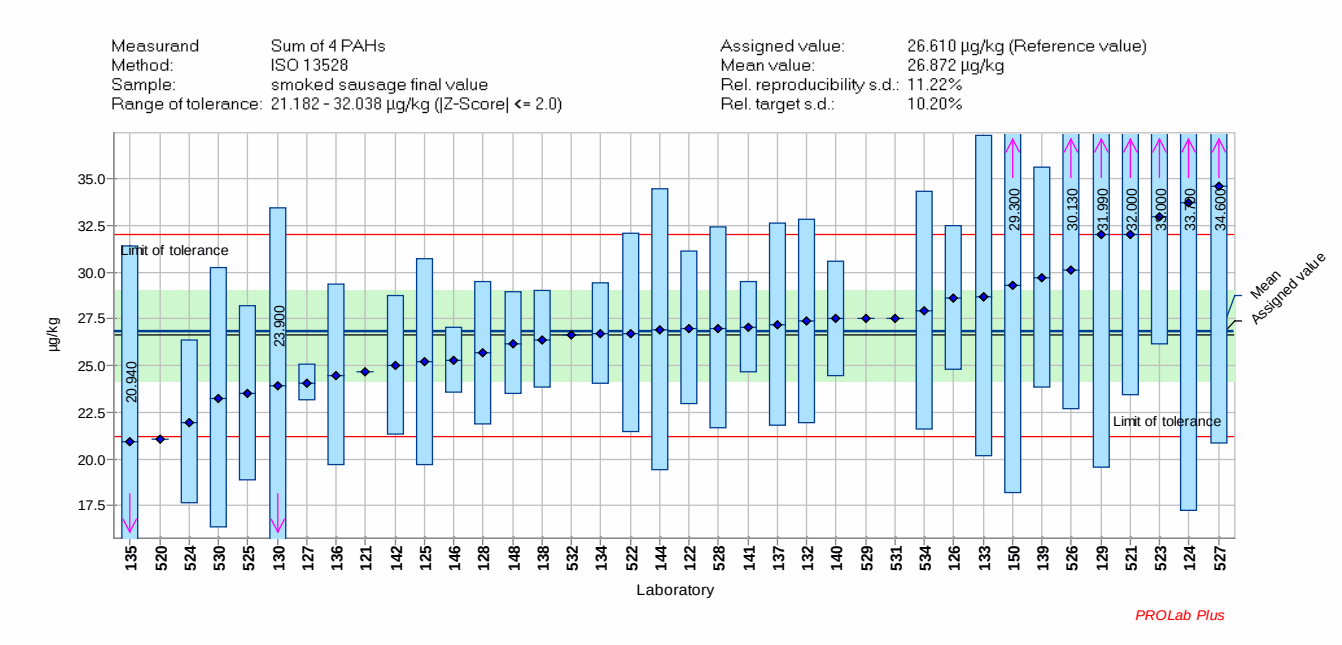
Results, as reported by the participants, for the content of chrysene (CHR) of the smoked meat test sample.
Assigned value is 6.70µg/kg. The uncertainty refers to the final value.

LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
121	CHR	5.75	5.7	5.74	5.73	4.6	GC-MS
122	CHR	7.75	7.65	7.94	7.8	30	HPLC-FLD
123	CHR	n.r	n.r	n.r	n.r	n.r	n.r
124	CHR	8.177	8.641	7.681	8.166	47	HPLC-FLD
125	CHR	7.02	7.15	6.84	7.00	22	GC-MS
126	CHR	7.0	7.8	7.3	7.4	31.5	HPLC-FLD
127	CHR	6.04	6.11	6.02	6.05	6.91	HPLC-FLD
128	CHR	6.64	6.47	6.90	6.67	22	HPLC-FLD
129	CHR	6.72	8.26	8.23	7.73	22	n.r
130	CHR	5.01	5.21	5.37	5.20	26	GC-MS
131	CHR	n.r	n.r	n.r	n.r	n.r	n.r
132	CHR	7.20	6.37	7.24	6.94	27.4	GC-MS/MS
133	CHR	8.57	8.50	8.48	8.52	58	HPLC-FLD
134	CHR	6.97	7.00	6.76	6.91	20.1	GC-MS
135	CHR	4.512	4.221	4.024	4.22	50	GC-MS/MS
136	CHR	5.38	5.25	6.11	5.58	20	HPLC-FLD
137	CHR	8.070	7.797	8.160	8.009	20	GC-MS/MS
138	CHR	6.5	6.8	6.6	6.7	5.4	GC-MS/MS
139	CHR	7.48	7.77	7.79	7.48	20	GC-HRMS
140	CHR	6.4	6.3	6.5	6.4	19.57	GC-MS
141	CHR	6.84	6.94	6.86	6.86	16	GC-MS
142	CHR	3.4	3.5	3.3	3.4	30	GC-MS/MS
144	CHR	7.14	7.02	6.90	7.02	18	HPLC-FLD
146	CHR	6.03	5.90	6.10	6.01	12.5	GC-MS
148	CHR	6.1	6.1	6.2	6.1	2.5	GC-MS
150	CHR	6.61	5.92	7.54	6.69	20	HPLC-FLD
520	CHR	5.69	5.85	6.19	5.85	n.r	GC-MS
521	CHR	10.3	9.2	9.7	9.7	22	GC-MS
522	CHR	7.39	6.28	6.87	6.85	20	HPLC-FLD
523	CHR	9.8	9.2	7.6	9.8	29	GC-MS
524	CHR	5.53	5.66	5.87	5.69	20	HPLC-FLD
525	CHR	6.53	5.74	5.56	5.94	20	GC-MS/MS
526	CHR	8.79	8.61	8.65	8.68	25	HPLC-FLD
527	CHR	11.5	11.9	10.8	11.4	41	GC-MS
528	CHR	7.29	6.75	6.86	6.96	20	HPLC-FLD
529	CHR	6.4	6.5	6.5	6.5	9.5	n.r
530	CHR	5.521	5.221	5.387	5.376	30	GC-MS/MS
531	CHR	6.2	6.6	5.9	6.2	40	GC-MS/MS
532	CHR	6.82	6.91	6.90	6.88	20	GC-MS/MS
534	CHR	6.81	6.82	6.81	6.81	12	GC-MS/MS

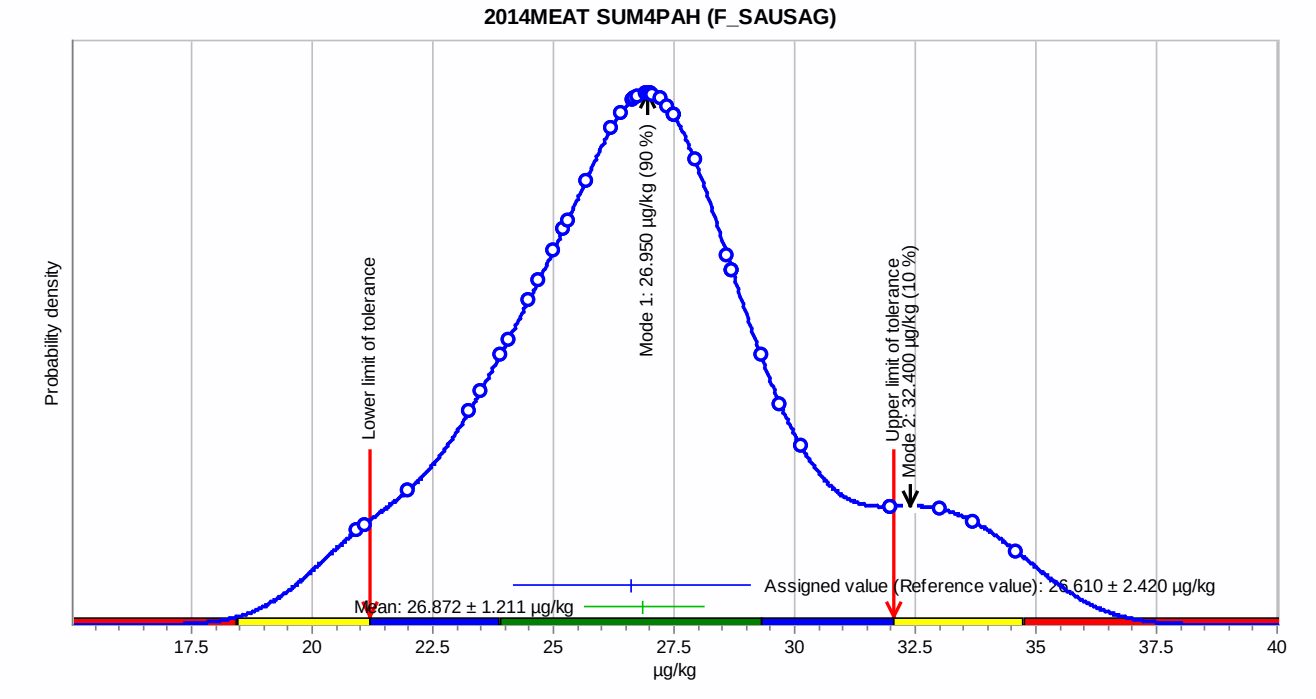
n.r.: not reported

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

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



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



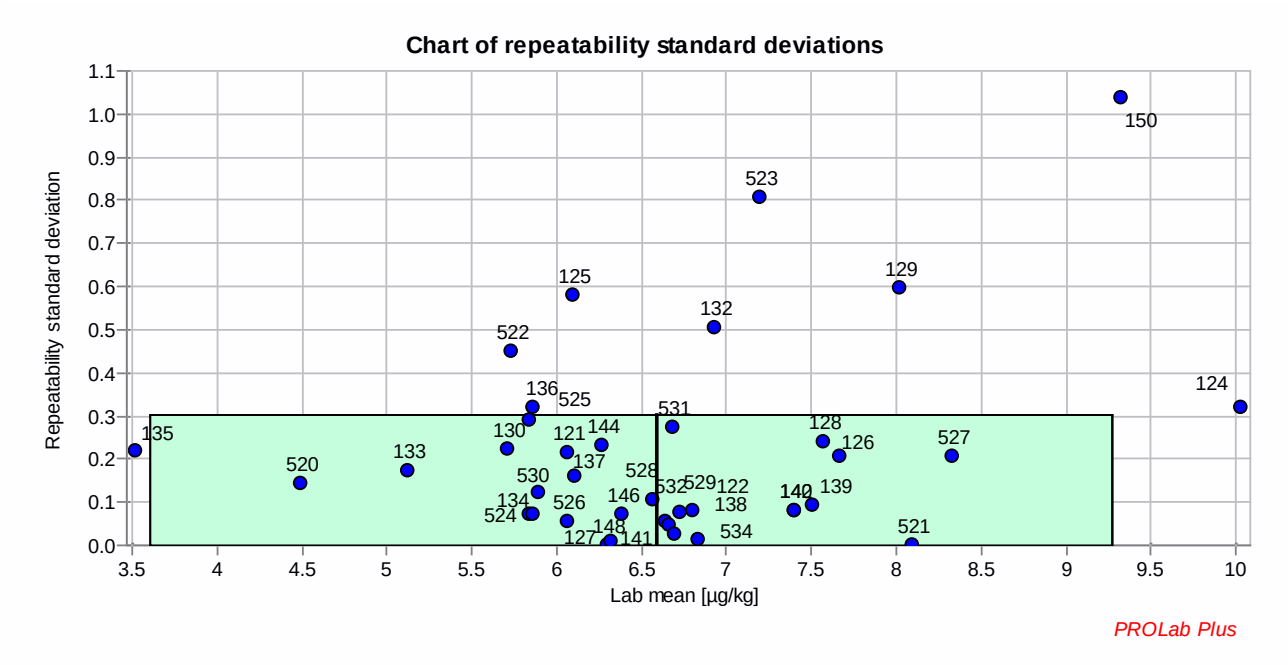
Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH) of the smoked meat test sample.
Assigned value is 26.61 µg/kg.

LCode	Measurant	Final value, µg/kg	Uncertainty, %	Analytical technique
121	SUM 4PAH	24.7	n.r	n.r
122	SUM 4PAH	27	15.3	HPLC-FLD
123	SUM 4PAH	n.r	n.r	n.r
124	SUM 4PAH	33.700	49	n.r
125	SUM 4PAH	25.21	22	GC-MS
126	SUM 4PAH	28.6	13.6	HPLC-FLD
127	SUM 4PAH	24.07	4.11	n.r
128	SUM 4PAH	25.67	15	HPLC-FLD
129	SUM 4PAH	31.99	39	n.r
130	SUM 4PAH	23.9	40	GC-MS
131	SUM 4PAH	n.r	n.r	n.r
132	SUM 4PAH	27.36	20.1	GC-MS/MS
133	SUM 4PAH	28.70	30	HPLC-FLD
134	SUM 4PAH	26.69	10.2	n.r
135	SUM 4PAH	20.94	50	GC-MS/MS
136	SUM 4PAH	24.5	20	HPLC-FLD
137	SUM 4PAH	27.216	20	GC-MS/MS
138	SUM 4PAH	26.4	10	GC-MS/MS
139	SUM 4PAH	29.7	20	GC-HRMS
140	SUM 4PAH	27.5	11.27	n.r
141	SUM 4PAH	27.05	9	n.r
142	SUM 4PAH	25	15	GC-MS/MS
144	SUM 4PAH	26.93	28	HPLC-FLD
146	SUM 4PAH	25.3	7	GC-MS
148	SUM 4PAH	26.2	10.5	GC-MS
150	SUM 4PAH	29.30	38	HPLC-FLD
520	SUM 4PAH	21.08	n.r	GC-MS
521	SUM 4PAH	32	27	GC-MS
522	SUM 4PAH	26.73	20	n.r
523	SUM 4PAH	33.0	21	GC-MS
524	SUM 4PAH	21.98	20	HPLC-FLD
525	SUM 4PAH	23.5	20	n.r
526	SUM 4PAH	30.13	25	HPLC-FLD
527	SUM 4PAH	34.6	40	GC-MS
528	SUM 4PAH	27.01	20	HPLC-FLD
529	SUM 4PAH	27.5	n.r	n.r
530	SUM 4PAH	23.256	30	n.r
531	SUM 4PAH	27.5	n.r	n.r
532	SUM 4PAH	26.65	n.r	GC-MS/MS
534	SUM 4PAH	27.93	23	GC-MS/MS

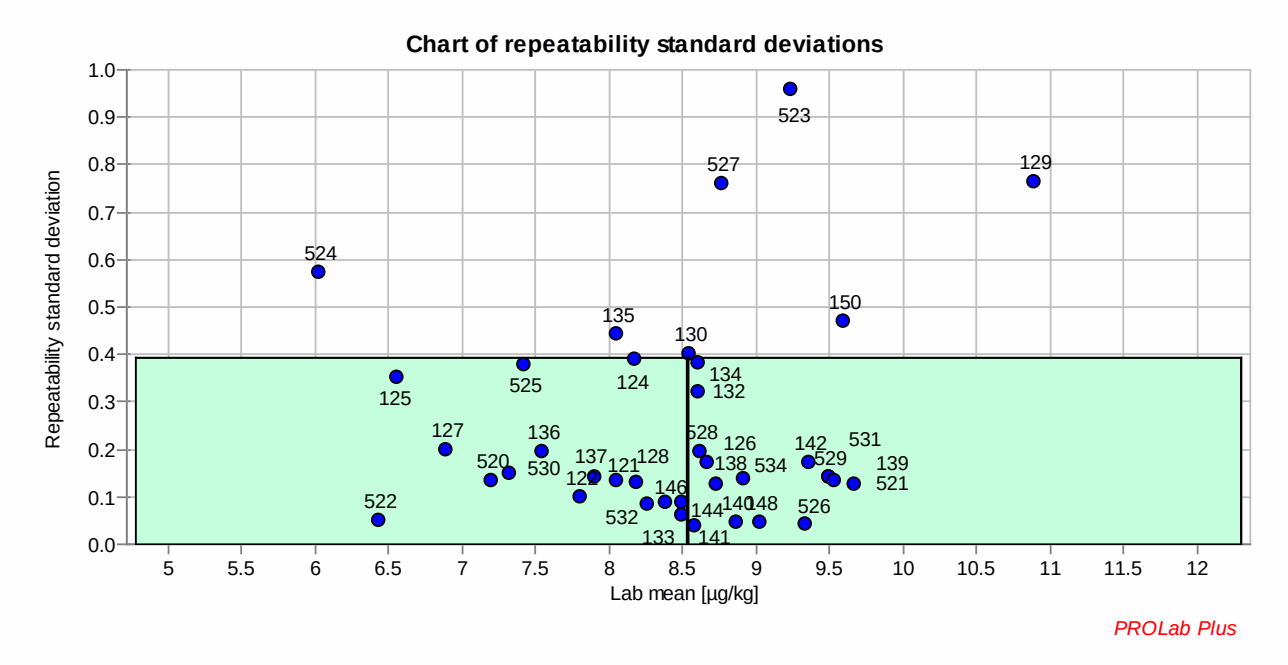
n.r.: not reported

ANNEX 11: Laboratory means and repeatability standard deviation

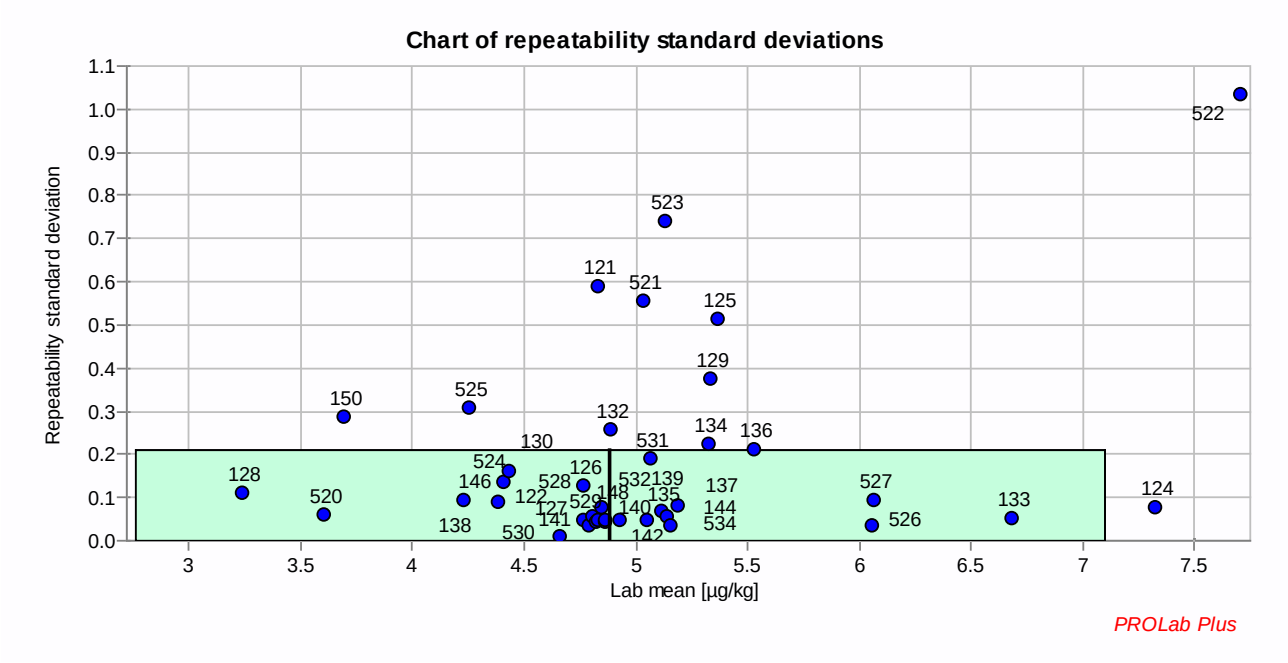
Lab means and repeatability standard deviation for the determination of BAA in the smoked meat test material



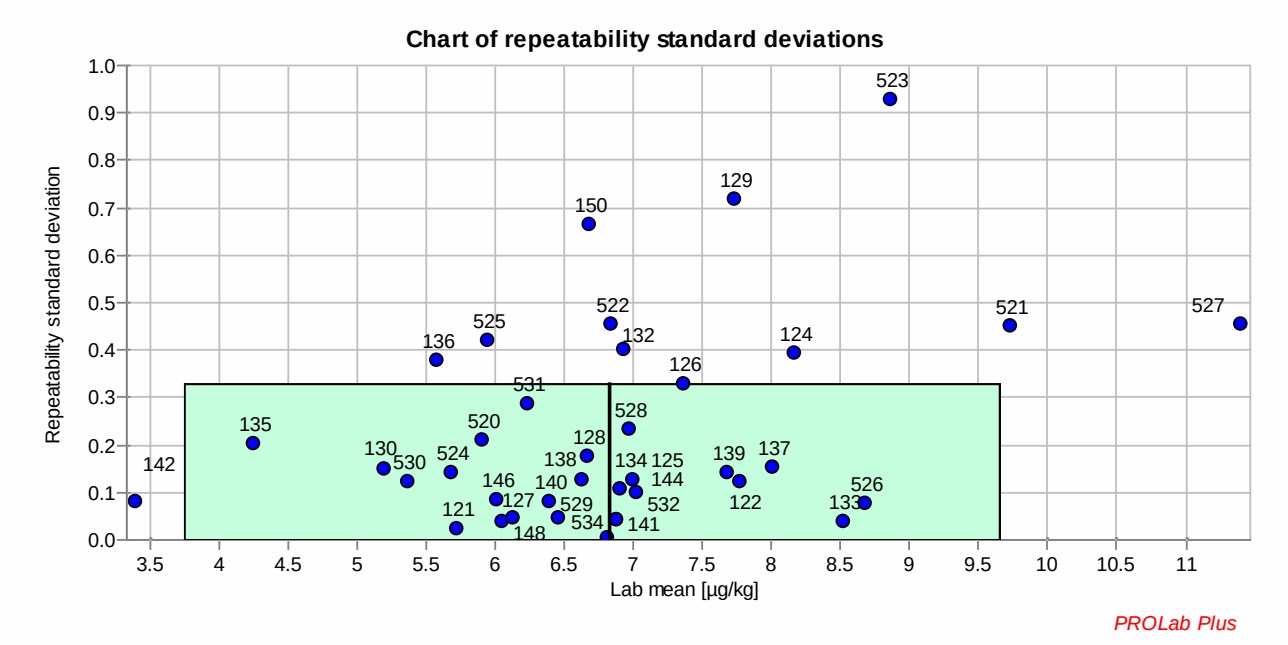
Lab means and repeatability standard deviation for the determination of BAP in the smoked meat test material



Lab means and repeatability standard deviation for the determination of BBF in the smoked meat test material



Lab means and repeatability standard deviation for the determination of CHR in the smoked meat test material



European Commission
EUR 26850 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: **Report on the 15th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons - Four marker PAHs in smoked meat**

Authors: Stefanka Bratinova, Zuzana Zelinkova, Thomas Wenzl

Luxembourg: Publications Office of the European Union

2014 – 55 pp. – 21.0 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424 (online)

ISBN 978-92-79-41238-7 (PDF)

doi:10.2787/99057

LA-NA-26850-EN-N

JRC Mission

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new methods, tools and standards, and sharing its know-how with the Member States, the scientific community and international partners.

Serving society
Stimulating innovation
Supporting legislation

doi:10.2787/99057

ISBN 978-92-79-41238-7

Publications Office