European Commission

JRC TECHNICAL REPORTS

Report on the 17th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in cocoa products

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2015

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JRC Science Hub
https://ec.europa.eu/jrc

JRC 97864

EUR 27573 EN

ISBN 978-92-79-53877-3 (PDF)

ISSN 1831-9424 (online)

doi: 10.2787/071922 (online)

How to cite: St. Bratinova, L. Karasek, G. Buttinger, Th. Wenzl, Report on the 17th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons, Four marker PAHs in cocoa products. EUR 27573 EN, doi: 10.2787/071922

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Executive summary

This report presents the results of the 17th inter-laboratory comparison (ILC) organised as a proficiency test (PT) by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL PAHs) on the determination of the four EU marker PAHs, benz[a]anthracene (BAA), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF) and chrysene (CHR) in cocoa products.

The test material used in this exercise was commercial milk chocolate and cocoa powder from a local supermarket. The milk chocolate was additionally spiked at the EURL PAH in order to increase the PAH content. Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with known PAH content for the verification of their instrument calibration.

The PT was conducted under ISO Standard 17043 accreditation. Both officially nominated National Reference Laboratories (NRLs) and official food control laboratories (OCLs) of the EU Member States were admitted as participants. Twenty-nine NRLs and 18 OCLs subscribed for participation.

The test material was characterised and value-assigned by the EURL PAH.

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

Seventy seven per cent of the reported test results were graded with z-scores that were below an absolute value of two, indicating acceptable agreement with the assigned reference values of the test material. The determination of the analytes in cocoa powder caused more problems than their determination in milk chocolate. This might be partially explained by the higher degree of difficulty related to low analyte contents, a low fat content and complexity of the cocoa powder matrix. However, it has also to be stressed that underperformance ratings accumulated for a few laboratories, indicating that these laboratories did not have their analysis procedures under control.

In addition to reporting analyte contents, the EURL PAH asked participants to assess the compliance of the sample with legislative limits.

Acknowledgements

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

1. Introduction

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

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

Of the many hundreds of PAHs, the most studied is benzo[a]pyrene, which is often used as a marker for PAHs in ambient air and food [5]. In 2012, based on the conclusions of the European Food Safety Authority (EFSA), the system of using benzo[a]pyrene as the only marker for the group of PAHs in food was changed. New maximum levels for the sum of four substances (PAH4) – benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene and chrysene, (Table 1) - have now been introduced whilst maintaining a separate maximum level for benzo[a]pyrene [6, 7]. This system ensures that PAH levels in food are kept at levels that do not cause health concerns and that the amount of PAH can also be controlled in those samples in which benzo(a)pyrene is not detectable, but where other PAHs are present

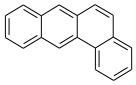
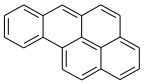
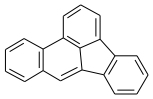
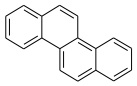
The manufacturing process of chocolate starts with the harvest of the ripe cocoa pods, culling of the cocoa beans from the pods and fermenting them. Afterwards the cocoa beans are dried, roasted, and winnowed. The collected cocoa nibs are alkalised and ground. Then the resulting cocoa liquor is blended with the other ingredients such as cocoa butter, sugar, milk, or emulsifiers and mechanically treated until the desired texture is reached. Conching, another mechanical treatment, and tempering follow next. Finally, the chocolate is moulded and packed. Within this manufacturing process are some critical steps during which cocoa and as a consequence chocolate may be contaminated with polycyclic aromatic hydrocarbons (PAH). The most critical step is drying of the cocoa seeds in their respective country of origin.

Cocoa butter might contain higher levels of PAH than other oils and fats [6]. This is mainly due to inappropriate drying practices of the cocoa beans and the fact that cocoa butter cannot be refined as is done with other vegetable oils and fats. Cocoa butter is a main constituent of raw cocoa products (e.g. cocoa beans, cocoa mass, cocoa nibs, or cocoa liquor) and is present in chocolate and other cocoa products often consumed by children. Therefore maximum levels for PAH in cocoa beans and derived products were established on a fat basis since PAH concentrate in the fat fraction, the cocoa butter (Commission Regulation (EC) No 835/2011). It shall be mentioned that cocoa beans and derived products is the only food category for which maximum levels for polycyclic aromatic hydrocarbons (PAHs) are based on the fat fraction.

To support the implementation of the regulated limits for cocoa products the EURL PAH organised in 2012 a proficiency test (PT) for the network of the National Reference Laboratories (NRLs) for the determination of the 4 markers PAHs in dark chocolate and cocoa butter. Reporting of the contents of the dark chocolate sample was required on product basis and on fat fraction basis. This aimed to identify the effect of the fat determination/fat extraction on the analysis results. Severe decline in performance for results expressed on fat basis has been noticed, which could be partially explained by a lack of experience for fat determinations within the NRLs for PAHs. Members of the Expert Committee on Industrial and Environmental Contaminants requested the Commission to repeat the proficiency test exercise, in order to elucidate the influence of fat determination on the analytical results.

Therefore, the EURL PAH agreed in October 2014 at the annual workshop with NRLs to re-organise in 2015 a EURL PAH PT on cocoa products.

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

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

2. Scope

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

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

The ILC was designed and evaluated under the umbrella of IRMM's accreditation according to ISO Standard 17043:2010 [8].

3. Setup of the exercise

3.1 Participating Laboratories

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

Table 2: List of participating National Reference Laboratories

Institute	*Country*
AGES - Österreichische Agentur für Gesundheit und Ernährungssicherheit, Kompetenzzentrum Cluster Chemie	AUSTRIA
Scientific Institute of Public Health	BELGIUM
SGL - State General Laboratory, Environmental and other Food Contamination Laboratory	CYPRUS
Nàrodní referenční laboratoř pro polycyklické aromatické uhlovodíky - Státní veterinární ústav Praha	CZECH REPUBLIC
Division of Food Chemistry, National Food Institute, Technical University of Denmark	DENMARK
Veterinary and Food Administration, Chemical Laboratory	DENMARK
Tartu Laboratory of Health Board	ESTONIA
EVIRA - Finnish Food Safety Authority	FINLAND
LABERCA - Laboratoire d'Etude des Résidus et des Contaminants dans les Aliments	FRANCE
BVL - Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	GERMANY
GCSL - General Chemical State Laboratory - Food Division - Laboratory	GREECE
Central Agricultural Office, Food & Feed Safety Directorate, Food Residues Toxicological Dept.	HUNGARY
Central Agricultural Office, Food and Feed Safety Directorate, Feed Investigation NRL	HUNGARY
The Public Analyst's Laboratory Dublin	IRELAND
Istituto Superiore di Sanità	ITALY
BIOR - Institute of Food Safety, Animal Health and Environment	LATVIA
National Veterinary Laboratory (National Food and Veterinary Risk Assessment Institute)	LITHUANIA
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
Departamento de Riscos Alimentares e Laboratorios	PORTUGAL
Sanitary Veterinary and Food Safety Direction, Brasov	ROMANIA
SVUPUDK - State Veterinary and Food Institute Dolný Kubín	SLOVAKIA
Zavod za zdravstveno varstvo Maribor	SLOVENIA
AESAN - Centro Nacional de Alimentaciòn (Spanish Food Safety and Nutrition Agency)	SPAIN
SLV - Livsmedelsverket	SWEDEN
FERA - The Food and Environment Research Agency	UNITED KINGDOM

From the 28 NRLs registered for participation, three NRLs did not report results.

Table 3: List of participating Official Food Control Laboratories

Institute	*Country*
Federal Laboratory for the Safety of the Food Chain	BELGIUM
CVUA-Münsterland-Emscher-Lippe	GERMANY
Institut für Lebensmittelchemie Speyer	GERMANY
Landesuntersuchungsamt für Chemie, Hygiene und Veterinärmedizin, Bremen	GERMANY
CVUA Rheinland	GERMANY
Berlin-Brandenburg State Laboratory	GERMANY
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit	GERMANY
Laboratorio de Salud Pública de Madrid	SPAIN
Service Commun des Laboratoires (SCL)	FRANCE
Staffordshire Scientific Services	UNITED KINGDOM
Public Analyst Scientific Services Limited	UNITED KINGDOM
Hrvatski veterinarski institut,Veterinarski zavod Split	CROATIA
Azienda Sanitaria Locale di Milano	ITALY

All thirteen participating OCLs reported results.

3.2 Time frame

The ILC was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on 17 April 2015 (see ANNEX 2) with deadline for registration via EU Survey webpage (see ANNEX 3) until 04 May 2015. Test samples were dispatched (see ANNEX 4) on 27 May 2015 and the deadline for reporting of results was set to 1st July 2015. The documents sent to the participants are presented in ANNEX 5.

3.3 Confidentiality

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

3.4 Design of the proficiency test

The design of the PT foresaw triplicate analysis of the test items and reporting on product basis of the individual results of replicate analyses for the single analytes. Additionally a "value for proficiency assessment", in the following denoted as "mean 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 EURL asked participants (NRLs and official control laboratories) to assess the compliance of the sample according to the current legislative limits

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

4. Test materials

4.1 Preparation

The test items of this PT were cocoa powder and milk chocolate. This matrices are representative for the food category 6.1.2 "Cocoa beans and derived products" specified in Commission Regulation (EC) No 836/2011 [6], with a maximum level for BAP and for the sum of the four PAHs (in the following indicated as SUM4PAH) of 5.0 µg/kg fat and 30.0 µg/kg fat respectively. The second maximum level for the SUM came into force on 1 April 2015.

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

The cocoa powder test samples were prepared at the EURL PAH starting from two kilos of commercial cocoa powder (acquired at local retail) with labelled fat contents of 21 %,. The material was homogenised and aliquots of about 22 g each were filled in amber glass bottles with PTFE-lined screw cap.

The milk chocolate test material (2 kg) with labelled fat contents of 29.5 %was acquired at local supermarkets too.. As the contents of some of the 4 markers PAHs were lower than the LOQ of 0.9 µg/kg fat, the milk chocolate was melted and spiked with a solution of PAHs. Afterwards the material was cryo-grinded to fine particles and homogenized by repetitive application of a sample divider. Aliquots of about 22 g each were packed in amber glass screw cap vials and stored in the refrigerator.

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

4.2 Homogeneity and stability

The cocoa and chocolate powder was tested for significant inhomogeneity, according to the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, and for sufficient homogeneity according to ISO 13528 [9]. 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 each 10 samples randomly selected among test samples prepared for dispatch. The duplicate analyses were performed in random order. The test materials were rated sufficiently homogenous and no trend was observed. Details of the homogeneity tests are given in ANNEX 7. Both tests requirements of the IUPAC protocol and the ISO standard proved sufficient homogeneity, meaning that the residual difference of the analyte content between vials (inhomogeneity) does not significantly influence the performance statement (z-score) of a particular laboratory.

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

The first set of 3 samples was stored at the recommended condition - refrigerator (~ 5 C°). The second set of 3 samples was stored at the reference conditions for the whole period of the study in a deep freezer (~ -80C°). At the end of the test period, all 6 samples were analysed in duplicate under repeatability conditions.

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

4.3 Assigned value and standard deviation for proficiency assessment

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

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

The standard deviation for proficiency assessment, σ_P, was set for the individual analytes equal to the maximum tolerable standard uncertainty (Uf), which is calculated according to Equation 1 [7]. A LOD value of 0.30 µg/kg fat, corresponding to 0.06 µg/kg for cocoa and 0.1 µg/kg chocolate, if expressed on product basis, and αequal to 0.2 were applied for this purpose. The standard deviation for proficiency testing was calculated for the SUM4PAH parameter from the σ_P - values of the individual analytes applying the law of error propagation.

Equation 1 $$U_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2}$$ [7]

where

Uf 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 Tables 4-7. The arithmetic mean values of twenty independent analyses of the test material were used as assigned reference values. Uncertainty contributions resulting from (i) the characterisation of the material (method precision and uncertainty, purity of labelled standards, preparation of calibration solutions and the calibration function), (ii) potential inhomogeneity and (iii) potential instability of the test items were considered for the estimation of the uncertainty of the assigned values.

Table 4: Assigned values and their associated expanded uncertainties (k=2) for the cocoa powder test item, expressed on product basis (LOD=0.06 µg/kg).

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	0.88	0.06	0.18	20.3
Chysene	CHR	1.23	0.07	0.25	20.1
Benzo[*b*]fluoranthene	BBF	0.46	0.04	0.10	21.0
Benzo[*a*]pyrene	BAP	0.44	0.03	0.09	21.2
Sum of the four marker PAHs	SUM4PAH	3.00	0.10	0.33	11.1

Table 5: Assigned values and their associated expanded uncertainties (k=2) for the cocoa powder test item, expressed on fat basis (LOD=0.3 µg/kg).

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	4.40	0.32	0.89	20.2
Chysene	CHR	6.16	0.39	1.24	20.1
Benzo[*b*]fluoranthene	BBF	2.32	0.21	0.49	21.1
Benzo[*a*]pyrene	BAP	2.19	0.17	0.46	21.0
Sum of the four marker PAHs	SUM4PAH	15.07	0.57	1.67	11.1

Table 6: Assigned values and their associated expanded uncertainties (k=2) for the chocolate test item, expressed on product basis (LOD=0.1 µg/kg).

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	1.37	0.07	0.28	20.4
Chysene	CHR	1.70	0.09	0.34	20.0
Benzo[*b*]fluoranthene	BBF	1.13	0.06	0.23	20.4
Benzo[*a*]pyrene	BAP	1.15	0.05	0.24	20.9
Sum of the four marker PAHs	SUM4PAH	5.36	0.14	0.55	10.3

Table 7: Assigned values and their associated expanded uncertainties (k=2) for the chocolate test item, expressed on fat basis (LOD=0.3 µg/kg).

Analyte	Analyte short name	Assigned value	U	σ_P	
		µg/kg	µg/kg	µg/kg	%
Benz[*a*]anthracene	BAA	4.66	0.27	0.94	20.2
Chysene	CHR	5.79	0.34	1.17	20.2
Benzo[*b*]fluoranthene	BBF	3.85	0.24	0.78	20.3
Benzo[*a*]pyrene	BAP	3.91	0.20	0.80	20.5
Sum of the four marker PAHs	SUM4PAH	18.2	0.54	1.87	10.3

5. Evaluation of laboratories

5.1 General

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the test materials, which was expressed by z-scores [8]. zeta-Scores were calculated in addition considering the uncertainty of the test results, as reported by each participant. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed.

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

The results reported by participants are listed in ANNEX 10.

5.2 Evaluation criteria

z-Scores

z-Scores were calculated based on the final values as reported by participants. Equation 2 presents the formula for calculation of z-scores.

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

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 3.

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

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

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

5.3 Evaluation of results

Each laboratory had to report a total of 68 results; therefore the expected number of results of the 41 participants was 2788. Three NRLs did however not at all report results due to technical problems. Some participants reported only final values without replicates. In total 2000 results were submitted. The results reported by participants are presented in ANNEX 10.

z-Scores (in total 726) were attributed to the final values only. The individual results of replicate analyses were not rated.

Statistical evaluation of the results was performed using the PROLab software [11]. Robust mean values and robust standard deviations were calculated according to Algorithm A+S of ISO 13528:2005 [9].

It should be noted that the confidence intervals of the robust means calculated from the participants' results (ANNEX 10) overlap with the confidence intervals of the assigned values for each analyte in the chocolate test sample. The agreement of assigned values with robust mean values of the reported results was for some analytes less pronounced for the cocoa powder test material. In all cases multimodality in the kernel plots were observed, in particular for the cocoa powder test item.

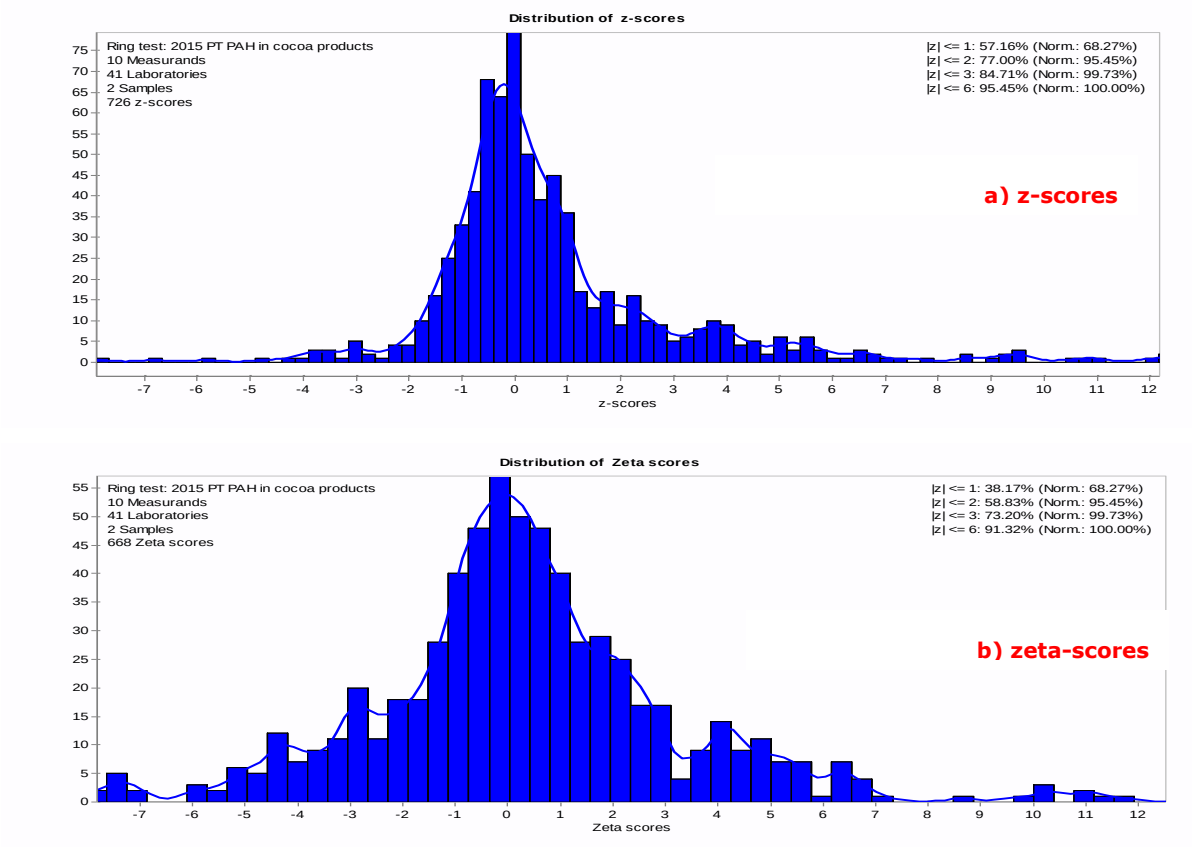
Robust reproducibility standard deviations were for milk chocolate equal or lower than σ_P for results expressed on product basis. They are slightly higher for the results expressed on fat basis. For cocoa powder however the robust reproducibility standard deviations were significantly higher than the respective σ_P . This could be explained with the higher complexity of the cocoa powder sample compared to the milk chocolate sample, which is manifested in lower PAH contents, lower fat content and some chromatographic interferences, as reported by the participants.

Seventy seven % of the results reported by the participants obtained satisfactory z-scores ≤ ±2.

Fifteen % of the results fell in the unsatisfactory field of z-scores > ±3 (Figure 1).

Figure 1 presents histograms and a Kernel density plots of the calculated a) z-scores and b) zeta-scores for the two samples and all the five measurands on product and on fat base, meaning all sample/measurand combinations and the resulting 726 z-scores (668 zeta scores). The percentages on the right side of the individual graphs indicate the percentage of the results falling within the different z- or zeta score ranges <=2, 3 or 6 and gives comparison with the normal distribution in brackets.

Figure 1: Histogram of a) z-scores and b) zeta- scores for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH expressed on product and fat base for both samples



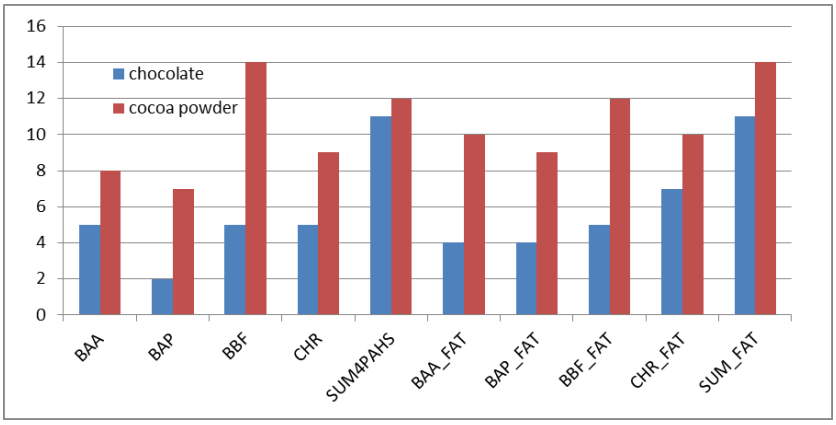
Twenty eight participants had more than 70% satisfactory z-scores and three participants did not report results. In general the overall performance of the participants could be summarised as reasonable.

Figure 2 and Figure 3 provide for both NRLs and OCLs an overview of the individual z-scores respectively zeta-scores assigned to the results for the cocoa powder and milk chocolate test materials. 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 8 and 9. All z-scores with an absolute value of ≥ 2 are highlighted in yellow and those higher than |3| in red.

It could be easily seen that the performance of the participants is better for the chocolate test material then for cocoa powder. Z-scores outside the satisfactory range were 28 on product base and 31 on fat base for the chocolate test sample, while for cocoa powder they are 47 and 55 respectively (Figure 4). The fact is in line with the previously mentioned complexity of the cocoa powder test sample with concentration levels for the analytes close to the LOQs for many of the methods used by the participants.

Figure 4. Number of z-scores outside satisfactory range defined by the tolerance limits of +/- 2



The graphical representations of the distribution of results for the individual analytes are given in ANNEX 11 together with the respective Kernel density plots.For each analyte the figures show the individual analysis results of the three replicate determinations.

The assessment of the performance of the participants based on the reported measurement uncertainty gave a less favourable picture. Table 10 presents the respective zeta-scores. Data outside the satisfactory performance range with an absolute value of ≥ 2 are highlighted in yellow and those higher than 3 - in red. 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. Only 58 % of the zeta-scores assigned for the four individual analytes and for the SUM4PAH were within the satisfactory performance range (Figure 1).

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, although improvement is noticed comparing previous years.

Unsatisfactorily large zeta-scores might be caused by underestimated measurement uncertainties, large bias, or a combination of both. Therefore reported uncertainties were checked against the uncertainty of the reference value. Those which were lower than the uncertainties of the reference values were highlighted in red as being non-adequate (Table 11).

Figure 2: Graphical overview of z-scores corresponding to the "final values" for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter expressed on product and fat base in the cocoa powder and milk chocolate test materials.

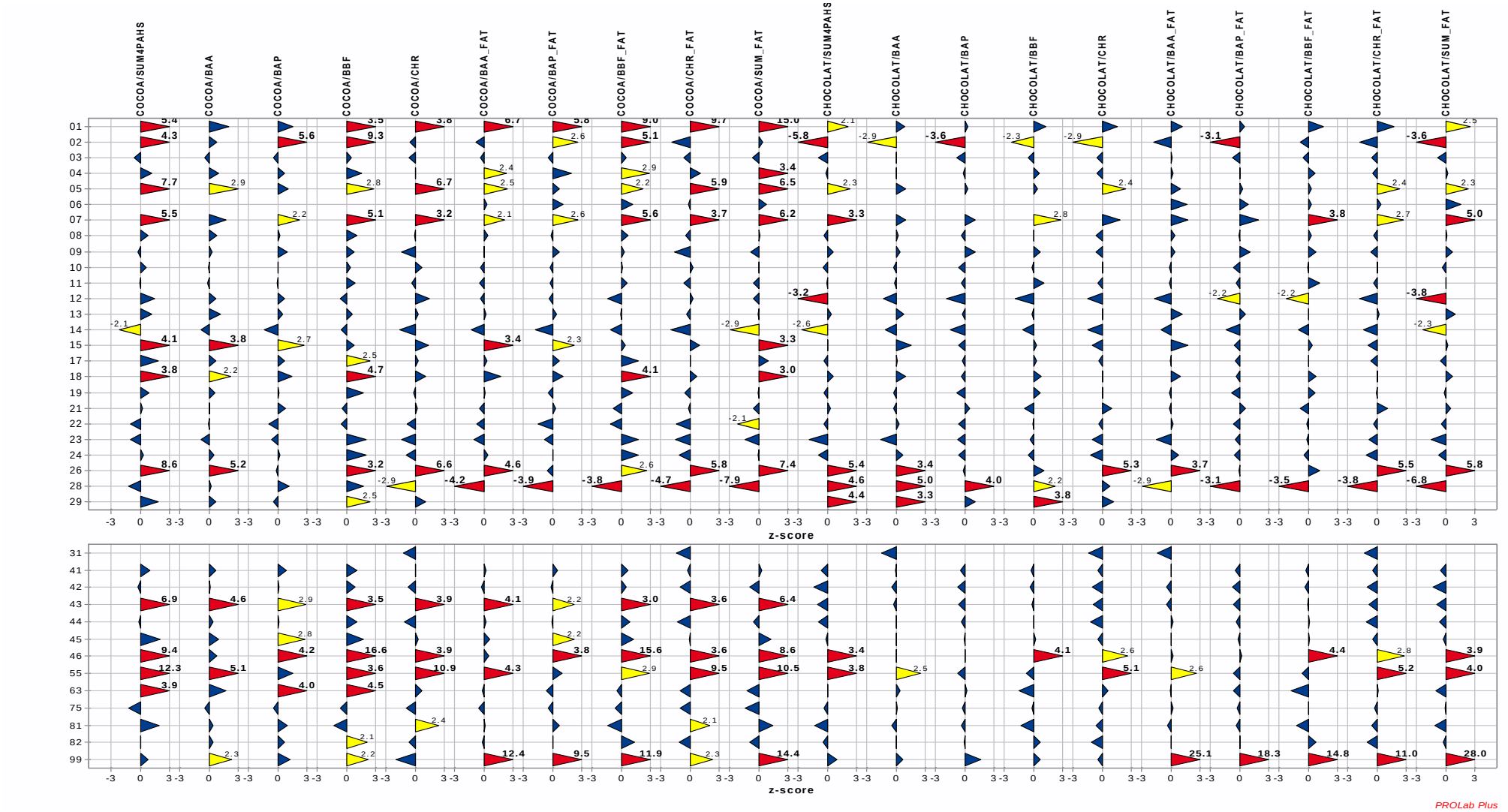


Figure 3: Graphical overview of zeta-scores corresponding to the "final values" for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter expressed on product and fat base in the cocoa powder and milk chocolate test materials.

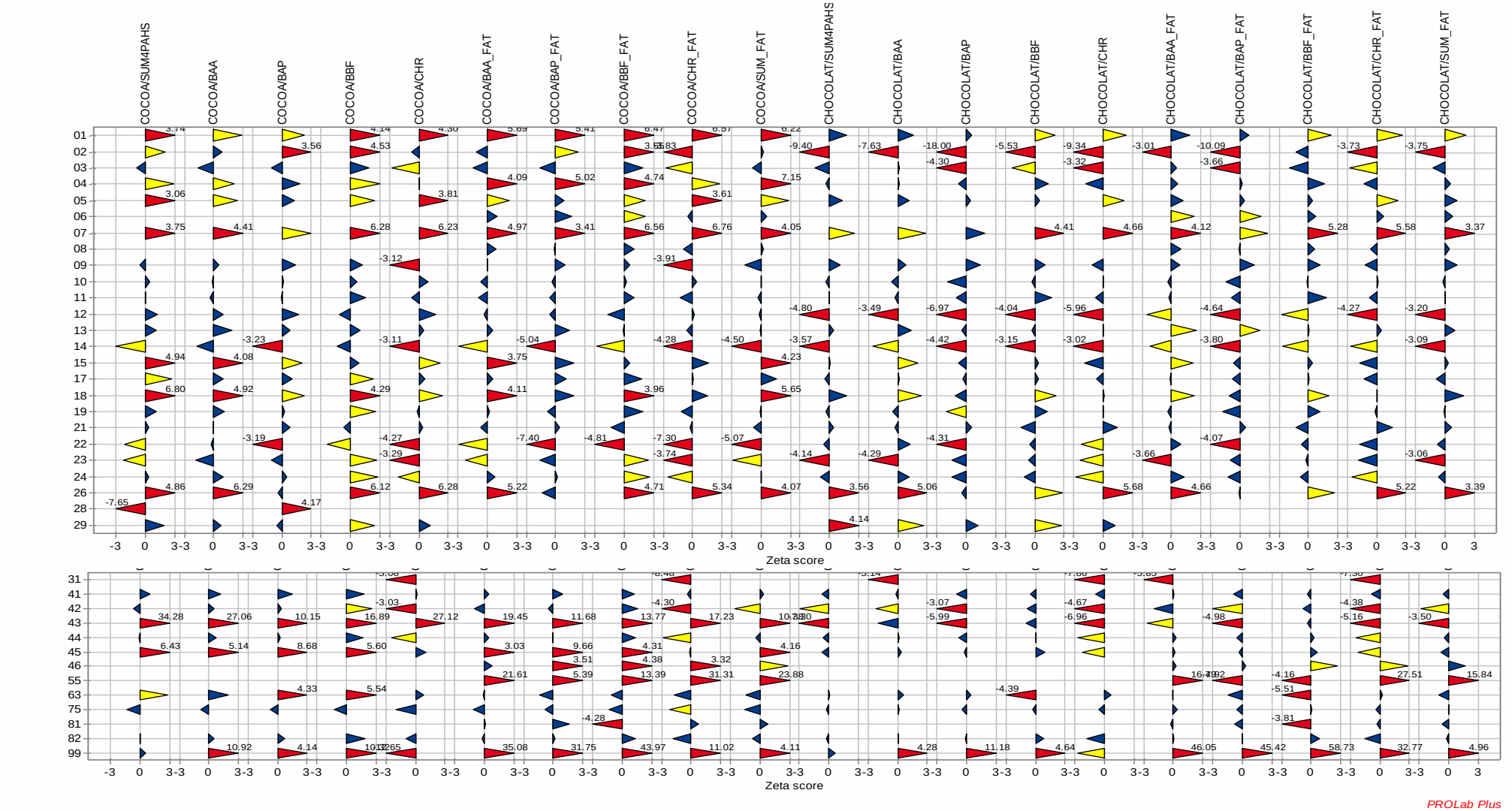


Table 8: Compilation of z-scores calculated from the "final values" reported by the participants for test material milk chocolate

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

Laboratory	BAA	BAP	BBF	CHR	SUM4PAHS	BAA_FAT	BAP_FAT	BBF_FAT	CHR_FAT	SUM_FAT
01	0.9	0.3	1.3	1.6	2.1	1.2	0.5	1.5	1.8	2.5
02	-2.9	-3.6	-2.3	-2.9	-5.8	-1.7	-3.1	-0.8	-1.8	-3.6
03	0	-0.8	-0.5	-0.6	-0.9	0.1	-0.8	-0.5	-0.5	-0.8
04	0.1	-0.1	0.6	-0.6	-0.1	0.2	0	0.8	-0.4	0.2
05	1	0.4	0.4	2.4	2.3	1	0.4	0.4	2.4	2.3
06						1.6	0.9	0.3	0.4	1.6
07	1	1.1	2.8	1.9	3.3	1.8	2	3.8	2.7	5
08	0.2	-0.3	0	-0.6	-0.3	0.5	0	0.3	-0.3	0.2
09	0.5	1	0.7	-0.6	0.6	0.5	1.1	0.8	-0.6	0.7
10	-0.3	-0.6	-0.1	0	-0.5	-0.2	-0.6	-0.1	0.1	-0.3
11	-0.1	-0.4	1.1	-0.4	-0.1	-0.1	-0.3	1.1	-0.3	0.1
12	-1.3	-1.9	-1.9	-1.5	-3.2	-1.7	-2.2	-2.2	-1.8	-3.8
13	0.8	-0.2	-0.1	0	0.4	1.2	0.6	0.1	0.3	1
14	-1.1	-1.5	-1.1	-1.5	-2.6	-1	-1.4	-1	-1.4	-2.3
15	1.6	-0.6	0.3	-1	0.1	1.7	-0.5	0.4	-0.9	0.3
16										
17	0.1	-0.2	0.3	-0.3	-0.3	-0.1	-0.4	0.1	-0.6	-0.5
18	1	-0.4	0.8	0	0.7	1	-0.4	0.8	0	0.7
19	-0.3	-0.8	0.7	0	-0.3	-0.2	-0.8	0.7	-0.1	-0.1
20										
21	-0.2	0.5	-0.9	1	0.3	-0.1	0.6	-0.8	1.1	0.5
22	0.3	-0.6	-0.1	-0.3	-0.3	0.2	-0.6	-0.1	-0.4	-0.4
23	-1.6	-0.7	-0.3	-1	-1.9	-1.4	-0.5	-0.1	-0.8	-1.5
24	0.7	-0.6	-0.5	-1.1	-0.9	0.8	-0.6	-0.4	-1.1	-0.7
25										
26	3.4	-0.1	1.1	5.3	5.4	3.7	0	1.2	5.5	5.8
28	5	4	2.2	0.8	4.6	-2.9	-3.1	-3.5	-3.8	-6.8
29	3.3	1	3.8	1.2	4.4					
31	-1.5			-1.4		-1.4			-1.3	
41	-0.1	-0.5	-0.3	-0.4	-0.7	0	-0.4	-0.2	-0.4	-0.5
42	-0.4	-0.7	-0.3	-1	-1.3	-0.4	-0.7	-0.3	-1	-1.3
43	-0.3	-0.6	-0.1	-0.9	-1	-0.4	-0.6	-0.1	-0.8	-0.9
44	0.1	-0.4	0	-1.2	-0.9	0.2	-0.3	0.2	-1.1	-0.6
45	0.1	-0.1	0.2	-0.4	-0.2	0	-0.1	0.2	-0.4	-0.2
46	0.1	0.1	4.1	2.6	3.4	0.2	0.3	4.4	2.8	3.9
55	2.5	-0.7	-0.7	5.1	3.8	2.6	-0.6	-0.7	5.2	4
63	0.5	0.2	-1.4	0.6	0.1	-0.1	-0.6	-1.7	0.2	-1
75	0.1	-0.2	-0.1	-0.3	-0.3	0.3	-0.3	0.1	-0.2	-0.1
81	-0.4	-0.4	-1.3	-0.6	-1.3	-0.3	-0.3	-1.2	-0.5	-1.1
82	0	-0.1	0.7	-1.1	-0.4	0.1	0	0.8	-1	-0.3
99	0.7	1.7	0.7	-0.4	1	25.1	18.3	14.8	11	28
–	–	–	–	–	–	–	–	–	–	–
No. of laboratories that submitted results	36	36	36	36	33	32	32	32	32	29
Assigned value	1.37	1.15	1.13	1.70	5.36	4.66	3.91	3.85	5.79	18.20
Mean	1.45	1.10	1.17	1.65	5.55	4.86	3.67	3.92	5.58	18.09
Reference value	1.37	1.15	1.13	1.70	5.36	4.66	3.91	3.85	5.79	18.20
Target s.d.	0.28	0.24	0.23	0.34	0.55	0.94	0.80	0.78	1.17	1.87
Reproducibility s.d.	0.25	0.16	0.22	0.39	1.11	1.06	0.52	0.78	1.38	3.27
Repeatability s.d.	0.07	0.06	0.06	0.11	0.20	0.24	0.19	0.19	0.34	0.70
Rel. target s.d.	20.4%	20.9%	20.4%	20.0%	10.3%	20.2%	20.5%	20.3%	20.2%	10.3%
Rel. reproducibility s.d.	18.5%	13.6%	19.2%	22.6%	20.7%	22.8%	13.3%	20.3%	23.8%	18.0%
Rel. repeatability s.d.	4.7%	5.3%	5.2%	6.2%	3.8%	5.1%	5.0%	5.0%	5.9%	3.9%
Reference s.d.	28.0%	24.0%	23.0%	34.0%	55.0%	94.0%	80.0%	78.0%	117.0%	187.0%
Number of labs with mean outside of tolerance limits	5	2	5	5	11	4	4	5	7	11

Table 9: Compilation of z-scores calculated from the "final values" reported by the participants for test materials cocoa powder

z-scores outside the satisfactory range (|z| > 3) are indicated by red (unsatisfactory) and yellow (questionable) background (|z| > 2); empty cells - z-score not calculated

Laboratory	BAA	BAP	BBF	CHR	SUM4PAHS	BAA_FAT	BAP_FAT	BBF_FAT	CHR_FAT	SUM_FAT
1	2	1.6	3.5	3.8	5.4	6.7	5.8	9	9.7	15
2	0.8	5.6	9.3	-0.5	4.3	-0.8	2.6	5.1	-1.8	0.4
3	-0.4	-0.4	0.5	-0.6	-0.6	-0.4	-0.4	0.5	-0.7	-0.7
4	1	0.7	1.5	0	1.2	2.4	1.9	2.9	1.1	3.4
5	2.9	1.1	2.8	6.7	7.7	2.5	0.7	2.2	5.9	6.5
6						0.3	1.1	1.2	-0.1	0.8
7	1.8	2.2	5.1	3.2	5.5	2.1	2.6	5.6	3.7	6.2
8	0.8	0.3	1.1	-0.1	0.8	0.4	-0.1	0.7	-0.4	0.1
9	0.3	1	0.8	-1.3	-0.3	0	0.7	0.4	-1.6	-0.8
10	-0.1	0	0.4	0.7	0.6	-0.3	-0.2	0.2	0.4	0.1
11	-0.2	-0.1	0.9	-0.4	-0.1	-0.4	-0.3	0.6	-0.6	-0.5
12	0.7	0.7	-0.6	1.5	1.5	-0.4	-0.3	-1.4	0.3	-0.5
13	1.2	0.5	0.6	0.3	1.2	0.2	0.5	0	-0.3	0
14	-0.8	-1.4	-0.5	-1.5	-2.1	-1.3	-1.7	-1	-1.9	-2.9
15	3.8	2.7	0.8	1.4	4.1	3.4	2.3	0.4	1	3.3
16										
17	0.7	0.7	2.5	0.3	1.8	0.3	0.7	1.8	0	1
18	2.2	1.5	4.7	1.1	3.8	1.8	1	4.1	0.7	3
19	0.6	0.2	1.7	-0.1	0.9	0.1	-0.4	1.2	-0.5	0
20										
21	0	0.8	-0.4	0.3	0.3	-0.4	0.3	-0.8	-0.2	-0.5
22	-0.1	-0.9	-0.5	-0.8	-1	-0.7	-1.5	-1.1	-1.4	-2.1
23	-0.8	-0.6	2	-1.3	-1	-1	-0.8	1.8	-1.5	-1.3
24	0.6	0.3	2	-0.9	0.3	0.4	0.1	1.8	-1	0
25										
26	5.2	-0.2	3.2	6.6	8.6	4.6	-0.5	2.6	5.8	7.4
28	0.3	1.2	1.8	-2.9	-1.2	-4.2	-3.9	-3.8	-4.7	-7.9
29	0.7	-0.4	2.5	1.1	1.8					
31				-1.2					-1.4	
41	0.7	0.9	1.1	0.1	1	0.3	0.5	0.7	-0.2	0.3
42	0.1	0.2	0.9	-0.7	-0.2	-0.2	-0.2	0.5	-1	-0.9
43	4.6	2.9	3.5	3.9	6.9	4.1	2.2	3	3.6	6.4
44	0.4	0.2	1.1	-1.1	-0.2	0.3	0	0.9	-1.2	-0.5
45	1	2.8	1.7	0.3	2	0.6	2.2	1.3	0	1.3
46	0.8	4.2	16.6	3.9	9.4	0.6	3.8	15.6	3.6	8.6
55	5.1	1.6	3.6	10.9	12.3	4.3	1	2.9	9.5	10.5
63	1.8	4	4.5	0.7	3.9	-0.1	-0.6	-0.4	-1	-1.2
75	-0.4	-0.4	-0.6	-0.9	-1.2	-0.6	-0.4	-0.7	-1	-1.4
81	0.4	1	-1.3	2.4	1.9	0.2	0.7	-1.4	2.1	1.4
82	0.4	0.7	2.1	-0.6	0.1	-0.1	0.1	1.4	-1.1	-0.9
99	2.3	1.2	2.2	-1.9	0.8	12.4	9.5	11.9	2.3	14.4
–	–	–	–	–	–	–	–	–	–	–
No. of laboratories that submitted results	36	36	36	36	33	32	32	32	32	29
Assigned=Reference value	0.88	0.44	0.46	1.23	3.00	4.40	2.19	2.32	6.16	15.07
Mean	1.04	0.52	0.64	1.34	3.65	4.94	2.46	3.00	6.41	17.13
Target s.d.	0.18	0.09	0.10	0.25	0.33	0.89	0.46	0.49	1.24	1.67
Reproducibility s.d.	0.22	0.12	0.18	0.49	1.03	1.44	0.73	1.16	2.68	6.09
Repeatability s.d.	0.05	0.04	0.05	0.07	0.21	0.29	0.16	0.26	0.35	0.89
Rel. target s.d.	20.5%	21.1%	21.0%	20.1%	11.1%	20.3%	21.0%	21.1%	20.1%	11.1%
Rel. reproducibility s.d.	24.8%	28.1%	38.2%	40.1%	34.2%	32.7%	33.4%	49.8%	43.5%	40.4%
Rel. repeatability s.d.	6.0%	8.6%	11.5%	6.0%	7.0%	6.6%	7.2%	11.0%	5.7%	5.9%
Reference s.d.	0.18	0.09	0.10	0.25	0.33	0.89	0.46	0.49	1.24	1.67
Number of labs with mean outside of tolerance limits	7	7	14	9	12	10	9	12	10	14

Table 10: Compilation of zeta-scores calculated from the "final values" reported by the NRLs and OCLs for test matrials cocoa powder and chocolate

zeta-scores outside the satisfactory range (|z| > 3) are indicated by red (unsatisfactory) and yellow (questionable) background (|z| > 2); empty cells - zeta-score not calculated

Lab code	COCOA/BAA	COCOA/BAP	COCOA/BBF	COCOA/CHR	COCOA/SUM4PAHS	COCOA/BAA_FAT	COCOA/BAP_FAT	COCOA/BBF_FAT	COCOA/CHR_FAT	COCOA/SUM_FAT	CHOCOLAT/BAA	CHOCOLAT/BAP	CHOCOLAT/BBF	CHOCOLAT/CHR	CHOCOLAT/SUM4PAHS	CHOCOLAT/BAA_FAT	CHOCOLAT/BAP_FAT	CHOCOLAT/BBF_FAT	CHOCOLAT/CHR_FAT	CHOCOLAT/SUM_FAT
	NATIONAL REFERENCE LABORATORIES (NRLs)																			
01	2.8	2.3	4.1	4.3	3.7	5.7	5.4	6.5	6.6	6.2	1.6	0.6	2.1	2.4	1.8	1.8	0.9	2.3	2.6	2.1
02	0.8	3.6	4.5	-0.8	2.1	-1.1	2.3	3.5	-3.8	0.3	-7.6	-18.0	-5.5	-9.3	-9.4	-3.0	-10.1	-1.3	-3.7	-3.8
03	-1.6	-1.1	1.9	-2.8	-0.9	-1.4	-1.6	2.0	-2.7	-0.9	0.2	-4.3	-2.3	-3.3	-1.5	0.5	-3.7	-2.0	-2.8	-1.2
04	2.1	1.8	3.0	0.0	2.9	4.1	5.0	4.7	2.7	7.2	0.2	-0.8	1.4	-1.8	-0.3	0.6	0.2	1.7	-1.3	0.6
05	2.5	1.2	2.4	3.8	3.1	2.2	0.9	2.1	3.6	2.8	1.2	0.5	0.5	2.2	1.3	1.1	0.5	0.5	2.1	1.3
06						1.1	1.7	2.2	-0.5	0.5						2.3	2.2	0.8	0.7	0.8
07	4.4	3.0	6.3	6.2	3.8	5.0	3.4	6.6	6.8	4.1	2.9	1.9	4.4	4.7	2.5	4.1	2.8	5.3	5.6	3.4
08						0.9	-0.2	1.1	-1.0	0.3						1.0	-0.1	0.6	-0.7	0.4
09	0.6	1.4	1.2	-3.1	-0.5	0.0	1.0	0.6	-3.9	-1.7	0.8	1.5	1.1	-1.2	1.1	0.8	1.5	1.2	-1.2	1.2
10	-0.1	0.1	0.7	1.0	0.5	-0.7	-0.4	0.3	0.4	0.1	-0.7	-1.9	-0.3	0.0	-0.4	-0.3	-1.4	-0.1	0.1	-0.2
11	-0.4	-0.1	1.5	-0.7	0.0	-0.9	-0.6	1.0	-1.2	-0.3	-0.3	-1.0	1.8	-0.8	0.0	-0.3	-0.9	1.8	-0.7	0.0
12	1.0	1.7	-1.2	1.7	1.3	-0.3	-0.6	-1.6	0.2	-0.3	-3.5	-7.0	-4.0	-6.0	-4.8	-2.5	-4.6	-2.7	-4.3	-3.2
13	1.9	0.8	1.0	0.5	1.2	0.5	1.4	-0.1	-0.6	-0.1	1.4	-0.4	-0.3	0.0	0.4	2.5	2.0	0.1	0.5	1.0
14	-1.7	-3.2	-1.3	-3.1	-3.0	-2.9	-5.0	-2.8	-4.3	-4.5	-2.5	-4.4	-3.2	-3.0	-3.6	-2.2	-3.8	-2.6	-2.7	-3.1
15	4.1	2.1	0.9	2.2	4.9	3.8	1.9	0.5	1.6	4.2	2.1	-0.8	0.4	-1.9	0.1	2.2	-0.6	0.5	-1.8	0.4
17	1.0	1.0	2.3	0.6	2.7	0.5	1.1	1.8	0.1	1.6	0.2	-0.4	0.4	-0.6	-0.5	-0.1	-0.8	0.1	-1.3	-1.0
18	4.9	2.3	4.3	2.4	6.8	4.1	1.8	4.0	1.6	5.6	2.4	-1.1	2.2	0.1	1.8	2.3	-1.1	2.1	0.1	1.8
19	1.1	0.3	2.5	-0.2	1.1	0.2	-0.9	1.9	-1.1	-0.1	-0.5	-2.0	1.3	0.0	-0.4	-0.3	-1.8	1.2	-0.2	-0.1
21	0.0	0.8	-0.6	0.4	0.4	-0.6	0.4	-1.3	-0.3	-0.7	-0.3	0.6	-1.4	1.5	0.4	-0.2	0.6	-1.3	1.6	0.6
22	-0.2	-3.2	-2.4	-4.3	-2.2	-2.9	-7.4	-4.8	-7.3	-5.1	1.3	-4.3	-0.5	-2.2	-0.6	1.0	-4.1	-0.7	-1.8	-0.8
23	-1.8	-1.1	2.7	-3.3	-2.2	-2.2	-1.6	2.4	-3.7	-2.9	-4.3	-1.5	-0.6	-2.3	-4.1	-3.7	-1.0	-0.2	-1.8	-3.1
24	1.0	0.4	2.8	-2.1	0.3	0.7	0.1	2.6	-2.5	0.0	1.2	-1.4	-1.0	-2.8	-1.0	1.3	-1.2	-0.8	-2.6	-0.7
26	6.3	-0.4	6.1	6.3	4.9	5.2	-1.4	4.7	5.3	4.1	5.1	-0.4	2.8	5.7	3.6	4.7	-0.1	2.7	5.2	3.4
28		4.2			-7.7															
29	0.8	-0.6	2.5	1.2	1.9						2.6	1.2	2.8	1.3	4.1					
	OFFICIAL CONTROL LABORATORIES (OCLs)																			
31				-5.1					-8.5		-5.1			-7.9		-5.9			-7.3	
41	1.1	1.4	1.8	0.2	1.0	0.5	0.9	1.2	-0.4	0.3	-0.1	-1.0	-0.5	-0.9	-0.7	0.1	-0.8	-0.4	-0.9	-0.6
42	0.6	0.3	2.5	-3.0	-0.7	-1.0	-0.5	1.5	-4.3	-2.6	-2.2	-3.1	-0.9	-4.7	-3.0	-1.9	-3.0	-0.8	-4.4	-2.8
43	27.1	10.2	16.9	27.1	34.3	19.5	11.7	13.8	17.2	10.4	-2.0	-6.0	-0.9	-7.0	-7.3	-2.6	-5.0	-0.4	-5.2	-3.5
44	0.7	0.3	1.6	-2.4	-0.1	0.4	-0.1	1.4	-2.8	-0.4	0.1	-0.8	0.1	-2.7	-0.6	0.3	-0.6	0.3	-2.4	-0.5
45	5.1	8.7	5.6	1.1	6.4	3.0	9.7	4.3	-0.1	4.2	0.3	-0.2	0.9	-2.2	-0.7	0.1	-0.3	0.7	-2.2	-0.8
46						0.8	3.5	4.4	3.3	2.8						0.3	0.4	2.7	2.9	1.6
55						21.6	5.4	13.4	31.3	23.9						16.8	-4.9	-4.2	27.5	15.8
63	1.9	4.3	5.5	0.8	2.9	-0.2	-1.4	-1.1	-1.7	-1.4	0.6	0.4	-4.4	0.7	0.1	-0.1	-1.4	-5.5	0.2	-1.0
75	-0.9	-0.7	-1.3	-2.0	-1.4	-1.1	-0.8	-1.3	-2.2	-1.6	0.2	-0.4	-0.2	-0.6	-0.3	0.4	-0.5	0.1	-0.5	0.0
81						0.2	1.6	-4.3	0.7	0.8						-0.3	-0.8	-3.8	-0.3	-0.7
82	0.6	0.7	1.9	-1.0	0.1	-0.2	0.1	1.3	-1.8	-0.7	0.0	-0.1	0.8	-1.8	-0.3	0.1	0.0	0.8	-1.6	-0.2
99	10.9	4.1	10.3	-12.6	0.5	35.1	31.8	44.0	11.0	4.1	4.3	11.2	4.6	-2.7	0.6	46.1	45.4	58.7	32.8	5.0

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 1). Individual maximum tolerated measurement uncertainties were calculated for each reported result as the outcome of Equation 1 depends besides of the LOD also of the analyte content in the sample. The final values reported by the participants and the maximum tolerated LOD of 0.30 µg/kg for contents expressed on fat basis, which corresponds on product basis to 0.06 µg/kg for cocoa powder and 0.1

µg/kg for milk chocolate were used for the calculation of the respective maximum threshold values. Non-compliant reported uncertainties are highlighted in Table 11.

Estimating realistic measurement uncertainty values still causes problem for some participants, although improvement is noticed compared to previous PTs. Attention should be paid to unrealistic low uncertainties, reported by some participants. It should be mentioned that probably some laboratories reported absolute uncertainty instead of the relative measurement uncertainty as required, resulting in very low unrealistic values for that parameter. However, 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.

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.

Table 11. Relative expanded uncertainties, as reported by the participants

	chocolate										cocoa powder									
Lab	Uncertainty on product base					Uncertainty on fat base					Uncertainty on product base					Uncertainty on fat base				
code	BaA	BaP	BbF	CHR	SUM	BaA_fat	BaP_fat	BbF_fat	CHR_fat	SUM_FAT	BaA	BaP	BbF	CHR	SUM	BaA_fat	BaP_fat	BbF_fat	CHR_fat	SUM_FAT
LOD	0.3	0.6	0.3	0.6		0.1	0.3	0.1	0.3		0.3	0.6	0.3	0.6		0.06	0.18	0.06	0.18	
1	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
2	35	30	29	28	31	35	30	29	28	31	35	30	29	28	31	35	30	29	28	31
3	5.4	7.6	8.4	5	13.5	5.6	7.8	8.6	5.2	13.9	8	9.2	5.8	8.4	15.9	8.2	9.4	6.2	8.6	16.4
4	15	5	15	12.5	6.5	15	5	15	12.5	6.5	15	10	15	12.5	7.2	15	10	15	12.5	7.2
5	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
6						21	13	15	22	36						10	22	17	7.4	30
7	11	20	16	11	20	12	20	16	12	20	11	20	16	12	20	11	20	16	12	20
8						16	25	21	17	9						16	35	24	16	10
9	21	24	23	22	11	21	24	23	22	11	21	24	23	22	11	21	24	23	22	11
10	15	15	20	25	25	20	20	25	30	30	15	15	20	25	25	20	20	25	30	30
11	17	16	20	20	37.6	17	16	20	20	37.6	17	18	20	20	37.6	17	18	20	20	37.6
12	20	17	29	12	20	40	34	58	25	40	24	11	25	27	22	47	22	50	54	44
13	20	20	20	20	20	15	10	20	20	17	20	20	20	20	20	15	10	20	20	17
14	22.3	18.8	16.5	27.4	20.1	22.3	18.8	16.5	27.4	20.1	22.3	18.8	16.5	27.4	20.1	22.3	18.8	16.5	27.4	20.1
15	23.8	34.9	34.8	25.2	14.4	23.8	34.9	34.8	25.2	14.4	21.2	33.4	31.4	19.7	12.4	21.2	33.4	31.4	19.7	12.4
16																				
17	23.9	22.2	29.1	19.3	11.8	23.9	22.2	29.1	19.3	11.8	23.9	22.17	29.08	19.29	11.85	23.9	22.17	29.08	19.29	11.85
18	13.3	14	11.5	11.8	6.5	13.3	14	11.5	11.8	6.5	11.8	18.8	22.8	14.6	8.4	11.8	18.8	22.8	14.6	8.4
19	20	20	20	20	16	20	20	20	20	16	20	20	20	20	16	20	20	20	20	16
20																				
21	26	34	30	22	15	26	34	30	22	15	26	34	30	22	15	26	34	30	22	15
22	5.4	7.6	8.4	5	13.5	5.6	7.8	8.6	5.2	13.9	7.3	4.1	4.5	5.9	11.2	7.3	4.1	4.5	5.9	11.2
23	20.7	20.6	20.6	20.3	11.1	20.7	20.6	20.6	20.3	11.1	21.15	23.99	21.37	20.76	10.37	21.15	23.99	21.37	20.76	11.05
24	20.1	20.2	20.2	20.1	20	20	20	20	20	20	20.2	21	20.5	20.2	20	20	20	20	20	20
25																				
26	16	12	12	18	20	18	14	14	20	22	16	12	12	18	20	18	14	14	20	22
28												0.096			0.74					
29	31	30	31	30	15						29	29	27	30	17					
31	15	13	8	7		11	13	8	6	10	13	12	17	10		13	13	13	2	10
41	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
42	6.8	10.1	16.4	9.1	10.1	6.8	10.1	16.4	9.1	10.1	4.2	14.5	10.4	8.1	6.9	4.2	14.5	10.4	8.1	6.9
43	0.4	0.3	0.3	0.4	1.4	1.4	1	1.1	1.4	4.9	0.5	0.2	0.2	0.7	1.6	2.5	1	1.2	3.2	7.7
44	22	22	22	22	30	22	22	22	22	30	22	22	22	22	30	22	22	22	22	30
45	6.7	18.8	7.7	5.1	5	6.7	18.8	7.7	5.1	5	3.4	3.9	7.1	10	5	3.4	3.9	7.1	10	5
46						25	25	35	25	35						25	25	35	25	35
55						1.6	0.7	0.7	2.4	3.05						1.8	0.6	0.8	3.6	4.15
63	27	20	17	29	21	27	20	17	29	21	27	20	17	29	21	27	20	17	29	21
75	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
81						40	15	15	83	33.7						40	15	15	83	33.7
82	29	34	32	30	30	30	29	34	32	30	29	34	32	30	30	30	29	34	32	30
99	3.5	3.3	2	3.8	29.9	3.5	3.3	2	3.8	29.9	3.5	3.3	2	3.8	29.9	3.5	3.3	2	3.8	29.9

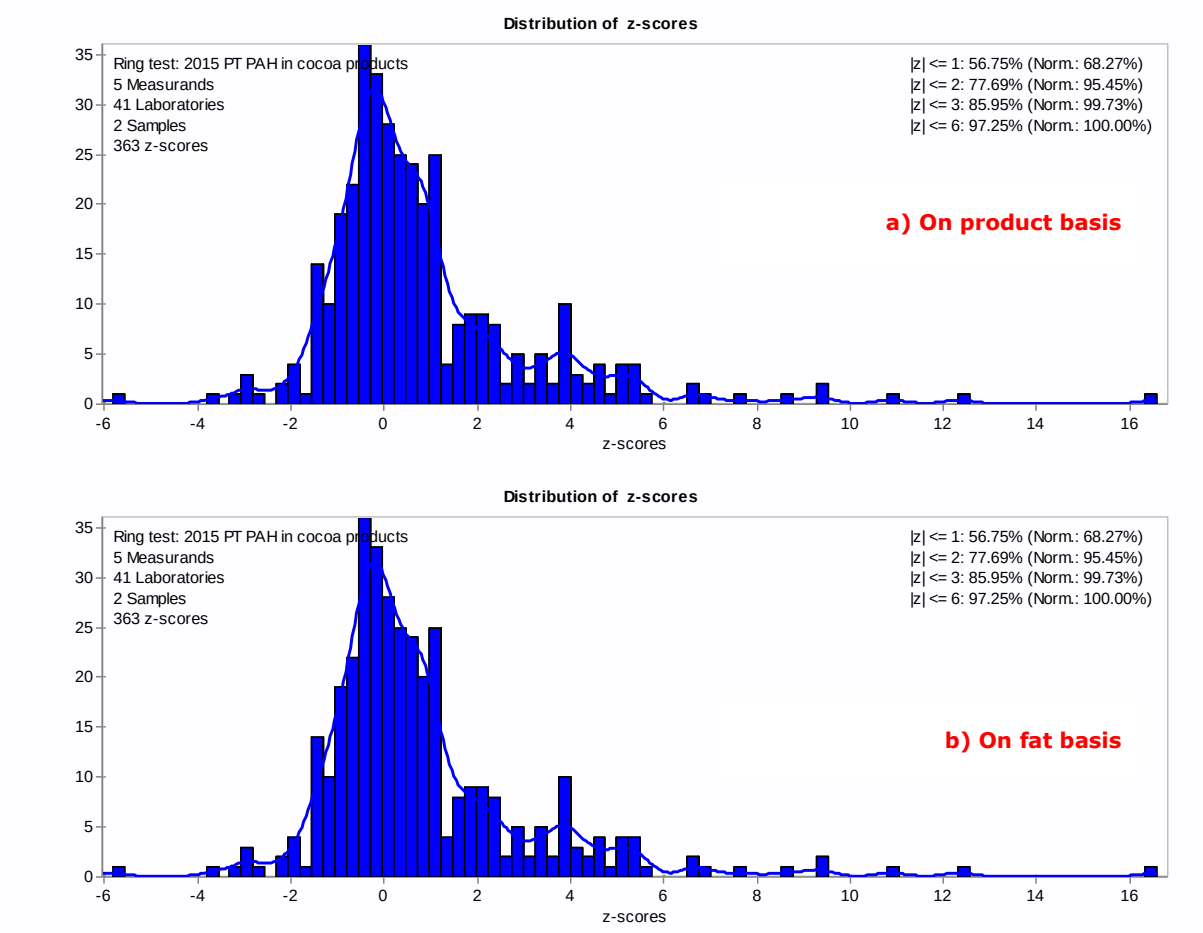
Of particular interest was the evaluation of the influence of the fat determination on the accuracy of results. Both the contribution of the fat determination to bias and comparability of results were evaluated.

Figure 5 provides the histograms of z-score distributions of results expressed on product basis (upper graph), and on fat basis (lower graph), showing non statistical difference between two ways of expressing results.

According to the answers from the questionnaire, six participants performed the analysis on the fat fraction after extracting it from the cocoa product. However most of the

participant analysed the cocoa product directly followed by transformation of the analyte contents expressed on product basis into expression on fat basis, applying a separately determined fat content ratio.

Figure 5. Comparison of the z-score distributions and Kernel density plots for results expressed a) on product and b) on fat basis.



This step introduced additional uncertainty to the reported value but does not lead to statistically significant increase in unsatisfactory z-scores.

As could be seen from the Kernel density plots the distributions of results for most of the analytes in both samples are monomodal and close to the Gaussian distribution. This supports the conclusion that, from the statistical point of view, the measurement of PAHs in cocoa products samples is under control.

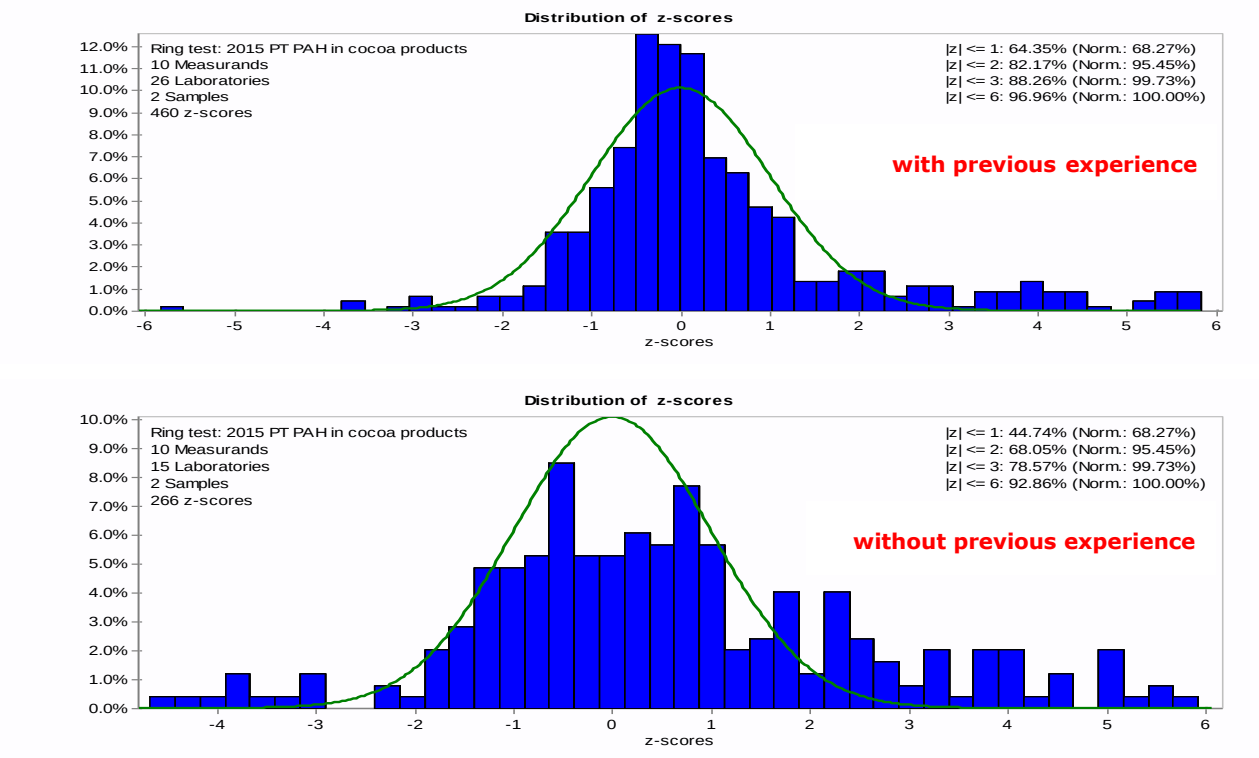
5.4 Additional information extracted from the questionnaire

Additional information on the determination of PAHs in cocoa products 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 in the determination of PAHs in similar products. However nine participants did not have previous experience with cocoa products, while another 7 did not analyse this matrix in routine, which is indicated by analysing around 5 samples/year. 13 laboratories are not accredited for the determination of the four marker PAHs in cocoa products. Figure 6 demonstrates clearly the effect of experience in the analysis of a food matrix on the laboratory performance.

The first graph shows the distribution of z-scores for laboratories, which were either accredited for that matrix or had some previous experience with similar matrices, while the second graphs shows the same distribution for the non-accredited laboratories or those with no experience. The experienced participant obtained an average 81% satisfactory z-scores against 68% for the non-experienced one.

Figure 6. Distributions of z-scores for laboratories with and without previous experience in the determination of PAHs in cocoa products.



Half of the participants (16) answering to the questionnaire used GC with different types of mass spectrometric detectors and 17 laboratories used HPLC-FLD for the determination of PAHs. The analysis of all data showed that laboratory performance was not linked to any analytical technique or sample preparation method used.

The survey related to instrument calibration revealed that 12 participant did not use internal standards. However, those are mainly laboratories applying HPLC/FLD as measurement technique. Four participants reported the application of standard addition technique.

Most participants (except participant #9) reported results corrected for recovery (on purpose, or implicitly corrected by internal standards).

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]. The maximum tolerated LOD and LOQ laid down in the legislation are related to the fat content of the cocoa products. Therefore, when the analysis is performed on the entire product instead of the fat fraction the maximum tolerated LOD/LOQ should be recalculated, taking into account the respective fat content in the samples. The resulting maximum tolerated LODs/LOQs are shown in the table in Annex 10. The same table presents an overview of the LODs/LOQs reported by participants, highlighting in red those, not complying with the provisions set in legislation. From 41 participants, 30 reported LODs/LOQ on product basis. Twenty one of them (70%) were non-compliant, as their LODs/LOQs transformed to the fat fraction exceeded the thresholds given in legislation. This was especially the

case for the cocoa powder test sample, for which the fat content was lower compared to milk chocolate.

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

5.5 Compliance assessment

As important as the correct analysis of the test sample is the interpretation of results. The test items of this PT were cocoa powder and milk chocolate. These matrices are representative for the food category 6.1.2 "Cocoa beans and derived products" specified in Commission Regulation (EC) No 835/2011 [6], with a maximum level for BAP and for the sum of the four PAHs (in the following indicated as SUM4PAH) of 5.0 µg/kg fat and 30.0 µg/kg fat respectively. The maximum level for the SUM came into force on 1 April 2015.

The assigned analyte contents for BaP and the sum of four PAHs, expressed on fat basis did not exceed the abovementioned maximum levels for none of the test materials studied in this PT. Both test samples were compliant with the legislative limits.

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. Figure 6 presents the distribution of the reported results with associated uncertainties for BaP and the sum of four PAHs in relation to the maximum levels defined in legislation (indicated by red lines).

The decision criterion for non-compliance is specified in Commission Regulation (EC) No 836/2011 [7]. 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 measurement uncertainty. A laboratory should reject the tested sample as being non-compliant if the lower end of the error bar (representing the expanded measurement uncertainty) associated with the reported result (black dot) in Figure 7 is above the regulated limit represented by the red line.

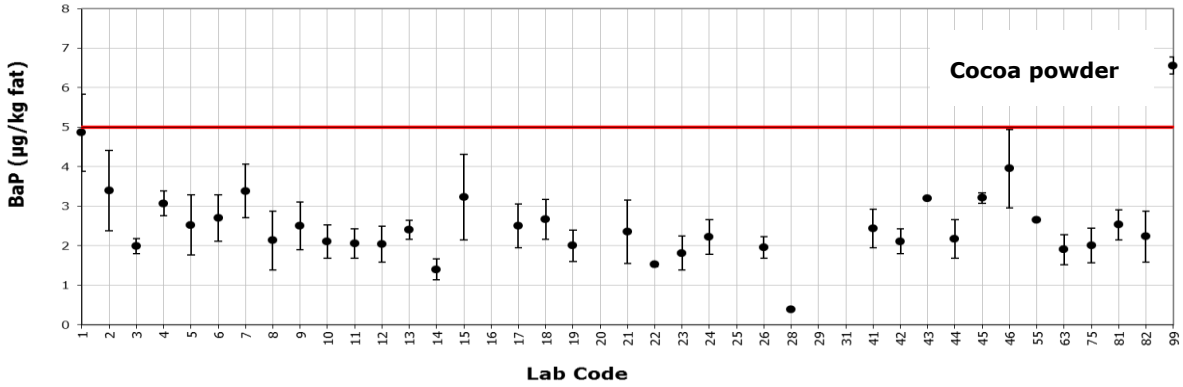
Thirty two laboratories classified the test samples correctly as compliant. One participant (#29) did not provide a compliance statement. One laboratory (#99) correctly classified it as non-compliant based on its results; however, the result of this laboratory was biased. One laboratory (#46) wrongly classified them as non-compliant although correctly explained that their results were below the legislative limits.

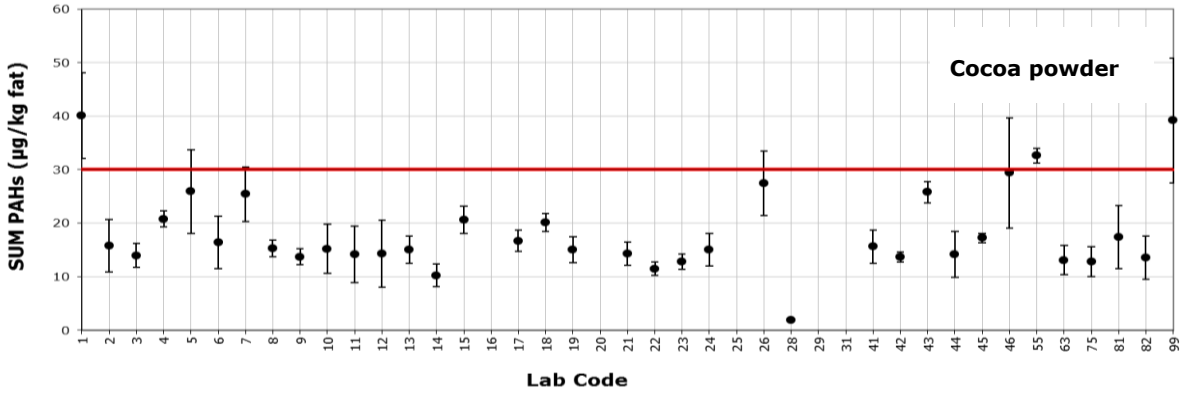
The compliance decision of laboratory #1 and #55 were not supported by their data. Based on their own measurements, they should have come to the conclusion that the SUMPAH content of the cocoa powder test sample is beyond reasonable doubt above the maximum level – resulting in a "non-compliant" statement.

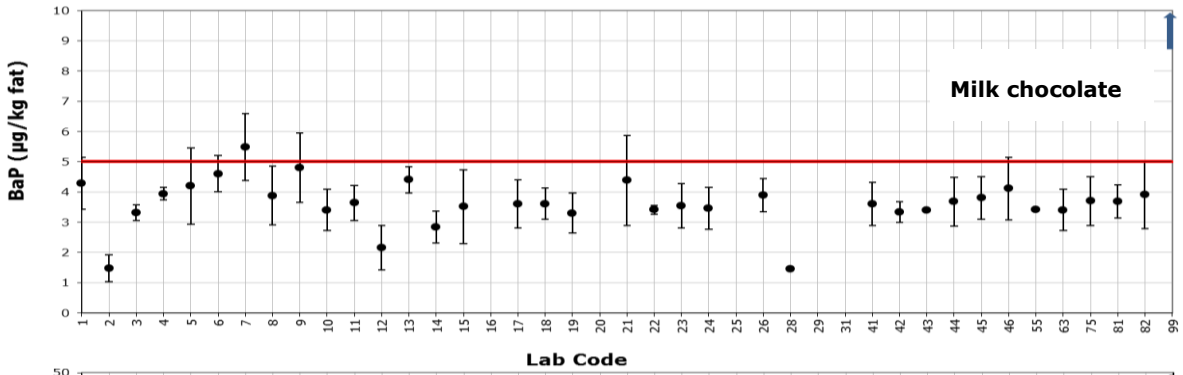
This study revealed that the interpretation of results provided problems to some participants. They are therefore requested to familiarise with the rules for interpretation of analysis results provided in [13]. They might also wish to consult the EURACHEM/CITAC Guide "Use of uncertainty information in compliance assessment" [14].

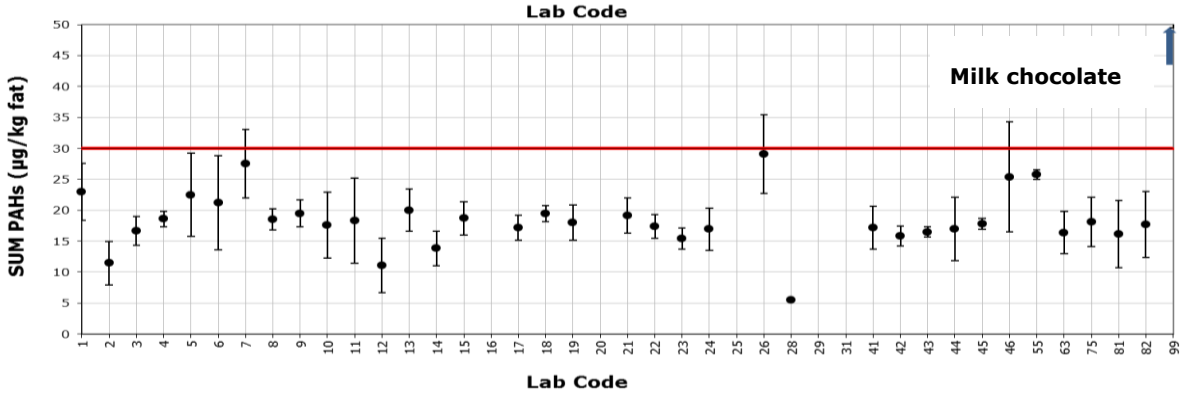
Figure 7. Results reported by the participants for BaP and the SUM PAHs for the test samples , Results are expressed on fat basis and associated by their expanded

measurement uncertainties (whiskers). Applicable maximum levels are indicated by red lines.









6. Follow-up actions for underperforming laboratories

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

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

Conclusion

Forty one participants reported analysis results. The performance of most participants was satisfactory. More than 77% of the results reported by NRLs and OCLs respectively obtained satisfactory performance ratings.

Participants are urged to pay attention to the estimation of realistic measurement uncertainty values and its way of reporting. Additionally, LODs/LOQs of the majority of the participants' method should be improved in order to comply with the requirement of legislation, especially for the analysis of cocoa products with low fat content.

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

Based on these findings the EURL PAH intends to repeat this proficiency test exercise in the years to come.

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

List of abbreviations and definitions

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

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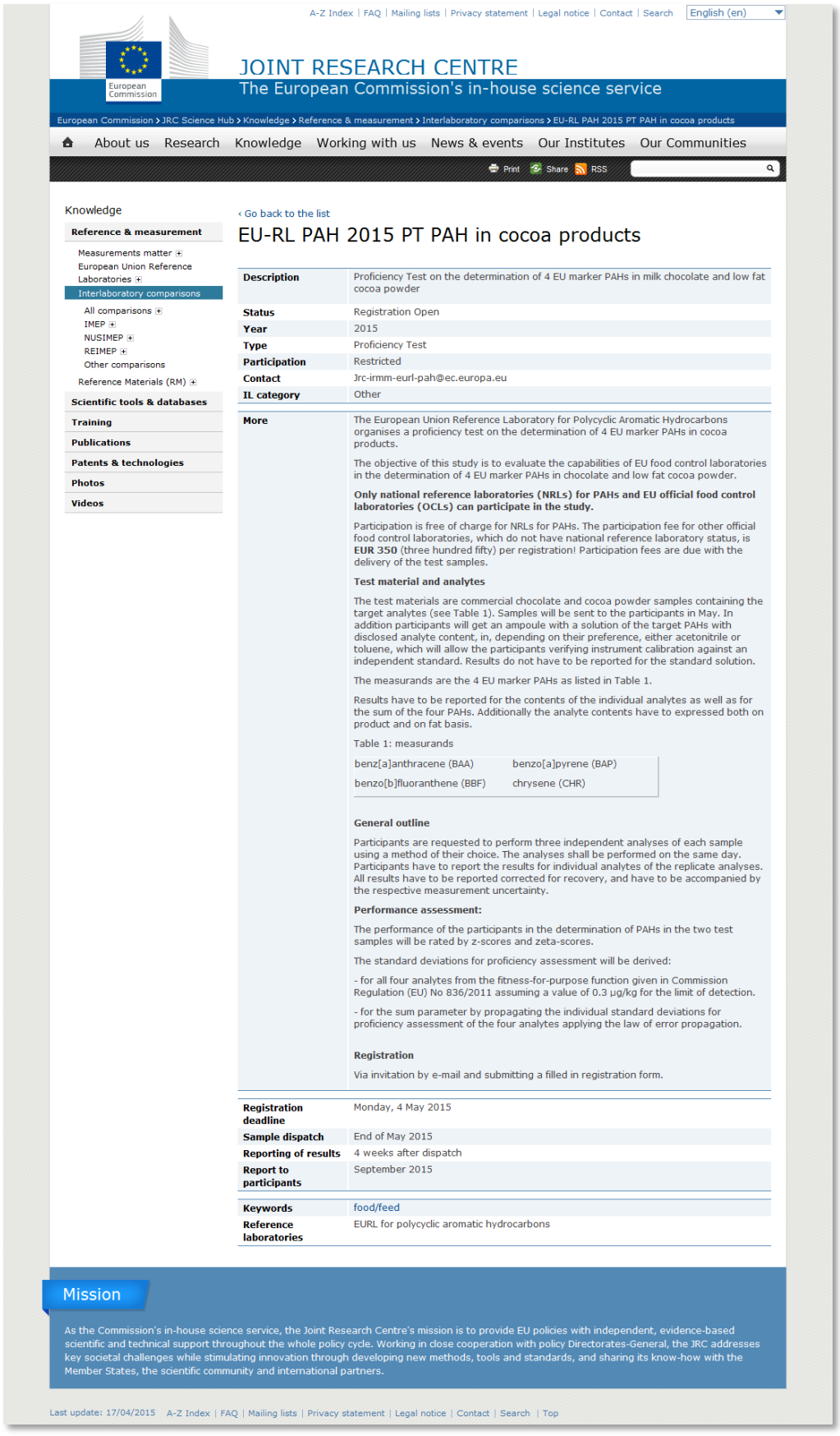
ANNEXES

ANNEX 1: Announcement of the PT on the IRMM webpage



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EU-RL PAH 2015 PT PAH in cocoa products

Description	Proficiency Test on the determination of 4 EU marker PAHs in milk chocolate and low fat cocoa powder
Status	Registration Open
Year	2015
Type	Proficiency Test
Participation	Restricted
Contact	Jrc-irmm-eurl-pah@ec.europa.eu
IL category	Other

More

The European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons organises a proficiency test on the determination of 4 EU marker PAHs in cocoa products.

The objective of this study is to evaluate the capabilities of EU food control laboratories in the determination of 4 EU marker PAHs in chocolate and low fat cocoa powder.

Only national reference laboratories (NRLs) for PAHs and EU official food control laboratories (OCLs) can participate in the study.

Participation is free of charge for NRLs for PAHs. The participation fee for other official food control laboratories, which do not have national reference laboratory status, is **EUR 350** (three hundred fifty) per registration! Participation fees are due with the delivery of the test samples.

Test material and analytes

The test materials are commercial chocolate and cocoa powder samples containing the target analytes (see Table 1). Samples will be sent to the participants in May. In addition participants will get an ampoule with a solution of the target PAHs with disclosed analyte content, in, depending on their preference, either acetonitrile or toluene, which will allow the participants verifying instrument calibration against an independent standard. Results do not have to be reported for the standard solution.

The measurands are the 4 EU marker PAHs as listed in Table 1.

Results have to be reported for the contents of the individual analytes as well as for the sum of the four PAHs. Additionally the analyte contents have to expressed both on product and on fat basis.

Table 1: measurands

benz[a]anthracene (BAA)	benzo[a]pyrene (BAP)
benzo[b]fluoranthene (BBF)	chrysene (CHR)

General outline

Participants are requested to perform three independent analyses of each sample using a method of their choice. The analyses shall be performed on the same day. Participants have to report the results for individual analytes of the replicate analyses. All results have to be reported corrected for recovery, and have to be accompanied by the respective measurement uncertainty.

Performance assessment:

The performance of the participants in the determination of PAHs in the two test samples will be rated by z-scores and zeta-scores.

The standard deviations for proficiency assessment will be derived:

- for all four analytes from the fitness-for-purpose function given in Commission Regulation (EU) No 836/2011 assuming a value of 0.3 µg/kg for the limit of detection.

- for the sum parameter by propagating the individual standard deviations for proficiency assessment of the four analytes applying the law of error propagation.

Registration

Via invitation by e-mail and submitting a filled in registration form.

Registration deadline	Monday, 4 May 2015
Sample dispatch	End of May 2015
Reporting of results	4 weeks after dispatch
Report to participants	September 2015

Keywords	food/feed
Reference laboratories	EURL for polycyclic aromatic hydrocarbons

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: 17/04/2015 A-Z Index | FAQ | Mailing lists | Privacy statement | Legal notice | Contact | Search | Top

ANNEX 2: Announcement of the PT via e-mail

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 17/04/2015
Ref. Ares(2014) – 17/04/2015

Interlaboratory comparison on the determination of four EU marker PAHs in cocoa products

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 cocoa products is **open until 4 May 2015**.

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

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

The target analytes are listed in the following Table.

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

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

Each participant will be provided with two samples: 30 g milk chocolate powder and 30 g low fat cocoa powder.

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

Registration procedure:

You are invited to register via following link:
https://ec.europa.eu/eusurvey/runner/EURL_PAH_2015_PT_cocoa_products

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

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

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

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

1) *NRL enrols OCLs and covers participation fee.*
   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

EURL PAH 2015 Proficiency Test on the determination of 4 marker PAHs in cocoa products

Fields marked with * are mandatory.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

EURL PAH 2015 PT PAH in cocoa products - Registration

This inter-laboratory comparison targets the analysis of the 4 EU marker PAHs (benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, and chrysene) in a cocoa products. The set of test samples will be distributed in May and will consisting of milk chocolate and low fat cocoa powder.

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 350 Euro for Official Food Control Laboratories per participation

* Organisation

1

Department

Address

City

*
Country

*
Name of the contact person

*Email

*
NRL or OCL

- NRL
- OCL

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

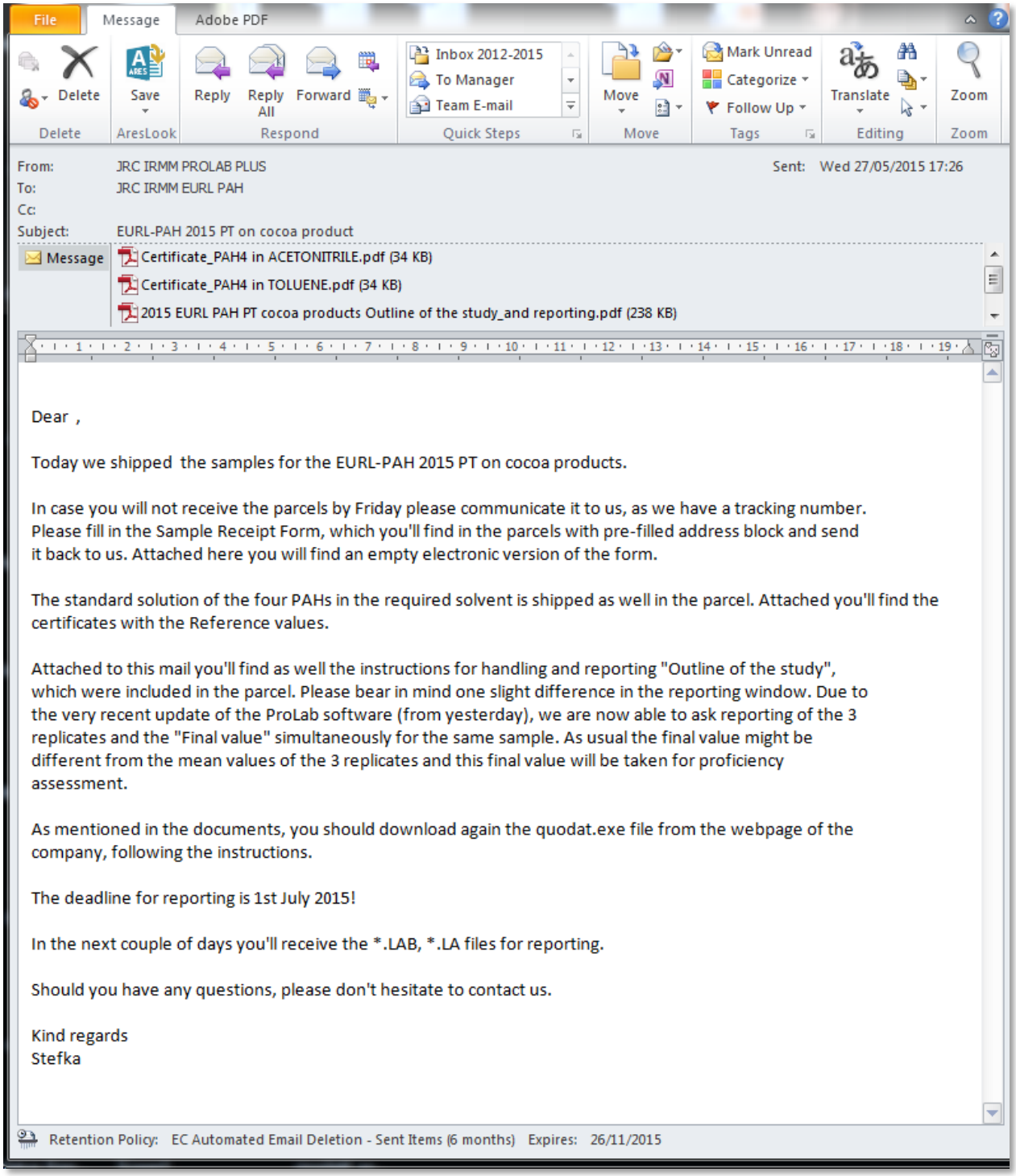
- enrolled by OCL itself (invoice sent to the avovementioned address)
- enrolled by the respective NRL (invoice sent to the respective NRL)

*
Prefered solvent for the standard solution

- acetonitrile
- toluene

2

ANNEX 4: Announcement of material dispatch



File Message Adobe PDF

Delete | Save | Reply | Reply All | Forward | Inbox 2012-2015 | To Manager | Team E-mail | Move | Mark Unread | Categorize | Follow Up | Translate | Zoom

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

From: JRC IRMM PROLAB PLUS
Sent: Wed 27/05/2015 17:26
To: JRC IRMM EURL PAH
Cc:
Subject: EURL-PAH 2015 PT on cocoa product

Message
Certificate_PAH4 in ACETONITRILE.pdf (34 KB)
Certificate_PAH4 in TOLUENE.pdf (34 KB)
2015 EURL PAH PT cocoa products Outline of the study_and reporting.pdf (238 KB)

Dear ,

Today we shipped the samples for the EURL-PAH 2015 PT on cocoa products.

In case you will not receive the parcels by Friday please communicate it to us, as we have a tracking number. Please fill in the Sample Receipt Form, which you'll find in the parcels with pre-filled address block and send it back to us. Attached here you will find an empty electronic version of the form.

The standard solution of the four PAHs in the required solvent is shipped as well in the parcel. Attached you'll find the certificates with the Reference values.

Attached to this mail you'll find as well the instructions for handling and reporting "Outline of the study", which were included in the parcel. Please bear in mind one slight difference in the reporting window. Due to the very recent update of the ProLab software (from yesterday), we are now able to ask reporting of the 3 replicates and the "Final value" simultaneously for the same sample. As usual the final value might be different from the mean values of the 3 replicates and this final value will be taken for proficiency assessment.

As mentioned in the documents, you should download again the quodat.exe file from the webpage of the company, following the instructions.

The deadline for reporting is 1st July 2015!

In the next couple of days you'll receive the *.LAB, *.LA files for reporting.

Should you have any questions, please don't hesitate to contact us.

Kind regards
Stefka

Retention Policy: EC Automated Email Deletion - Sent Items (6 months) Expires: 26/11/2015

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

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements (Geel)

Geel, 21 May 2015

EURL PAH 2015 PT- PAHs in cocoa products

Dear Madame/Sir,

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

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

Each participant is provided with two amber glass vials containing a cocoa powder and milk chocolate powder and an ampoule with known standard solution in either toluene or acetonitrile for checking of the instrument calibration against an external reference.

Outline of the study.

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

The laboratories shall report the results by **1st July 2015 at the latest** following the instructions provided further on in this document.

The participants are requested to report for both the cocoa powder and milk chocolate powder samples the results obtained from three replicate analyses. They also have to report a final value for proficiency assessment and the sum of the contents of the four analytes. The "final value" for the cocoa powder and milk chocolate powder samples shall be reported both on product basis (µg/kg cocoa powder or milk chocolate powder) and on fat basis (µg/kg fat), as the latter is required by Commission Regulation (EU) No 835/2011.

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.

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

Test material and analytes

1. Two amber vials, labelled as *"EU-RL PAHs PT 2015 Interlaboratory comparison 431, 4 EU PAHs in cocoa powder"* containing about 20 g of a naturally contaminated cocoa powder. 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".
2. Two amber vials, labelled as *"EU-RL PAHs PT 2015 Interlaboratory comparison 431, 4 EU PAHs in milk chocolate"* containing about 20 g of milk chocolate powder, spiked additionally with the four markers PAHs as the level of natural contamination was very low for some of the measurands. The analyte content shall be determined in triplicate. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value".

   Store the samples in refrigerator, protected of light.

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

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

Reporting the results

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

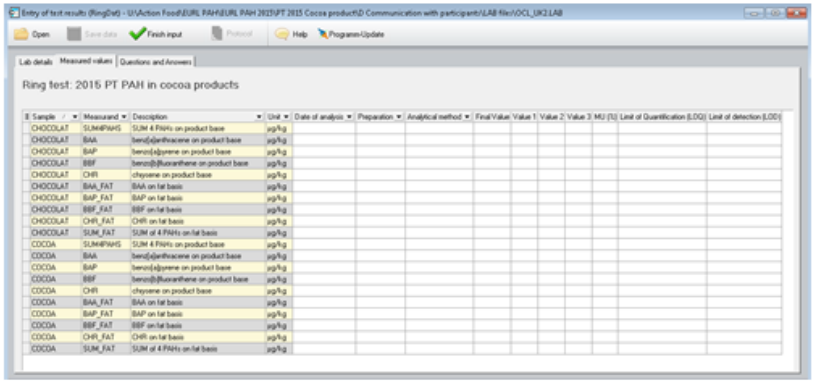
1. Please download the updated data entry program RingDat free from the QuoData web page using following link:
http://quodata.de/ringdat_en.php
User: *ringdat*
Password: *prolabdata*

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

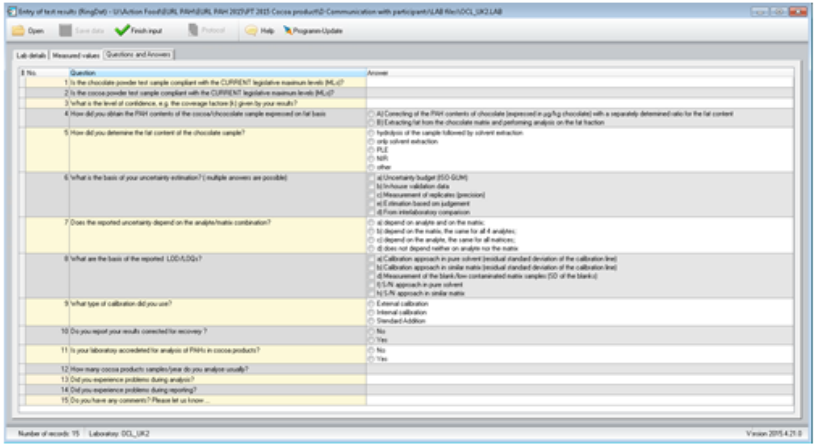
2. Save to the same folder the two lab specific files with the extension **"*.LAB"** and **"*.LA2"**, generated by the ProLab software and provided to each laboratory individually (personal files) by mail.

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

4. Fill in the result table with your data. Please report 3 replicates and one final value per sample/measurand, together with method uncertainty, information for the method used and respective LOD, LOQ.



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

Confirmation of the receipt of the samples: RECEIPT FORM

EURL PAH 2015 PT- PAHs in cocoa products

Lab Code	
Organization	
Short name	
Address	
City	
Country	
Contact person	

Content of the parcel

1. Two amber glass vial containing about 22 g of milk chocolate powder test sample
2. Two amber glass vial containing about 22 g of cocoa powder test sample
3. One brown glass ampoule with 1 ml standard solution of PAHs in solvent of choice (known concentrations)
4. A specification sheet for the item 3) content (standard solution), e-mailed as well
5. Material safety data sheets for acetonitrile / toluene
6. One inter-laboratory comparison sample receipt form (= this form), which is e-mailed as well to be filed and send electronically
7. Instructions for handling and reporting

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

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

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

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

Date

Signature field

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

ANNEX 6: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 26/05/2015

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

Standard solution composition:

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

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

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

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

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

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

TOLUENE SOLUTION

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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

Geel, 25/05/2015

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

Standard solution composition:

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

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

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

Solvent: Toluene

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

ANNEX 7a: Homogeneity of the cocoa powder test material

Analyte: **BAA**

	n =	10		
	mean =	0.8760	22%	**= σ-trg(%)**
0.000199452	**s_x =**	0.0141	0.1927	**= σ-trg**
√MSW =	**s_w =**	0.0375		
	s_s =	0.0225	0.0578	**= 0,3*s**

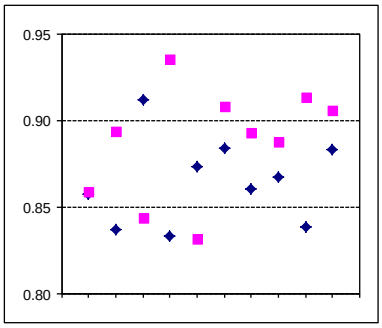
ISO-13528	passed		
F =	0.283229	3.0203829	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0005	0.0077	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	0.86	0.86	0.00	1.72	0.86
Ampoule 13	0.84	0.89	-0.06	1.73	0.87
Ampoule 18	0.91	0.84	0.07	1.76	0.88
Ampoule 28	0.83	0.94	-0.10	1.77	0.88
Ampoule 38	0.87	0.83	0.04	1.70	0.85
Ampoule 41	0.88	0.91	-0.02	1.79	0.90
Ampoule 58	0.86	0.89	-0.03	1.75	0.88
Ampoule 61	0.87	0.89	-0.02	1.76	0.88
Ampoule 80	0.84	0.91	-0.07	1.75	0.88
Ampoule 83	0.88	0.91	-0.02	1.79	0.89

∑(diff)^2 = 0.0281683

var(sum)/2 = 0.00040 =MSB



Analyte: **BBF**

	n =	10		
	mean =	0.4624	22%	**= σ-trg(%)**
5.55863E-05	**s_x =**	0.0075	0.1017	**= σ-trg**
√MSW =	**s_w =**	0.0252		
	s_s =	0.0162	0.0305	**= 0,3*s**

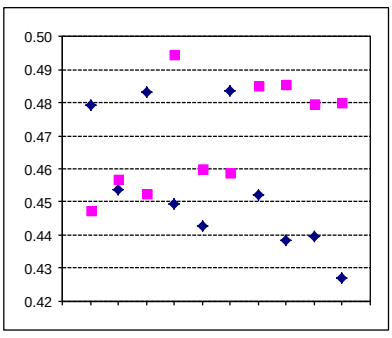
ISO-13528	passed		
F =	0.1754907	3.0203829	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0003	0.0024	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	0.48	0.45	0.03	0.93	0.46
Ampoule 13	0.45	0.46	0.00	0.91	0.46
Ampoule 18	0.48	0.45	0.03	0.94	0.47
Ampoule 28	0.45	0.49	-0.05	0.94	0.47
Ampoule 38	0.44	0.46	-0.02	0.90	0.45
Ampoule 41	0.48	0.46	0.02	0.94	0.47
Ampoule 58	0.45	0.49	-0.03	0.94	0.47
Ampoule 61	0.44	0.49	-0.05	0.92	0.46
Ampoule 80	0.44	0.48	-0.04	0.92	0.46
Ampoule 83	0.43	0.48	-0.05	0.91	0.45

∑(diff)^2 = 0.0126699

var(sum)/2 = 0.00011 =MSB



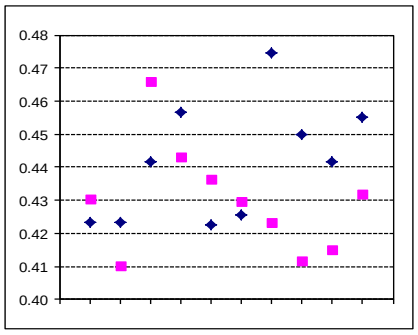
Analyte: **BAP**

	n =	10		
	mean =	0.4356	22%	**= σ-trg(%)**
0.000153938	**s_x =**	0.0124	0.0958	**= σ-trg**
√MSW =	**s_w =**	0.0181		
	s_s =	0.0030	0.0287	**= 0,3*s**

ISO-13528	passed		
F =	0.9444281	3.0203829	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	0.0000	0.0019	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	0.42	0.43	-0.01	0.85	0.43
Ampoule 13	0.42	0.41	0.01	0.83	0.42
Ampoule 18	0.44	0.47	-0.02	0.91	0.45
Ampoule 28	0.46	0.44	0.01	0.90	0.45
Ampoule 38	0.42	0.44	-0.01	0.86	0.43
Ampoule 41	0.43	0.43	0.00	0.86	0.43
Ampoule 58	0.47	0.42	0.05	0.90	0.45
Ampoule 61	0.45	0.41	0.04	0.86	0.43
Ampoule 80	0.44	0.41	0.03	0.86	0.43
Ampoule 83	0.46	0.43	0.02	0.89	0.44



∑(diff)^2 = 0.0065199

var(sum)/2 = 0.00031 =MSB

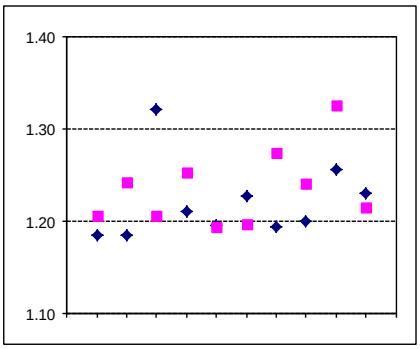
Analyte: **CHR**

	n =	10		
	mean =	1.2279	22%	**= σ-trg(%)**
0.000883478	**s_x =**	0.0297	0.2701	**= σ-trg**
√MSW =	**s_w =**	0.0405		
	s_s =	0.0079	0.0810	**= 0,3*s**

ISO-13528	passed		
F =	1.0765503	3.0203829	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	0.0001	0.0140	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	1.19	1.21	-0.02	2.39	1.20
Ampoule 13	1.18	1.24	-0.06	2.43	1.21
Ampoule 18	1.32	1.21	0.12	2.53	1.26
Ampoule 28	1.21	1.25	-0.04	2.46	1.23
Ampoule 38	1.20	1.19	0.00	2.39	1.20
Ampoule 41	1.23	1.20	0.03	2.42	1.21
Ampoule 58	1.19	1.27	-0.08	2.47	1.23
Ampoule 61	1.20	1.24	-0.04	2.44	1.22
Ampoule 80	1.26	1.33	-0.07	2.58	1.29
Ampoule 83	1.23	1.22	0.01	2.45	1.22



∑(diff)^2 = 0.0328262

var(sum)/2 = 0.00177 =MSB

ANNEX 7b: Homogeneity of the chocolate powder test material

Analyte: **BAA**

	n =	10		
	mean =	1.3712	22%	= **σ-trg(%)**
0.000416362	s_x =	0.0204	0.3017	= **σ-trg**
√MSW =	s_w =	0.0375		
	s_s =	0.0169	0.0905	= **0,3*s**

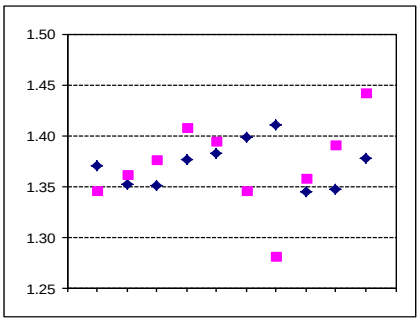
ISO-13528	passed		
F =	0.59262519	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0003	0.0168	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	1.37	1.35	0.02	2.72	1.36
Ampoule 13	1.35	1.36	-0.01	2.71	1.36
Ampoule 18	1.35	1.38	-0.03	2.73	1.36
Ampoule 28	1.38	1.41	-0.03	2.79	1.39
Ampoule 38	1.38	1.40	-0.01	2.78	1.39
Ampoule 41	1.40	1.35	0.05	2.75	1.37
Ampoule 58	1.41	1.28	0.13	2.69	1.35
Ampoule 61	1.34	1.36	-0.01	2.70	1.35
Ampoule 80	1.35	1.39	-0.04	2.74	1.37
Ampoule 83	1.38	1.44	-0.06	2.82	1.41

$\sum$**(diff)^2** = 0.02810292

var(sum)/2 = 0.00083 =MSB



Analyte: **BAP**

	n =	10		
	mean =	1.1496	22%	= **σ-trg(%)**
0.000667028	s_x =	0.0258	0.2529	= **σ-trg**
√MSW =	s_w =	0.0235		
	s_s =	0.0198	0.0759	= **0,3*s**

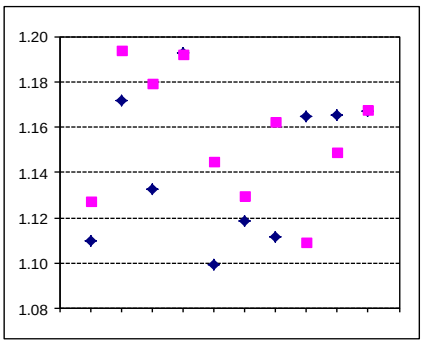
ISO-13528	passed		
F =	2.41781565	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	0.0004	0.0114	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	1.11	1.13	-0.02	2.24	1.12
Ampoule 13	1.17	1.19	-0.02	2.37	1.18
Ampoule 18	1.13	1.18	-0.05	2.31	1.16
Ampoule 28	1.19	1.19	0.00	2.38	1.19
Ampoule 38	1.10	1.15	-0.05	2.24	1.12
Ampoule 41	1.12	1.13	-0.01	2.25	1.12
Ampoule 58	1.11	1.16	-0.05	2.27	1.14
Ampoule 61	1.16	1.11	0.06	2.27	1.14
Ampoule 80	1.17	1.15	0.02	2.31	1.16
Ampoule 83	1.17	1.17	0.00	2.34	1.17

$\sum$**(diff)^2** = 0.01103522

var(sum)/2 = 0.00133 =MSB



Analyte: **BBF**

	n =	10		
	mean =	1.1329	22%	**= σ-trg(%)**
0.000274196	s_x =	0.0166	0.2492	**= σ-trg**
√MSW =	s_w =	0.0359		
	s_s =	0.0192	0.0748	**= 0,3*s**

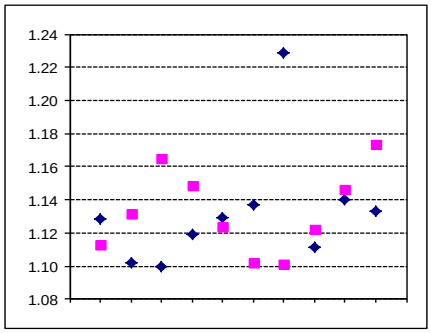
ISO-13528	passed		
F =	0.4263988	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0004	0.0118	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	1.13	1.11	0.01	2.24	1.12
Ampoule 13	1.10	1.13	-0.03	2.23	1.12
Ampoule 18	1.10	1.17	-0.07	2.27	1.13
Ampoule 28	1.12	1.15	-0.03	2.27	1.13
Ampoule 38	1.13	1.12	0.01	2.25	1.13
Ampoule 41	1.14	1.10	0.04	2.24	1.12
Ampoule 58	1.23	1.10	0.13	2.33	1.17
Ampoule 61	1.11	1.12	-0.01	2.23	1.12
Ampoule 80	1.14	1.15	-0.01	2.29	1.14
Ampoule 83	1.13	1.17	-0.04	2.31	1.15

$\sum$**(diff)^2** = 0.02572202

var(sum)/2 = 0.00055 =MSB



Analyte: **CHR**

	n =	10		
	mean =	1.7033	22%	**= σ-trg(%)**
0.000299878	s_x =	0.0173	0.3747	**= σ-trg**
√MSW =	s_w =	0.0526		
	s_s =	0.0329	0.1124	**= 0,3*s**

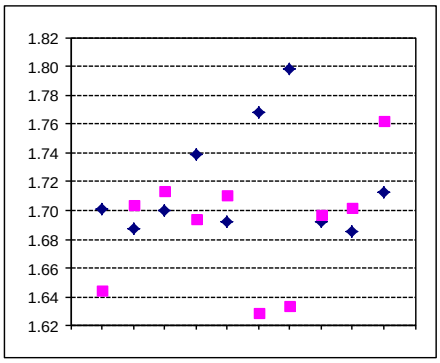
ISO-13528	passed		
F =	0.2171723	3.02038295	= Fcrit
	passed		

IUPAC			
(MSB-MSW)/2	-0.0011	0.0265	= F1*(0,3*s)^2+F2*MSW
	passed		

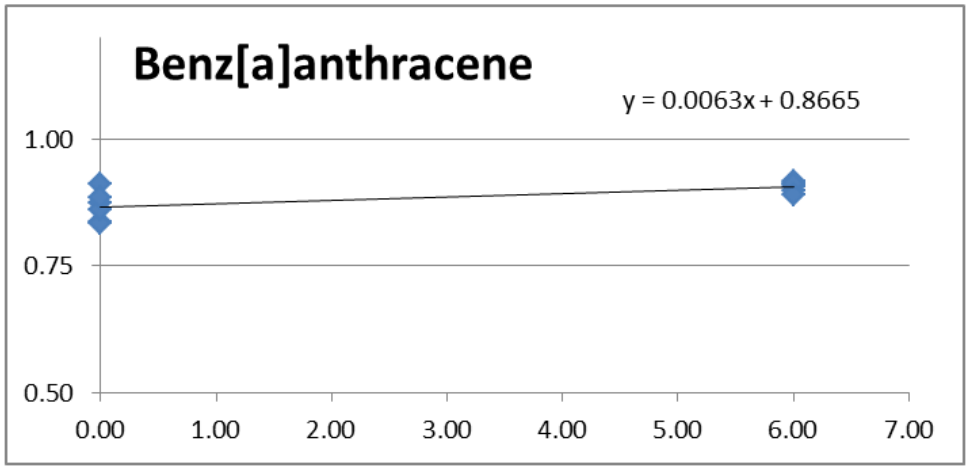
Bottle	Result a	Result b	diff	sum	avg
Ampoule 04	1.70	1.65	0.06	3.35	1.67
Ampoule 13	1.69	1.70	-0.02	3.39	1.70
Ampoule 18	1.70	1.71	-0.01	3.41	1.71
Ampoule 28	1.74	1.69	0.04	3.43	1.72
Ampoule 38	1.69	1.71	-0.02	3.40	1.70
Ampoule 41	1.77	1.63	0.14	3.40	1.70
Ampoule 58	1.80	1.63	0.16	3.43	1.72
Ampoule 61	1.69	1.70	-0.01	3.39	1.69
Ampoule 80	1.69	1.70	-0.02	3.39	1.69
Ampoule 83	1.71	1.76	-0.05	3.47	1.74

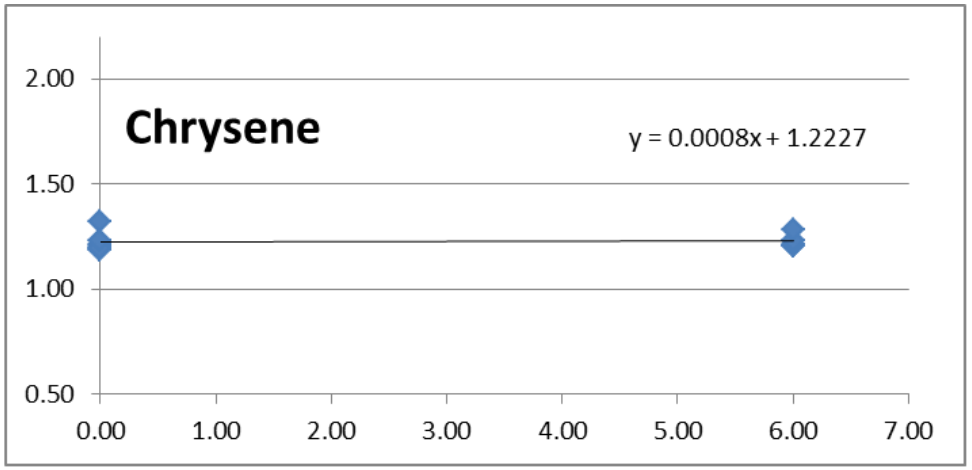
$\sum$**(diff)^2** = 0.05523313

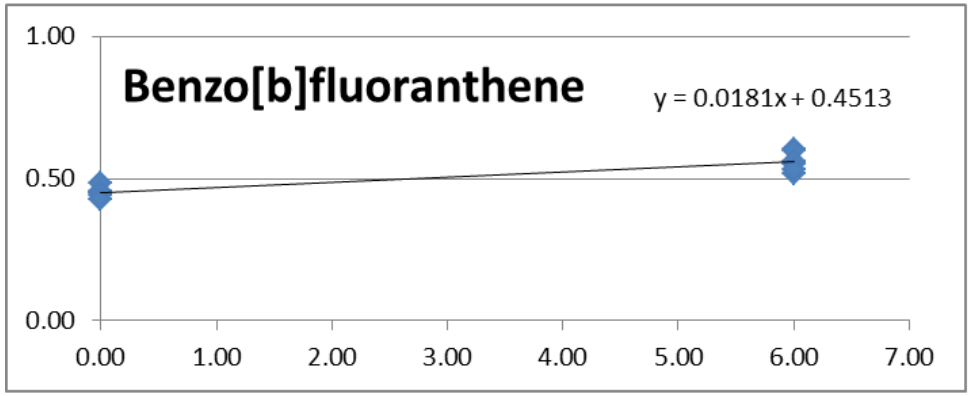
var(sum)/2 = 0.00060 =MSB

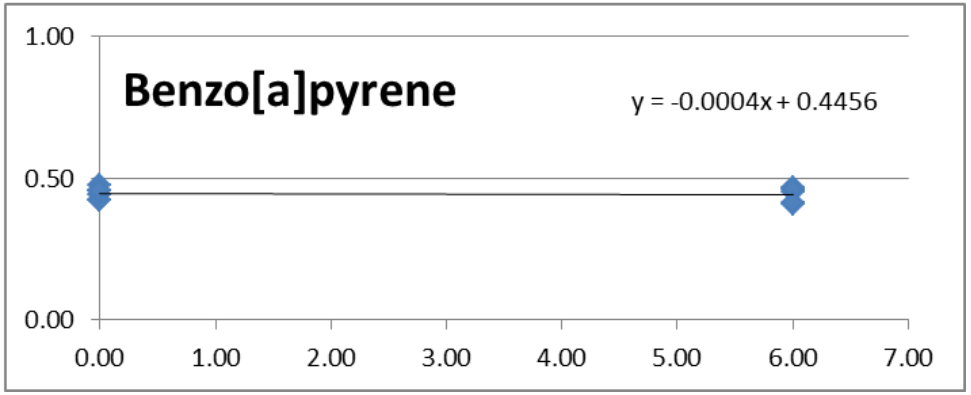


ANNEX 8a. Stability of the cocoa powder test material for the period of the study

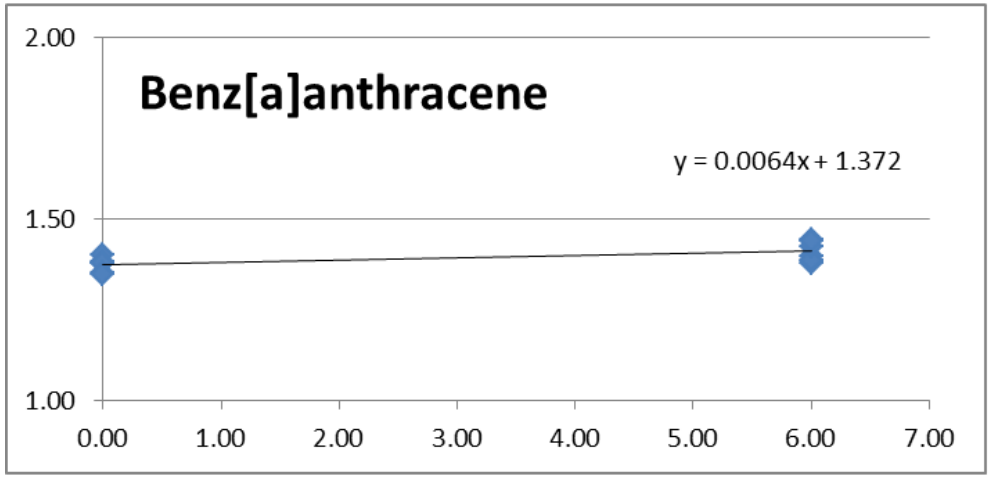


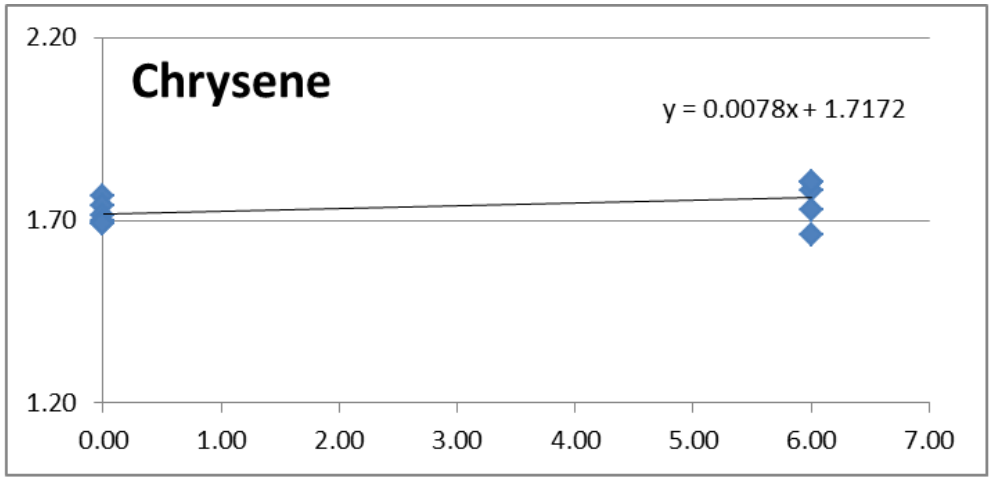


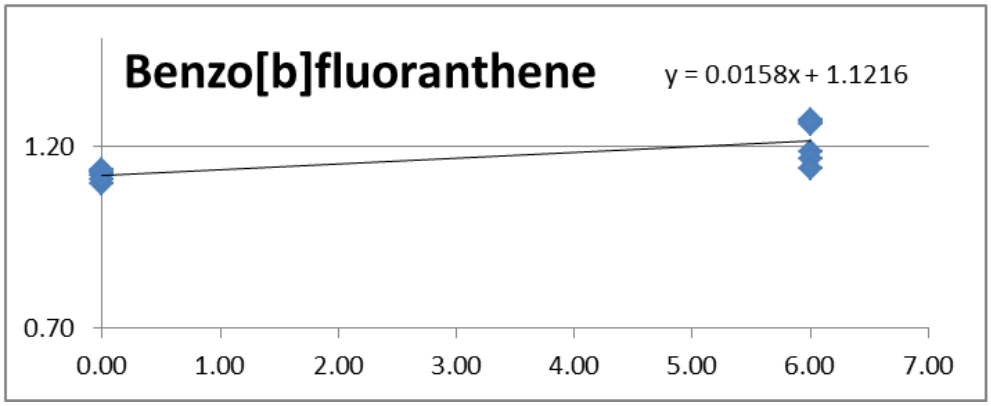


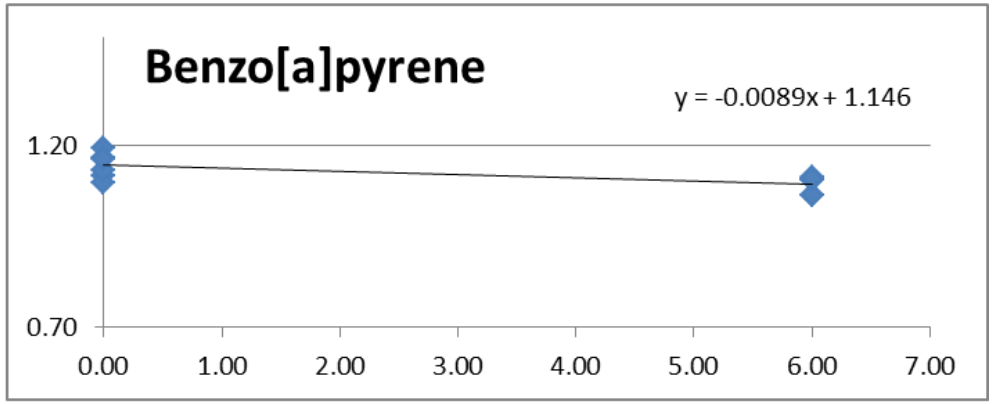


ANNEX 8b. Stability of the chocolate test material for the period of the study

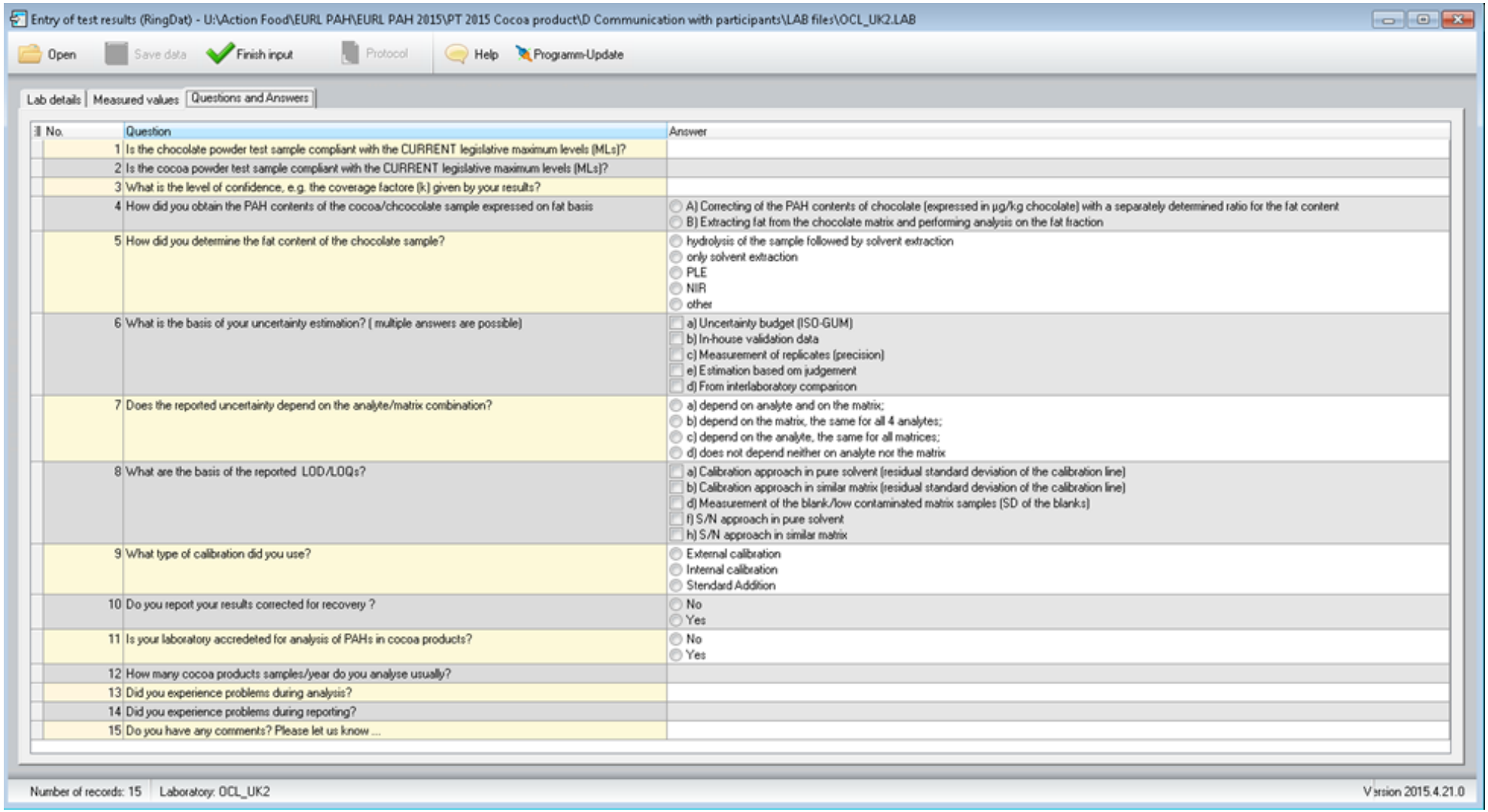








ANNEX 9. Questionnaire and answers from the participants



Lab Code	1. Compliance with the ML chocolate	2. Compliance with the ML cocoa	3. Level of confidence
1	Yes	Yes for Bap, No for SUM4PAH	
2	Yes for BaP and sum	Yes for BaP and sum	2
3	Yes (Please explain) ... the results are below the MLs	Yes (Please explain) ....the results are below the MLs	2
4	Yes (measured levels of benzo(a)pyrene and 4PAHs do not exceed the respective MLs taking into account the MU)	Yes (measured levels are below the current MLs taking into account the MU)	95
5	Yes (Please explain) ...	Yes (Please explain)	2
6	Yes, the ML levels don't exceed	Yes, the ML levels don't exceed	2
7	Yes, test result is clarely below current ML	Yes, test result is clarely below current ML	2
8	Yes	Yes	2k
9	Yes (because the results of the sum PAH not exceeding the limit of 30 ug/kg)	Yes (because the results of the sum PAH not exceeding the limit of 30 ug/kg)	k=2, 95%
10	Yes (Please explain) ...Maximum levels for BaP and SUM PAH4 are not exceeded.	Yes (Please explain) ....Maximum levels for BaP and SUM PAH4 are not exceeded.	95%, coverage factor k=2
11		Yes (Please explain)	95%
12	Yes - below limits	Yes - below limits	
13	Yes, the levels of SUM4PAH and BaP are below ML	Yes, the levels of SUM4PAH and BaP are below ML	k=2
14	Yes (Please explain) ...	Yes (Please explain)	k=2, level of confidence of 95%
15	Yes, according to the MLs of 5 and 30 ppb for cocoa beans and derived products	Yes, according to the MLs of 5 and 30 ppb for cocoa beans and derived products	2
17	Yes. BaP and Sum of PAH4 below 5.0 and 30.0 ppb limit.	Yes. BaP and Sum of PAH4 below 5.0 and 30.0 ppb limit.	2
18	Yes, the chocolate powder sample complies with the legislative maximum levels	Yes, the cocoa powder sample complies with the legislative maximum levels	2
19	Yes : BaP < ML of 5 µk/kg fat; Sum PAH4 < 30 mg/kg fat	Yes : BaP < ML of 5 µk/kg fat; Sum PAH4 < 30 mg/kg fat	2
21	Yes, BaP MLs is 5.0 ug/kg, PAH4 MLs is 30.0 ug/kg.	Yes, BaP MLs is 5.0 ug/kg, PAH4 MLs is 30.0 ug/kg.	
22	Yes (Please explain) ...B(a)p:5ug/kg fat result:3,41(3,13-3,68); PAH4:30 ug/kg fat, result: 17,4 (16,4-18,5)	Yes (Please explain) ....B(a)p:5ug/kg fat result:1,52(1,39-1,64); PAH4:30 ug/kg fat, result: 11,5 (10,7-12,3)	2
23	Yes (Please explain) ...EU limits 5 ug/kg for Benzo(a);yrene and 30 ug/kg for the summary of Benzo(a)pyrene, benzo(a)anthracene, chrysene and benzo(b)fluoranthene on fat basis	Yes (Please explain) EU limits 5 ug/kg for Benzo(a);yrene and 30 ug/kg for the summary of Benzo(a)pyrene, benzo(a)anthracene, chrysene and benzo(b)fluoranthene on fat basis	2
24	Yes (Please explain) ...<30.0 ug/kg fat	Yes (Please explain) .....<30.0 ug/kg fat	95%; k=2
26	Yes (Please explain) ... BaP below ML (5 ug/kg fat), sum of 4 PAHs below ML (30 ug/kg fat)	Yes (Please explain) ....BaP below ML (5 ug/kg fat), sum of 4 PAHs below ML (30 ug/kg fat)	2
28	Yes, the results are lower than the MLs.	Yes, the results are lower than the MLs.	
29			95%
31	Yes (Please explain) ...	Yes (Please explain)	2
41	compliant	compliant	K =2
42	Yes (Please explain) ...	Yes (Please explain)	2
43	Yes (Please explain) ...BaP<5; Sum 4 PAH <30	Yes (Please explain) ...BaP<5; Sum 4 PAH <30	
44	Yes. Mean value of 17.0 µg/kg fat for sum of PAH4 and 3.7 µg/kg fat for BaP is below limit of 30 µg/kg and 5 µg/kg fat respectively.	Yes. Mean value of 14.2 µg/kg fat for sum of PAH4 and 2.2 µg/kg fat for BaP is below limit of 30 µg/kg and 5 µg/kg fat respectively.	
45	Yes (Please explain) ...According to CR (EC) No 1881/2006 (Annex, Section 6) the maximum level in cocao beans and derived products for BAP is 5,0 µg/kg fat and for the sum of PAH4 it is 30,0 µg/kg fat. The results we achieved for the choclate powder do not exceed these legislative MLs.	Yes (Please explain) ...According to CR (EC) No 1881/2006 (Annex, Section 6) the maximum level in cocao beans and derived products for BAP is 5,0 µg/kg fat and for the sum of PAH4 it is 30,0 µg/kg fat. The results we achieved for the cocoa powder do not exceed these legislative MLs.	95%, k=2
46	No (Please explain) ... MLs for BAP is 5µg/kg, MLs sum of 4PAH: 30 µg/kg. Our values are under the current legislative maximum level	No (Please explain) ... MLs for BAP is 5µg/kg, MLs sum of 4PAH: 30 µg/kg. Our values are under the current legislative maximum level	Our level of confidence is 95% and the coverage factore (k) is 2
55	Yes, the final value with the uncertainty is< ML	Yes ,the final value with uncertainty is <ML	2
63	Yes (Please explain) ...	Yes (Please explain)	2
75	yes, the sample is compliant with the current legislative maximum level	yes, the sample is compliant with the current legislative maximum level	
81	Yes	Yes	
82	Yes (Please explain) ...Limits are 5 and 30	Yes (Please explain) ....Limits are 5 and 30	95% k-2
99	No (BAP is above 5 ppb fat and sum PAH is above 30 ppb)	No (BAP is above 5 ppb fat and sum PAH is above 30 ppb)	95 k=2

Lab Code	4. PAH content on fat basis	5. Fat content determination
1	Performing analysis on the fat fraction	Only solvent extraction
2	Performing analysis on the fat fraction	Only solvent extraction
3	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
4	Correcting of the PAH contents of chocolate	Other
5	Correcting of the PAH contents of chocolate	Only solvent extraction
6	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
7	Correcting of the PAH contents of chocolate	Only solvent extraction
8	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
9	Correcting of the PAH contents of chocolate	Only solvent extraction
10	Correcting of the PAH contents of chocolate	Other
11	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
12	Correcting of the PAH contents of chocolate	Only solvent extraction
13	Performing analysis on the fat fraction	Only solvent extraction
14	Correcting of the PAH contents of chocolate	PLE
15	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
17	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
18	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
19	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
21	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
22	Correcting of the PAH contents of chocolate	Only solvent extraction
23	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
24	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
26	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
28	Performing analysis on the fat fraction	Only solvent extraction
29		
31	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
41	Weibull-Stoldt according to § 64 LFGB ASU L 44.00-4	DIN ISO 11352:2013
42		Hydrolysis of the sample followed by solvent extraction
43	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
44	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
45	Correcting of the PAH contents of chocolate	Only solvent extraction
46	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
55	Performing analysis on the fat fraction	PLE
63	Performing analysis on the fat fraction	Only solvent extraction
75	calculation	fat extraction
81	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
82	Correcting of the PAH contents of chocolate	Hydrolysis of the sample followed by solvent extraction
99	Correcting of the PAH contents of chocolate	Only solvent extraction

Lab Code	6. Uncertainty estimate	7. Uncertainty dependence
1	– In-house validation data	– Depend on the matrix, the same for all 4 analytes
2	– In-house validation data	
3	– In-house validation data – Measurement of replicates (precision)	– Depend on the analyte and on the matrix
4	– In-house validation data – Measurement of replicates (precision)	– Depend on the analyte and on the matrix
5	– Measurement of replicates (precision) – Estimation based on judgement	– Depend on the analyte and on the matrix
6	– In-house validation data	
7	– Uncertainty budget	– Depend on the analyte and on the matrix
8	– In-house validation data	
9	– Estimation based on judgement – From interlaboratory comparison	– Depend on the analyte and on the matrix
10	– Estimation based on judgement	
11	– Measurement of replicates (precision)	– Depend on the analyte and on the matrix
12	– In-house validation data	– Depend on the analyte and on the matrix
13	– In-house validation data	
14	– Uncertainty budget	– Does not depend neither on the analyte nor on the matrix
15	– In-house validation data – Measurement of replicates (precision) – From interlaboratory comparison	
17	– Measurement of replicates (precision)	– Depend on the analyte and on the matrix
18	– In-house validation data – Measurement of replicates (precision)	
19	– In-house validation data	– Depend on the analyte, the same for all matrices
21	– In-house validation data	– Depend on the matrix, the same for all 4 analytes
22	– Uncertainty budget – In-house validation data	– Depend on the analyte and on the matrix
23	– In-house validation data	– Depend on the analyte, the same for all matrices
24	– In-house validation data – Measurement of replicates (precision)	– Depend on the analyte and on the matrix
26	– In-house validation data	– Depend on the analyte, the same for all matrices
28	– Uncertainty budget – Measurement of replicates (precision)	
29	– Measurement of replicates (precision)	
31	– analyte/matrix combination	– Depend on the analyte and on the matrix
41	– Measurement of replicates (precision)	– Depend on the analyte and on the matrix
42	– From interlaboratory comparison	
43	– In-house validation data – Measurement of replicates (precision) – Estimation based on judgement	– Depend on the analyte and on the matrix
44	– Measurement of replicates (precision)	– Depend on the analyte, the same for all matrices
45	– In-house validation data – Measurement of replicates (precision)	– Depend on the analyte and on the matrix
46	– In-house validation data – Measurement of replicates (precision)	
55	– Uncertainty budget – Measurement of replicates (precision)	– Depend on the analyte and on the matrix
63	– Horwitz	
75	– Measurement of replicates (precision)	– Depend on the analyte and on the matrix
81	– In-house validation data – Measurement of replicates (precision)	
82	– In-house validation data	– Depend on the analyte, the same for all matrices
99	–	– Depend on the analyte, the same for all matrices

Lab Code	8. Basis for LOD/LOQ	9. Calibration	10. Recovery rate	11. Laboratory accredited	12. Previous experience
1	– Calibration approach in pure solvent – S/N approach in similar matrix	Internal calibration	Yes	Yes	10
2	– S/N approach in pure solvent	Internal calibration	Yes	Yes	10
3	– Calibration approach in similar matrix	Internal calibration	Yes	Yes	20-30/year
4	– Calibration approach in similar matrix	Internal calibration	No	Yes	5
5	– S/N approach in pure solvent	External calibration	No	Yes	0
6	– Calibration approach in pure solvent	Standard Addition	Yes	No	0
7	– Measurement of the blank/low contaminated matrix samples	External calibration	Yes	No	0
8	– Measurement of the blank/low contaminated matrix samples	Internal calibration	Yes	Yes	>10
	– S/N approach in similar matrix				
9	– Measurement of the blank/low contaminated matrix samples – S/N approach in pure solvent	Internal calibration	No	No	100
10	–	Internal calibration	Yes	Yes	<10
11	– S/N approach in similar matrix	External calibration	Yes	Yes	20
12	– S/N approach in similar matrix	Standard Addition	No	No	none
13	– S/N approach in similar matrix	Internal calibration	Yes	Yes	5
14	– Measurement of the blank/low contaminated matrix samples	Internal calibration	Yes	Yes	0
15	– Measurement of the blank/low contaminated matrix samples	External calibration	Yes	No	5
17	– Measurement of the blank/low contaminated matrix samples	Internal calibration	Yes	Yes	20
18	– S/N approach in pure solvent	External calibration	Yes	Yes	
19	– Calibration approach in pure solvent – S/N approach in similar matrix	External calibration	No	Yes	<30
21	– Calibration approach in pure solvent	External calibration	Yes	Yes	<10
22	– Measurement of the blank/low contaminated matrix samples	Internal calibration	Yes	Yes	20
23	– Calibration approach in similar matrix	Standard Addition	Yes	Yes	20-30
24	– Calibration approach in pure solvent	Internal calibration	No	No	-
	– S/N approach in similar matrix				
26	– Measurement of the blank/low contaminated matrix samples	External calibration	Yes	Yes	05.окт
28	– Measurement of the blank/low contaminated matrix samples	Internal calibration	Yes	No	0 samples; the method validation for cocoa products is not completed.
29	– Calibration approach in pure solvent	External calibration	Yes	No	0
31	–	Standard Addition	No	No	Never
41	– solvent calibration	yes (ISTD for all PAH 4)	yes	yes	> 50
42	– Calibration approach in similar matrix	Internal calibration	No	Yes	0
43	– S/N approach in similar matrix	Internal calibration	Yes	Yes	30
44	– Calibration approach in similar matrix	Internal calibration	Yes	Yes	< 20
45	– Calibration approach in similar matrix	External calibration	No	Yes	up to 10
46	– Calibration approach in pure solvent	External calibration	Yes	Yes	10-50
55	– Measurement of the blank/low contaminated matrix samples	Internal calibration	Yes	No	<30
63	– Calibration approach in similar matrix	Internal calibration	Yes	No	5
75	– method validation	internal standard	30 - 150 %	no for cocoa products	25
81	– Measurement of the blank/low contaminated matrix samples	Standard Addition	Yes	Yes	
82	– Measurement of the blank/low contaminated matrix samples	External calibration	Yes	Yes	Few
99	– Measurement of the blank/low contaminated matrix samples	External calibration	Yes	No	5

Lab Code	13. Problems analysis	14. Problems reporting	15. Comment
1	No	No	No
2	no	interference BaA, contamination Chrysene	Q6 : estimation of uncertainty with RSD of control chart
3	No	-	-
4	no	no	
5	Yes.	No.	Yes (Please explain) ...
6	no	no	I suppose mean value=final value. The instructions talk about final value, but in this sheet it's mean value.
7	no	no	
8	No	No	
9	No	No	No
10	No	No	Sample for control of recovery is near 100%, so no correction is necessary.
11	No	No	No
12	yes - fat extraction (we never did before)	no	/
13	no	no	no
14	No	No	
15	NO	NO	NO
17	The fat determination is performed out of our control in another lab.	No	The quantity of material supplied is quite small.
18	No	No	Nº 6: The estimation of uncertainty is based not only in the precision, but also considering the bias contribution. Nº 8: LOQ was calculated s/r, but LOD was estimated on the lowest in house validated concentration. Nº 12: Depending if any survey study is carried out on this kind of products.
19	no	no	
21	No	No	No
22	No	No	No
23	In HPLC chrysene did not show a clear spectrum. Therefore the GC-MS was carried aout.	No	
24	No	No	
26	no	no	no
28		we do not have the uncertainty calculated for every Pah, only for BAP and SUM so i completed the column with 0	Our validated method is based on the SE EN ISO 15753. We need to mention that we didn't participate in any training for the detection of PAH's and we would like to know if there is any posibility to participate in a trainig organised by you. Our laboratory is acredited with SE EN ISO 17025/2005 . PAHs could be acreditated only after we participate in an interlaboratory comparison with acceptable results.
29	problems during extraction		We have no experience in this matix and 20 g is not enough for our usual fat determination
31	Yes		
41		There is no line for reporting the fat content. Fat content cocoa powder: 21,4 %; Fat content chocolate powder: 29,0 %	
42	bad flow of sovent of HRX-column (milk-chocolate]	no	no
43	no	no	usually we use for expressing on fat basis Extracting fat from the cocoa-matrix but in this case we used the other method because of not so much material und because of time and Lab organisation
44	no	no	Results are corrected for recovery automatically by calculating on an internal standard basis. They are not corrected for the recovery, observed with a spiked sample. LOD/LOQ were validated for chocolate and pure oil (on a calibration approach). Given values were smoothed afterwards.
45	triphenylene seemed to be in all samples, it slightly disturbed the chromatographic analysis of CHR; there seemed to be an interference peak influencing the chromatographic analysis of BAP		It was not quite obvious that there were only one sample per matrix for each vial had an separate ID. There was no instruction for pooling the vials.
46	No	No	No
55	Chrysene in PT is interfered; probably by Trifenilene	We would like to know the purpose of question n.10,considering that in the document you ask to correct the data for the recovery	The uncertainty is estimate by Horwitz method; LOD and LOQ are estimate with blank matrix spiked
63	No	No	
75	/	/	
81		Yes due to 'fire wall restrictions' NRL had to submit results for OCL.	
82	No	No	I did the results on both pots of each sample you sent assuming they were different. It seems you supplied duplicate pots. This should be made clearer
99	No	No	/

Annex 10. METHOD PERFORMANCE LOD and LOQs

With reference to Commission Regulation (EC) No 333/2007 as amended by Commission Regulation (EU) No 836/2011, non-compliant method performance characteristics are highlighted in red. Data reported by laboratory N 5, 10, 26, 42, 82 were corrected for typing mistakes with respect to the eventual swap between LOD and LOQ.

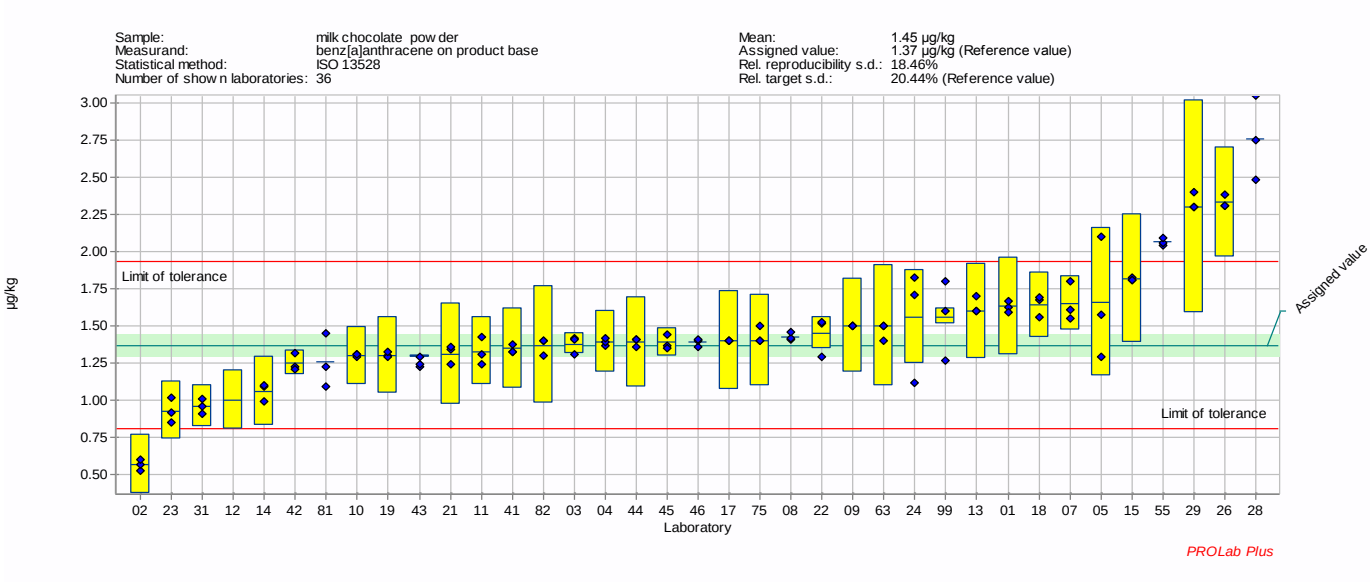
	CHOCOLATE																COCOA														
	BaA_product		BaA_fat		BaP_product		BaP_fat		BbF_product		BbF_fat		CHR_product		CHR_fat		BaA_product		BaA_fat		BaP_product		BaP_fat		BbF_product		BbF_fat		CHR_product		CHR_fat		
Lab Code	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	LOD [µg/kg]	LOQ [µg/kg]	Analytical method
legislation	0.1	0.3	0.3	0.9	0.1	0.3	0.3	0.9	0.1	0.3	0.3	0.9	0.1	0.3	0.3	0.9	0.06	0.18	0.3	0.9	0.06	0.18	0.3	0.9	0.06	0.18	0.3	0.9	0.06	0.18	0.3	0.9	
01			0.02	0.5			0.03	0.5			0.03	0.5			0.02	0.5			0.02	0.5			0.03	0.5			0.03	0.5			0.02	0.5	HPLC-UV/FLD
02			0.2	0.4			0.2	0.4			0.2	0.4			0.2	0.4			0.2	0.4			0.2	0.4			0.2	0.4			0.2	0.4	GC-MS/MS
03	0.07	0.24	0.24	0.79	0.07	0.26	0.24	0.86	0.08	0.27	0.28	0.88	0.07	0.24	0.24	0.8	0.02	0.08	0.13	0.39	0.02	0.08	0.12	0.39	0.02	0.08	0.12	0.41	0.03	0.09	0.12	0.44	GC-MS
04	0.1	0.3	0.35	1.05	0.1	0.3	0.35	1.05	0.1	0.3	0.35	1.05	0.1	0.3	0.35	1.05	0.1	0.3	0.6	1.8	0.1	0.3	0.6	1.8	0.1	0.3	0.6	1.8	0.1	0.3	0.6	1.8	HPLC-FLD
05	0.15	0.5	0.5	1.7	0.05	0.2	0.25	0.7	0.05	0.2	0.25	0.7	0.15	0.5	0.5	1.7	0.15	0.5	0.7	2.3	0.05	0.2	0.23	0.93	0.05	0.2	0.23	0.93	0.15	0.5	0.7	2.3	GC-MS/MS
06			0.26	0.78			0.26	0.78			0.26	0.78			0.26	0.78			0.26	0.78			0.26	0.78			0.26	0.78			0.26	0.78	GC-MS
07	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5	GC-MS
08			0.05	0.05			0.33	0.33			0.2	0.2			0.06	0.06			0.05	0.05			0.35	0.35			0.22	0.22			0.06	0.06	GC-MS
09	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	0.3	0.5	GC-MS
10			0.3	0.9			0.3	0.9			0.3	0.9			0.3	0.9			0.3	0.9			0.3	0.9			0.3	0.9			0.3	0.9	HPLC-FLD
11	0.08	0.24	0.08	0.24	0.07	0.21	0.08	0.24	0.12	0.36	0.12	0.36	0.1	0.3	0.1	0.3	0.07	0.21	0.07	0.21	0.08	0.24	0.08	0.24	0.11	0.33	0.11	0.33	0.12	0.36	0.12	0.36	GC-MS/MS
12	0.01	0.1	0.03	0.3	0.1	0.2	0.3	0.6	0.05	0.1	0.15	0.3	0.01	0.1	0.03	0.3	0.01	0.1	0.04	0.4	0.1	0.3	0.4	1.2	0.1	0.2	0.4	0.8	0.01	0.1	0.04	0.4	GC-HRMS
13	0.004	0.4	0.004	0.1	0.004	0.1	0.004	0.1	0.002	0.1	0.003	0.1	0.004	0.1	0.004	0.1	0.004	0.1	0.004	0.1	0.004	0.1	0.004	0.1	0.002	0.1	0.003	0.1	0.004	0.1	0.004	0.1	GC-MS/MS
14	0.03	0.09	0.11	0.32	0.03	0.09	0.11	0.32	0.03	0.09	0.11	0.32	0.03	0.09	0.11	0.32	0.03	0.09	0.13	0.4	0.03	0.09	0.13	0.4	0.03	0.09	0.13	0.4	0.03	0.09	0.13	0.4	HPLC-FLD
15	0.15	0.5	0.15	0.5	0.1	0.33	0.1	0.33	0.1	0.33	0.1	0.33	0.24	0.8	0.24	0.8	0.15	0.5	0.15	0.5	0.1	0.33	0.1	0.33	0.1	0.33	0.1	0.33	0.24	0.8	0.24	0.8	HPLC-FLD
16																																	
17			0.2	0.5			0.2	0.5			0.2	0.5			0.2	0.5			0.2	0.5			0.2	0.5			0.2	0.5			0.2	0.5	
18	0.01	0.4	0.03	1.36	0.01	0.4	0.02	1.36	0.03	0.4	0.11	1.36	0.02	0.4	0.05	1.36	0.01	0.4	0.04	1.87	0.01	0.4	0.02	1.87	0.03	0.4	0.15	1.87	0.02	0.4	0.07	1.87	HPLC-FLD
19	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.1	0.3	0.1	0.3	0.03	0.1	0.03	0.1	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.1	0.3	0.1	0.3	0.03	0.1	0.03	0.1	HPLC-FLD
20																																	
21	0.03	0.05	0.03	0.05	0.03	0.05	0.03	0.05	0.05	0.1	0.05	0.1	0.03	0.05	0.03	0.05	0.03	0.05	0.03	0.05	0.03	0.05	0.03	0.05	0.05	0.1	0.05	0.1	0.03	0.05	0.03	0.05	
22	0.1	0.2	0.3	0.7	0.1	0.3	0.3	1	0.1	0.3	0.3	1	0.1	0.3	0.3	1	0.1	0.2	0.4	0.9	0.1	0.3	0.4	1.3	0.1	0.3	0.4	1.3	0.1	0.3	0.4	1.3	
23	0.1	0.3	0.36	1.07	0.1	0.3	0.36	1.07	0.1	0.3	0.36	1.07	0.1	0.3	0.36	1.07	0.1	0.3	0.48	1.44	0.1	0.3	0.48	1.44	0.1	0.3	0.48	1.44	0.1	0.3	0.48	1.44	HPLC-FLD
24	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.2	0.5	0.2	0.5	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.06	0.2	0.2	0.5	0.2	0.5	HPLC-FLD
25																																	
26	0.25	0.5	0.25	0.5	0.08	0.16	0.08	0.16	0.2	0.4	0.2	0.4	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.08	0.16	0.08	0.16	0.2	0.4	0.2	0.4	0.25	0.5	0.25	0.5	HPLC-FLD
28	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	0.25	0.7	HPLC-UV/FLD
29	0.2	0.5			0.2	0.3			0.2	0.5			0.2	0.5			0.2	0.5			0.2	0.3			0.2	0.5			0.2	0.5			HPLC-FLD
31	0.3	0.9	1.04	3.12	0.3	0.9	1.04	3.12	0.3	0.9	1.04	3.12	0.3	0.9	1.04	3.12	0.3	0.9	1.43	4.31	0.3	0.9	1.43	4.31	0.3	0.9	1.43	4.31	0.3	0.9	1.43	4.31	GC-MS/MS
41	0.03	0.05	0.1	0.17	0.03	0.05	0.1	0.17	0.03	0.05	0.1	0.17	0.03	0.05	0.1	0.17	0.03	0.05	0.14	0.23	0.03	0.05	0.14	0.23	0.03	0.05	0.14	0.23	0.03	0.05	0.14	0.23	GC-MS/MS
42	0.15	0.3	0.5	1	0.15	0.3	0.5	1	0.2	0.4	0.7	1.4	0.15	0.3	0.5	1	0.15	0.3	0.7	1.4	0.15	0.3	0.7	1.4	0.2	0.4	0.9	1.8	0.15	0.3	0.7	1.4	GC-MS/MS
43	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	HPLC-FLD
44	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	0.1	0.3	0.2	0.6	HPLC-FLD
45	0.1	0.3	0.47	1.4	0.1	0.3	0.47	1.4	0.2	0.5	0.93	2.34	0.2	0.5	0.93	2.34	0.1	0.3	0.47	1.4	0.1	0.3	0.47	1.4	0.2	0.5	0.93	2.34	0.2	0.5	0.93	2.34	GC-MS
46	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	0.25	0.5	HPLC-FLD
55	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	GC-MS
63	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	0.3	0.9	GC-MS
75	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	0.03	0.1	GC-MS/MS
81			0.6	1.79			0.23	0.68			0.21	0.63			1.26	3.78			0.6	1.79			0.23	0.68			0.21	0.63			1.26	3.78	HPLC-FLD
82			0.6	1.5			0.6	1.5			0.6	1.5			0.6	1.5			0.6	1.5		0.5	0.6	1.5			0.6	1.5			``	1.5	
99	0.04	0.13	0.04	0.13	0.04	0.12	0.04	0.12	0.07	0.13	0.07	0.13	0.04	0.17	0.04	0.17	0.04	0.13	0.04	0.13	0.04	0.12	0.04	0.12	0.07	0.13	0.07	0.13	0.04	0.17	0.04	0.17	HPLC-FLD

ANNEX 11: Data reported by participants

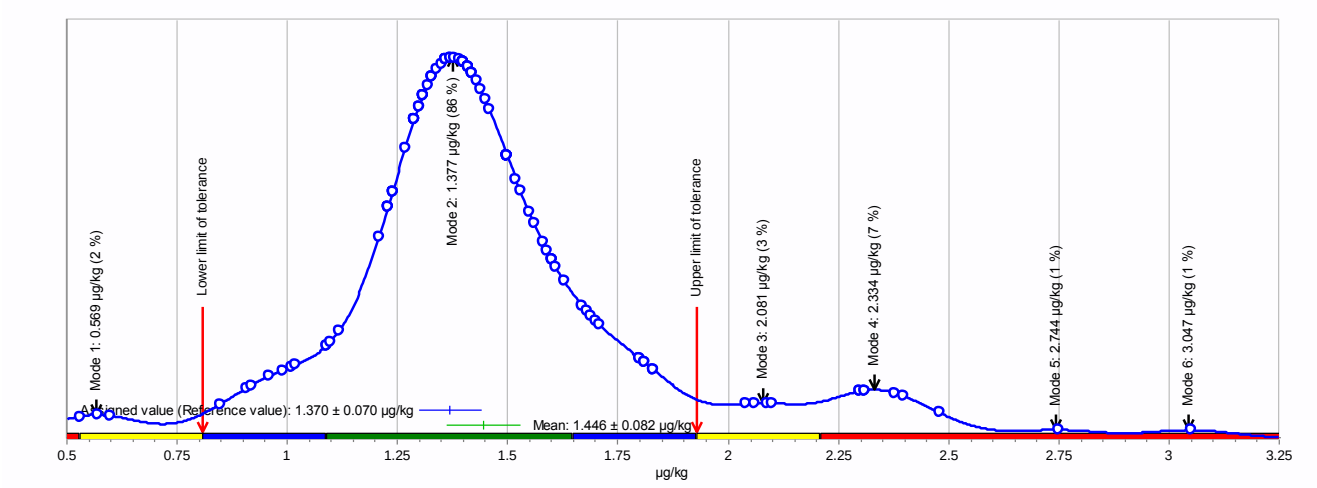
The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores. "Mean values" and "Rel. reproducibility s.d." represent the robust mean values and the robust standard deviations of the participants data, calculated according to the ISO 13528 algorithm.

Distribution of individual results, expressed on product basis, of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the milk chocolate test sample

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



Kernel density plot of the "mean value" for the benz[*a*]anthracene (BAA) content, expressed on product basis, of the milk chocolate test sample



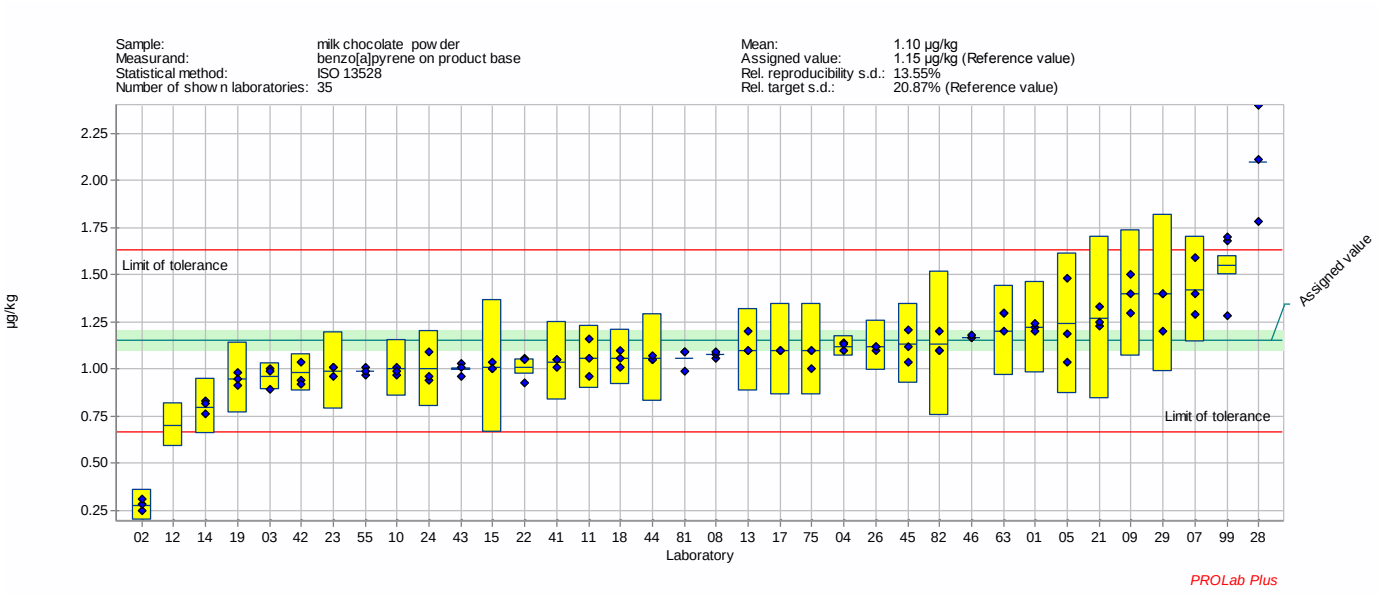
Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA), expressed on product basis, of the milk chocolate test sample .

Assigned value is 1.37 µg/kg**.** The uncertainty refers to the "final value".

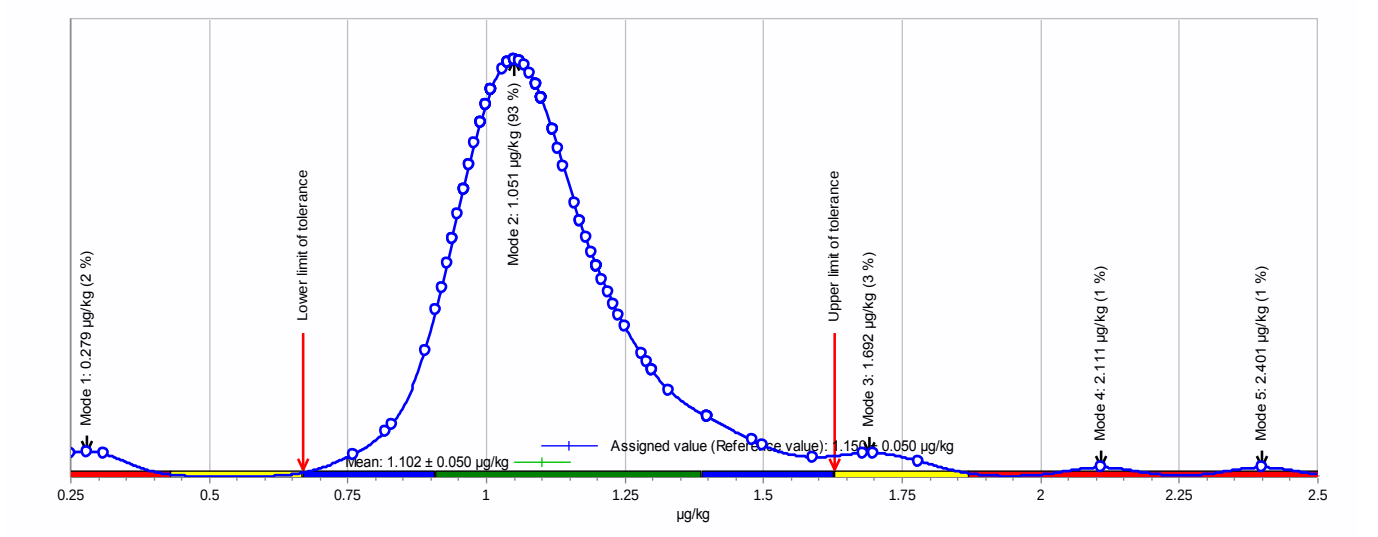
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BAA	1.63	1.59	1.67	1.631	20	GC-MS/MS
2	BAA	0.53	0.57	0.6	0.567	35	HPLC-UV/FLD
3	BAA	1.42	1.41	1.31	1.38	5.4	GC-MS/MS
4	BAA	1.37	1.39	1.42	1.39	15	GC-MS
5	BAA	2.1	1.58	1.29	1.66	30	HPLC-FLD
6	BAA						GC-MS/MS
7	BAA	1.8	1.55	1.61	1.65	11	GC-MS
8	BAA	1.41	1.42	1.46	1.43		GC-MS
9	BAA	1.5	1.5	1.5	1.5	21	GC-MS
10	BAA	1.31	1.29	1.31	1.3	15	GC-MS
11	BAA	1.43	1.24	1.31	1.33	17	HPLC-FLD
12	BAA				1	20	GC-MS/MS
13	BAA	1.7	1.6	1.6	1.6	20	GC-HRMS
14	BAA	0.99	1.09	1.1	1.06	22.3	GC-MS/MS
15	BAA	1.83	1.81	1.81	1.82	23.8	HPLC-FLD
16	BAA						
17	BAA	1.4	1.4	1.4	1.4	23.9	GC-MS
18	BAA	1.56	1.68	1.69	1.64	13.3	HPLC-FLD
19	BAA	1.3	1.29	1.33	1.3	20	HPLC-FLD
20	BAA						
21	BAA	1.34	1.24	1.36	1.31	26	HPLC-FLD
22	BAA	1.29	1.52	1.53	1.45	7.3	GC-MS
23	BAA	0.85	1.02	0.92	0.93	20.71	HPLC-FLD
24	BAA	1.83	1.71	1.12	1.56	20.1	HPLC-FLD
25	BAA						
26	BAA	2.31	2.31	2.38	2.33	16	HPLC-FLD
28	BAA	3.05	2.48	2.75	2.757		HPLC-UV/FLD
29	BAA	2.3	2.4	2.3	2.3	31	HPLC-FLD
31	BAA	0.91	0.96	1.01	0.959	15	GC-MS/MS
41	BAA	1.33	1.33	1.38	1.35	20	GC-MS/MS
42	BAA	1.32	1.23	1.21	1.25	6.8	GC-MS/MS
43	BAA	1.29	1.23	1.24	1.3	0.4	HPLC-FLD
44	BAA	1.36	1.41	1.41	1.39	22	HPLC-FLD
45	BAA	1.44	1.37	1.35	1.39	6.7	GC-MS
46	BAA	1.36	1.4	1.41	1.39		HPLC-FLD
55	BAA	2.04	2.06	2.09	2.063		GC-MS
63	BAA	1.5	1.5	1.4	1.5	27	GC-MS
75	BAA	1.4	1.5	1.4	1.4	22	GC-MS/MS
81	BAA	1.45	1.23	1.09	1.26		HPLC-FLD
82	BAA	1.3	1.4	1.4	1.37	29	
99	BAA	1.27	1.6	1.8	1.56	3.5	HPLC-FLD

Distribution of individual results expressed on product basis of replicate determinations reported for the benzo[*a*] pyrene (BAP) content of the milk chocolate test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the milk chocolate test sample



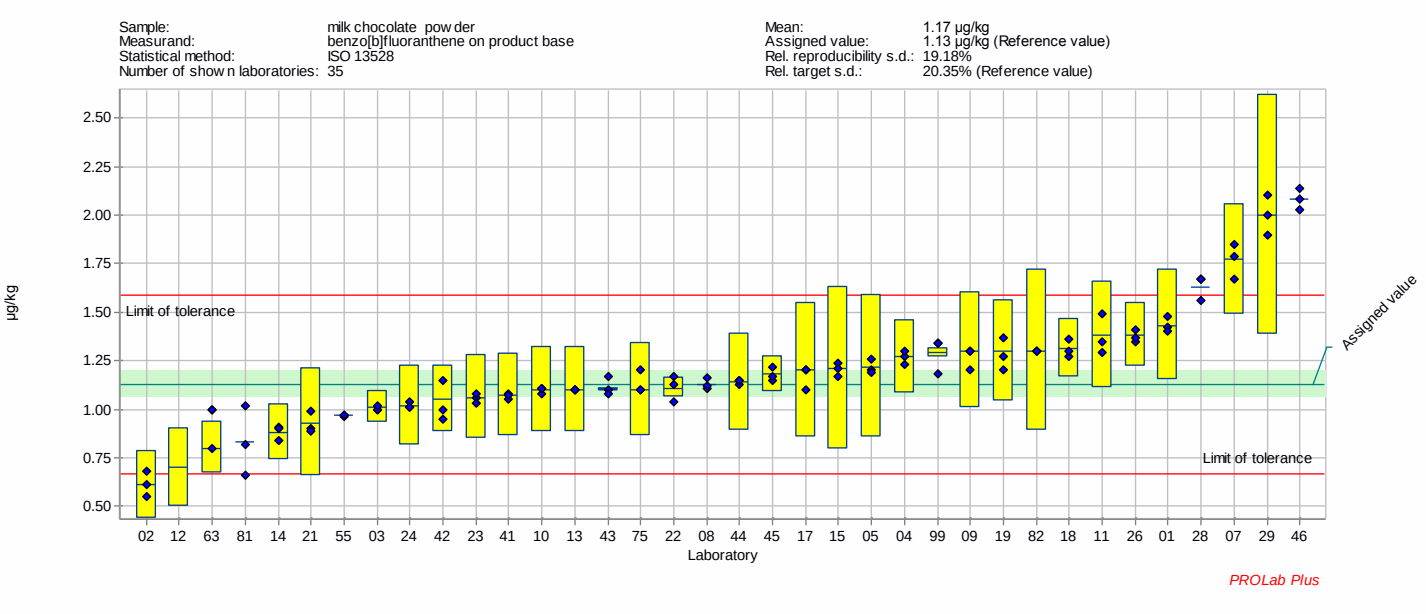
Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP), expressed on product basis, of the milk chocolate test sample.

Assigned value is 1.15 µg/kg**.** The uncertainty refers to the final value.

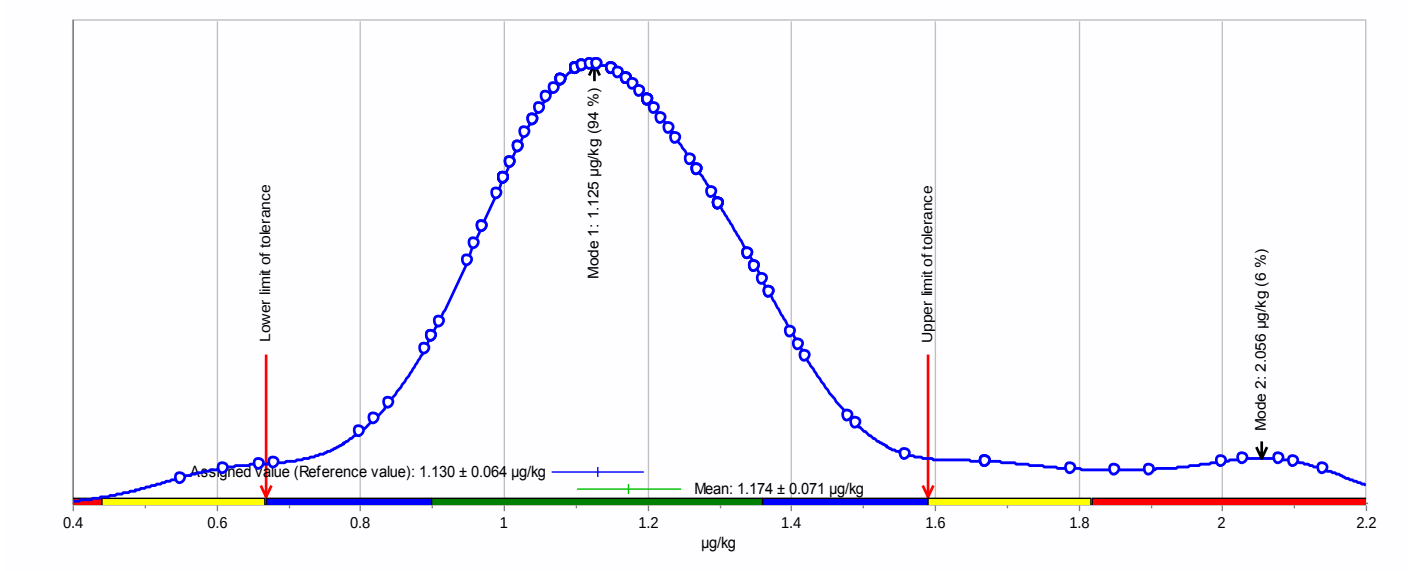
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BAP	1.22	1.2	1.24	1.219	20	GC-MS/MS
2	BAP	0.25	0.28	0.31	0.277	30	HPLC-UV/FLD
3	BAP	1	0.89	0.99	0.96	7.6	GC-MS/MS
4	BAP	1.1	1.14	1.13	1.12	5	GC-MS
5	BAP	1.48	1.19	1.04	1.24	30	HPLC-FLD
6	BAP						GC-MS/MS
7	BAP	1.4	1.29	1.59	1.42	20	GC-MS
8	BAP	1.06	1.08	1.09	1.08		GC-MS
9	BAP	1.3	1.5	1.4	1.4	24	GC-MS
10	BAP	1.01	0.97	0.99	1	15	GC-MS
11	BAP	0.96	1.16	1.06	1.06	16	HPLC-FLD
12	BAP				0.7	17	GC-MS/MS
13	BAP	1.1	1.1	1.2	1.1	20	GC-HRMS
14	BAP	0.76	0.83	0.82	0.8	18.8	GC-MS/MS
15	BAP	1.04	1	1	1.01	34.9	HPLC-FLD
16	BAP						
17	BAP	1.1	1.1	1.1	1.1	22.17	GC-MS
18	BAP	1.01	1.06	1.1	1.06	14	HPLC-FLD
19	BAP	0.98	0.91	0.95	0.95	20	HPLC-FLD
20	BAP						
21	BAP	1.33	1.23	1.25	1.27	34	HPLC-FLD
22	BAP	0.93	1.06	1.05	1.01	4.1	GC-MS
23	BAP	0.96	1.01	1.01	0.99	20.62	HPLC-FLD
24	BAP	0.94	1.09	0.96	1	20.2	HPLC-FLD
25	BAP						
26	BAP	1.1	1.12	1.12	1.12	12	HPLC-FLD
28	BAP	2.4	2.11	1.78	2.099		HPLC-UV/FLD
29	BAP	1.2	1.4	1.4	1.4	30	HPLC-FLD
31	BAP	< 0.90	< 0.90	< 0.90		13	GC-MS/MS
41	BAP	1.05	1.01	1.05	1.04	20	GC-MS/MS
42	BAP	1.04	0.94	0.92	0.98	10.1	GC-MS/MS
43	BAP	1.03	1.01	0.96	1	0.3	HPLC-FLD
44	BAP	1.05	1.05	1.07	1.06	22	HPLC-FLD
45	BAP	1.21	1.12	1.04	1.13	18.8	GC-MS
46	BAP	1.17	1.17	1.18	1.17		HPLC-FLD
55	BAP	1.01	0.97	0.99	0.99		GC-MS
63	BAP	1.2	1.3	1.3	1.2	20	GC-MS
75	BAP	1.1	1.1	1	1.1	22	GC-MS/MS
81	BAP	1.09	1.09	0.99	1.06		HPLC-FLD
82	BAP	1.1	1.1	1.2	1.13	34	
99	BAP	1.28	1.68	1.7	1.55	3.3	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content, expressed on product basis, of the milk chocolate test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the milk chocolate test sample



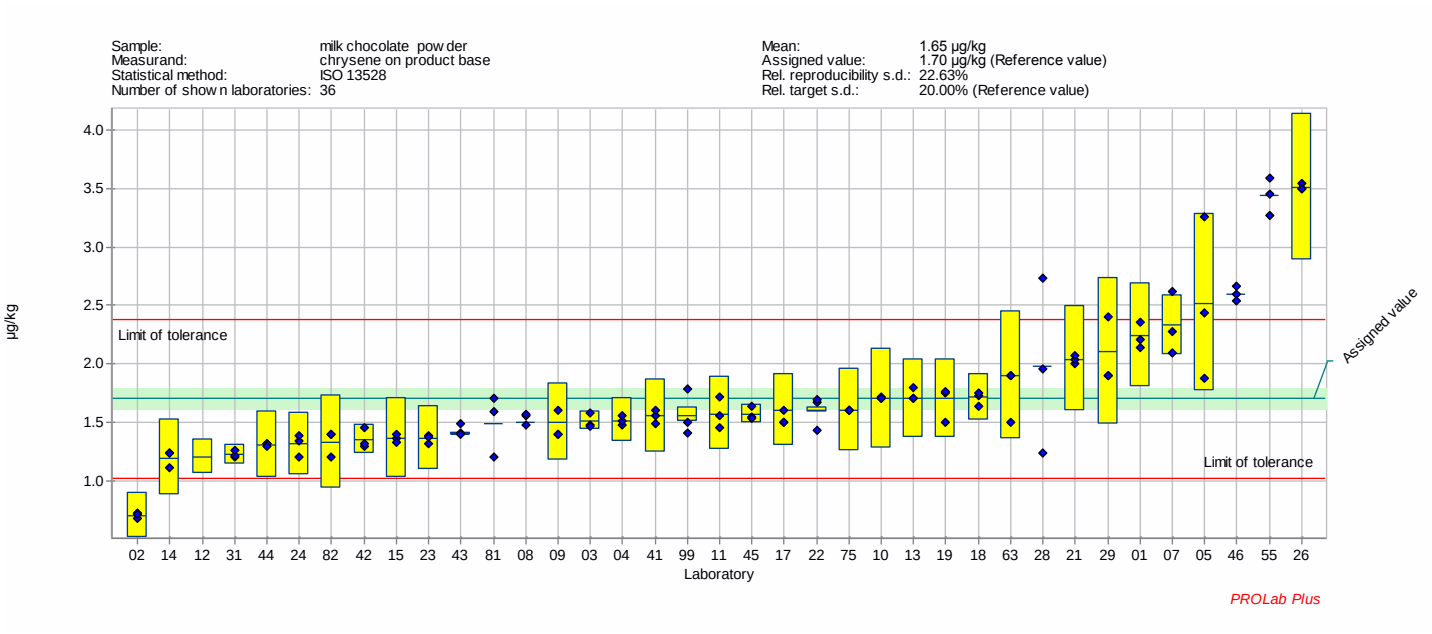
Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF), expressed on product basis, of the milk chocolate test sample.

Assigned value is 1.13 µg/kg. The uncertainty refers to the final value.

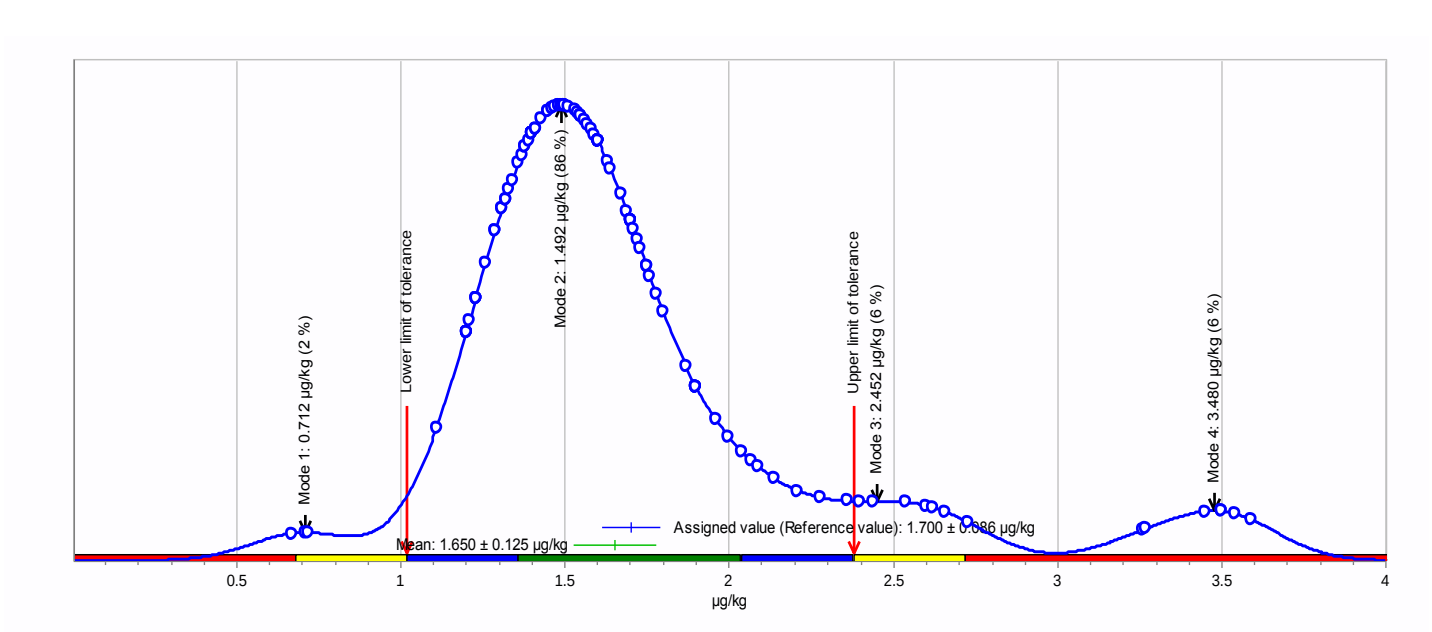
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BBF	1.42	1.4	1.48	1.433	20	GC-MS/MS
2	BBF	0.55	0.61	0.68	0.61	29	HPLC-UV/FLD
3	BBF	1	1	1.02	1.01	8.4	GC-MS/MS
4	BBF	1.23	1.27	1.3	1.27	15	GC-MS
5	BBF	1.2	1.26	1.19	1.22	30	HPLC-FLD
6	BBF						GC-MS/MS
7	BBF	1.79	1.67	1.85	1.77	16	GC-MS
8	BBF	1.11	1.12	1.16	1.13		GC-MS
9	BBF	1.2	1.3	1.3	1.3	23	GC-MS
10	BBF	1.08	1.11	1.11	1.1	20	GC-MS
11	BBF	1.49	1.29	1.35	1.38	20	HPLC-FLD
12	BBF				0.7	29	GC-MS/MS
13	BBF	1.1	1.1	1.1	1.1	20	GC-HRMS
14	BBF	0.84	0.91	0.9	0.88	16.5	GC-MS/MS
15	BBF	1.24	1.21	1.17	1.21	34.8	HPLC-FLD
16	BBF						
17	BBF	1.2	1.1	1.2	1.2	29.08	GC-MS
18	BBF	1.27	1.36	1.3	1.31	11.5	HPLC-FLD
19	BBF	1.27	1.37	1.2	1.3	20	HPLC-FLD
20	BBF						
21	BBF	0.99	0.9	0.89	0.93	30	HPLC-FLD
22	BBF	1.04	1.13	1.17	1.11	4.5	GC-MS
23	BBF	1.06	1.03	1.08	1.06	20.55	HPLC-FLD
24	BBF	1.01	1.04	1.01	1.02	20.2	HPLC-FLD
25	BBF						
26	BBF	1.41	1.35	1.37	1.38	12	HPLC-FLD
28	BBF	1.67	1.67	1.56	1.632		HPLC-UV/FLD
29	BBF	1.9	2	2.1	2	31	HPLC-FLD
31	BBF	< 0.90	< 0.90	< 0.90		8	GC-MS/MS
41	BBF	1.08	1.05	1.07	1.07	20	GC-MS/MS
42	BBF	1.15	1	0.95	1.05	16.4	GC-MS/MS
43	BBF	1.17	1.1	1.08	1.1	0.3	HPLC-FLD
44	BBF	1.13	1.15	1.15	1.14	22	HPLC-FLD
45	BBF	1.22	1.15	1.17	1.18	7.7	GC-MS
46	BBF	2.08	2.14	2.03	2.08		HPLC-FLD
55	BBF	0.97	0.96	0.97	0.967		GC-MS
63	BBF	1	1	0.8	0.8	17	GC-MS
75	BBF	1.1	1.2	1.1	1.1	22	GC-MS/MS
81	BBF	1.02	0.82	0.66	0.83		HPLC-FLD
82	BBF	1.3	1.3	1.3	1.3	32	
99	BBF	1.18	1.34	1.34	1.29	2	HPLC-FLD

Distribution of individual results of replicate determinations reported for the chrysene (CHR) content, expressed on product basis, of the milk chocolate test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the milk chocolate test sample



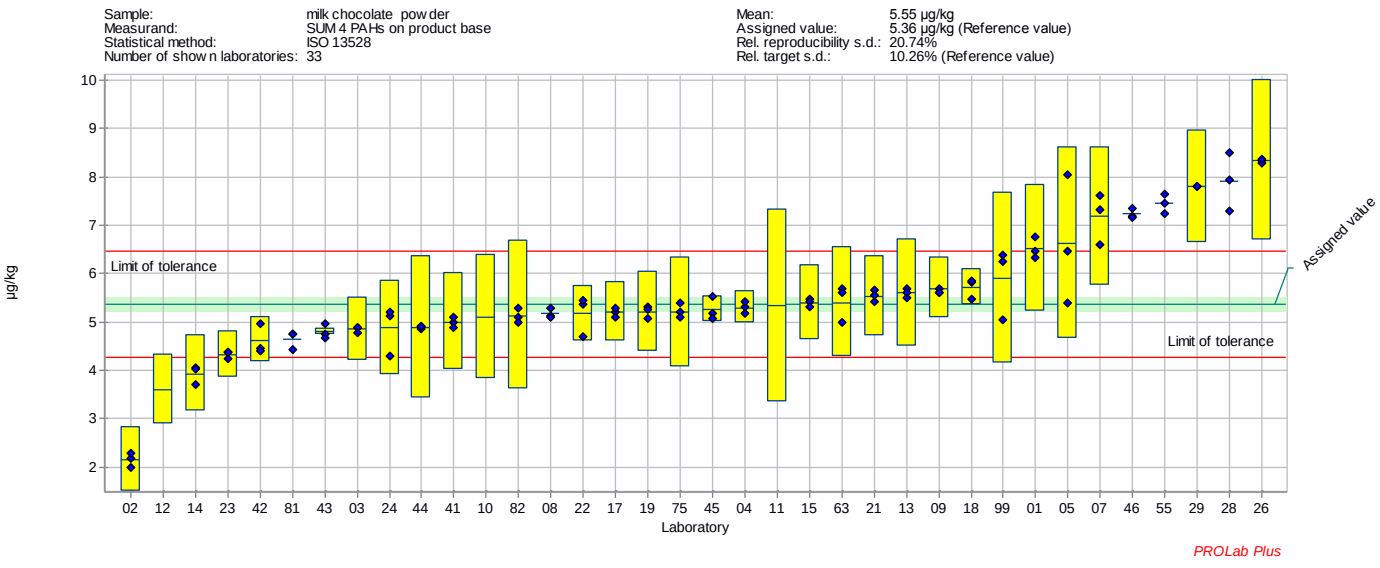
Results, as reported by the participants, for the content of chrysene (CHR), expressed on product basis, of the milk chocolate test sample.

Assigned value is 1.70µg/kg. The uncertainty refers to the final value.

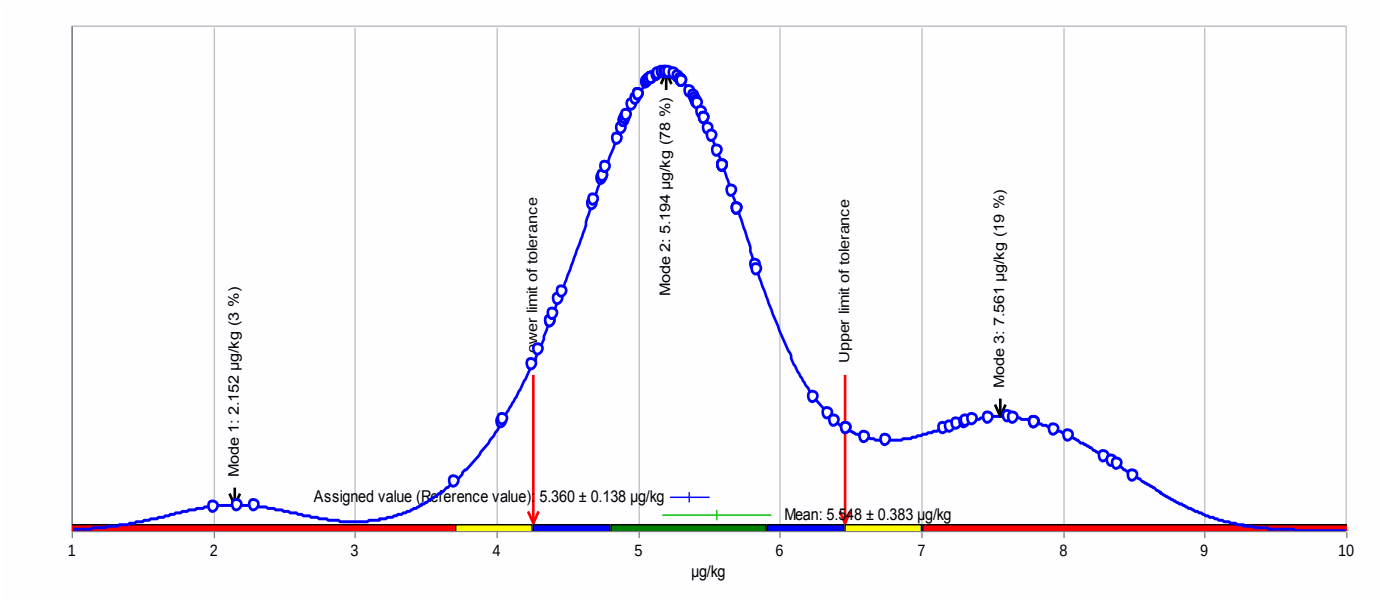
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	CHR	2.21	2.14	2.36	2.238	20	GC-MS/MS
2	CHR	0.67	0.72	0.71	0.7	28	HPLC-UV/FLD
3	CHR	1.48	1.58	1.46	1.51	5	GC-MS/MS
4	CHR	1.47	1.51	1.56	1.51	12.5	GC-MS
5	CHR	3.26	2.44	1.87	2.52	30	HPLC-FLD
6	CHR						GC-MS/MS
7	CHR	2.62	2.09	2.28	2.33	11	GC-MS
8	CHR	1.55	1.48	1.57	1.5		GC-MS
9	CHR	1.6	1.4	1.4	1.5	22	GC-MS
10	CHR	1.7	1.72	1.7	1.7	25	GC-MS
11	CHR	1.71	1.55	1.45	1.57	20	HPLC-FLD
12	CHR				1.2	12	GC-MS/MS
13	CHR	1.8	1.7	1.7	1.7	20	GC-HRMS
14	CHR	1.11	1.23	1.23	1.19	27.4	GC-MS/MS
15	CHR	1.36	1.39	1.33	1.36	25.2	HPLC-FLD
16	CHR						
17	CHR	1.5	1.5	1.6	1.6	19.29	GC-MS
18	CHR	1.63	1.73	1.75	1.71	11.8	HPLC-FLD
19	CHR	1.75	1.5	1.76	1.7	20	HPLC-FLD
20	CHR						
21	CHR	2	2.04	2.07	2.04	22	HPLC-FLD
22	CHR	1.43	1.67	1.69	1.6	1.6	GC-MS
23	CHR	1.38	1.32	1.37	1.36	20.34	HPLC-FLD
24	CHR	1.34	1.38	1.2	1.31	20.1	HPLC-FLD
25	CHR						
26	CHR	3.54	3.5	3.5	3.51	18	HPLC-FLD
28	CHR	2.73	1.23	1.96	1.974		HPLC-UV/FLD
29	CHR	2.4	1.9	1.9	2.1	30	HPLC-FLD
31	CHR	1.2	1.21	1.26	1.223	7	GC-MS/MS
41	CHR	1.55	1.49	1.6	1.55	20	GC-MS/MS
42	CHR	1.45	1.29	1.32	1.35	9.1	GC-MS/MS
43	CHR	1.49	1.41	1.4	1.4	0.4	HPLC-FLD
44	CHR	1.31	1.31	1.29	1.3	22	HPLC-FLD
45	CHR	1.64	1.54	1.53	1.57	5.1	GC-MS
46	CHR	2.6	2.66	2.54	2.6		HPLC-FLD
55	CHR	3.45	3.27	3.59	3.437		GC-MS
63	CHR	1.5	1.9	1.9	1.9	29	GC-MS
75	CHR	1.6	1.6	1.6	1.6	22	GC-MS/MS
81	CHR	1.2	1.59	1.7	1.49		HPLC-FLD
82	CHR	1.4	1.2	1.4	1.33	30	
99	CHR	1.41	1.5	1.78	1.56	3.8	HPLC-FLD

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content, expressed on product basis, of the milk chocolate test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the milk chocolate test sample

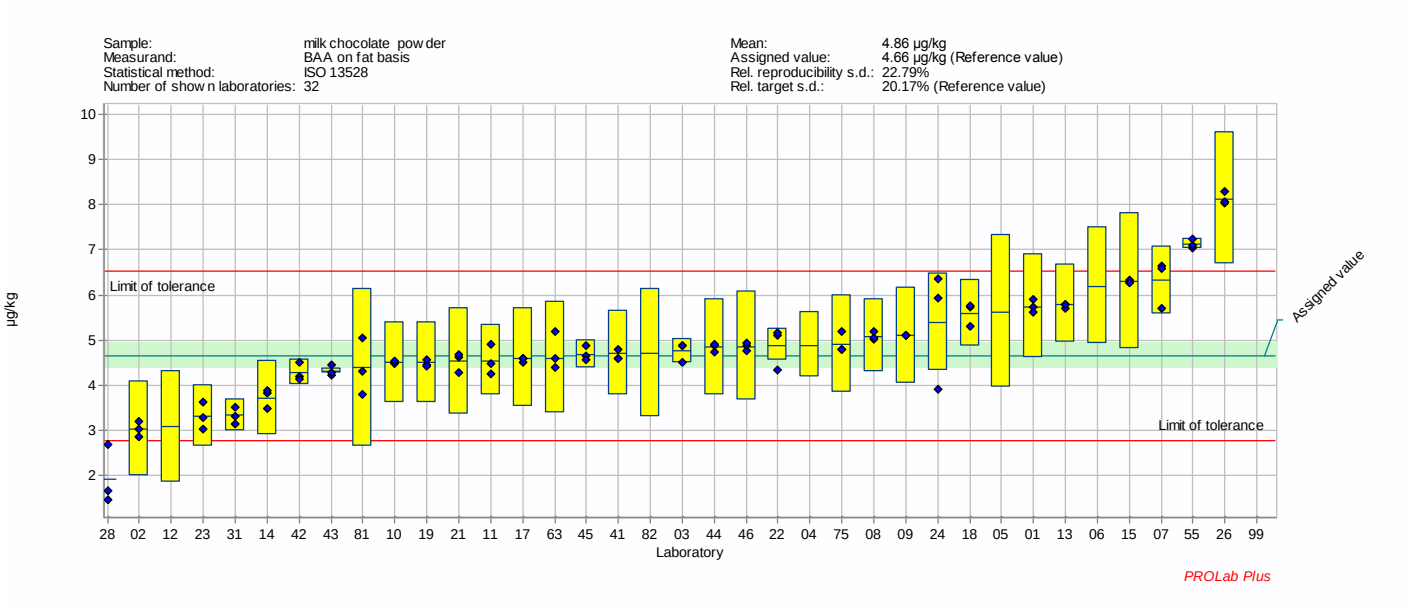


Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH), expressed on product basis, of the milk chocolate test sample .
Assigned value is 5.36 µg/kg.

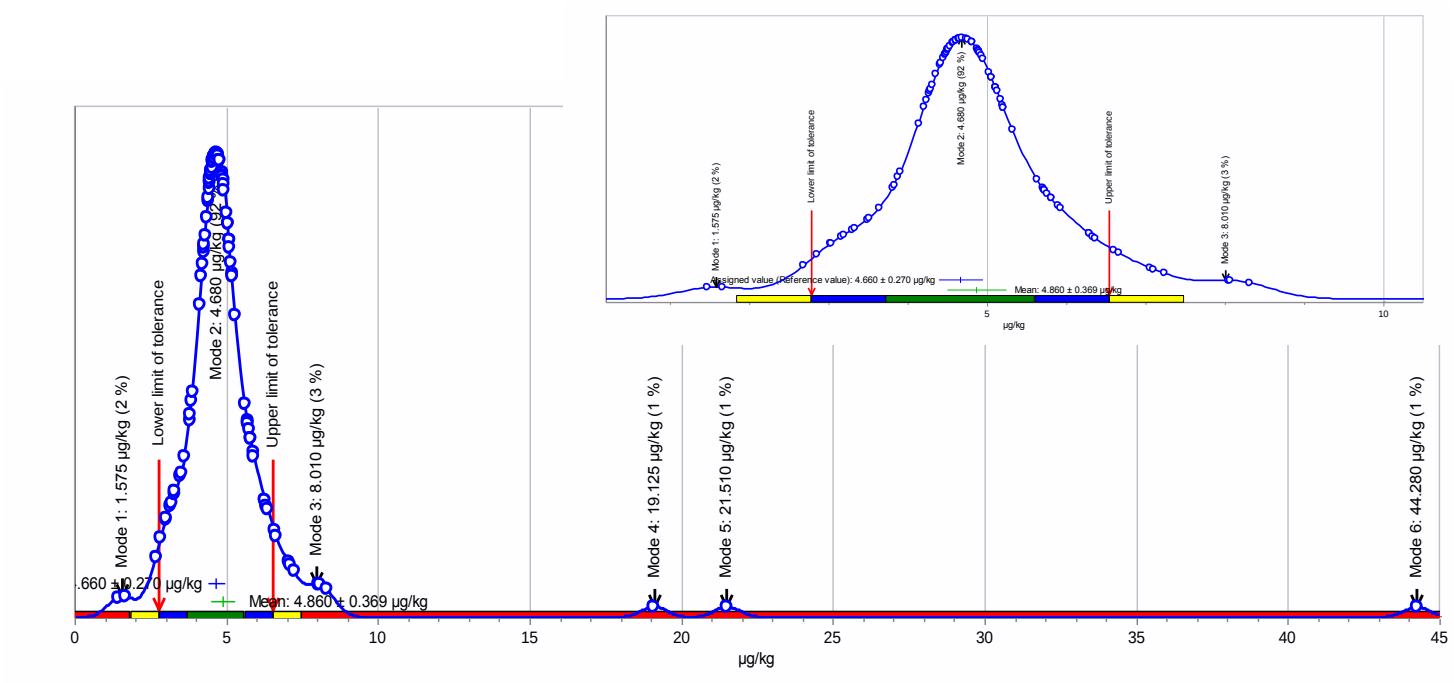
LCode	Measurand	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	%	
1	SUM4PAHS	6.52	20	GC-MS/MS
2	SUM4PAHS	2.155	31	HPLC-UV/FLD
3	SUM4PAHS	4.86	13.5	GC-MS/MS
4	SUM4PAHS	5.3	6.5	GC-MS
5	SUM4PAHS	6.63	30	HPLC-FLD
6	SUM4PAHS			GC-MS/MS
7	SUM4PAHS	7.18	20	GC-MS
8	SUM4PAHS	5.17		GC-MS
9	SUM4PAHS	5.7	11	GC-MS
10	SUM4PAHS	5.1	25	GC-MS
11	SUM4PAHS	5.33	37.6	HPLC-FLD
12	SUM4PAHS	3.6	20	GC-MS/MS
13	SUM4PAHS	5.6	20	GC-HRMS
14	SUM4PAHS	3.93	20.1	GC-MS/MS
15	SUM4PAHS	5.4	14.4	HPLC-FLD
16	SUM4PAHS			
17	SUM4PAHS	5.2	11.76	
18	SUM4PAHS	5.72	6.5	HPLC-FLD
19	SUM4PAHS	5.2	16	HPLC-FLD
20	SUM4PAHS			
21	SUM4PAHS	5.54	15	HPLC-FLD
22	SUM4PAHS	5.17	11.2	
23	SUM4PAHS	4.33	11.05	HPLC-FLD
24	SUM4PAHS	4.88	20	HPLC-FLD
25	SUM4PAHS			
26	SUM4PAHS	8.34	20	HPLC-FLD
28	SUM4PAHS	7.916		HPLC-UV/FLD
29	SUM4PAHS	7.8	15	HPLC-FLD
31	SUM4PAHS			GC-MS/MS
41	SUM4PAHS	5	20	GC-MS/MS
42	SUM4PAHS	4.63	10.1	GC-MS/MS
43	SUM4PAHS	4.8	1.4	HPLC-FLD
44	SUM4PAHS	4.89	30	HPLC-FLD
45	SUM4PAHS	5.26	5	GC-MS
46	SUM4PAHS	7.24		HPLC-FLD
55	SUM4PAHS	7.46		GC-MS
63	SUM4PAHS	5.4	21	GC-MS
75	SUM4PAHS	5.2	22	GC-MS/MS
81	SUM4PAHS	4.64		HPLC-FLD
82	SUM4PAHS	5.13	30	
99	SUM4PAHS	5.9	29.9	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content, expressed on fat basis, of the milk chocolate test sample

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



Kernel density plot of the reported values for proficiency assessment for the benz[*a*]anthracene (BAA) content, expressed on fat basis, of the milk chocolate test sample



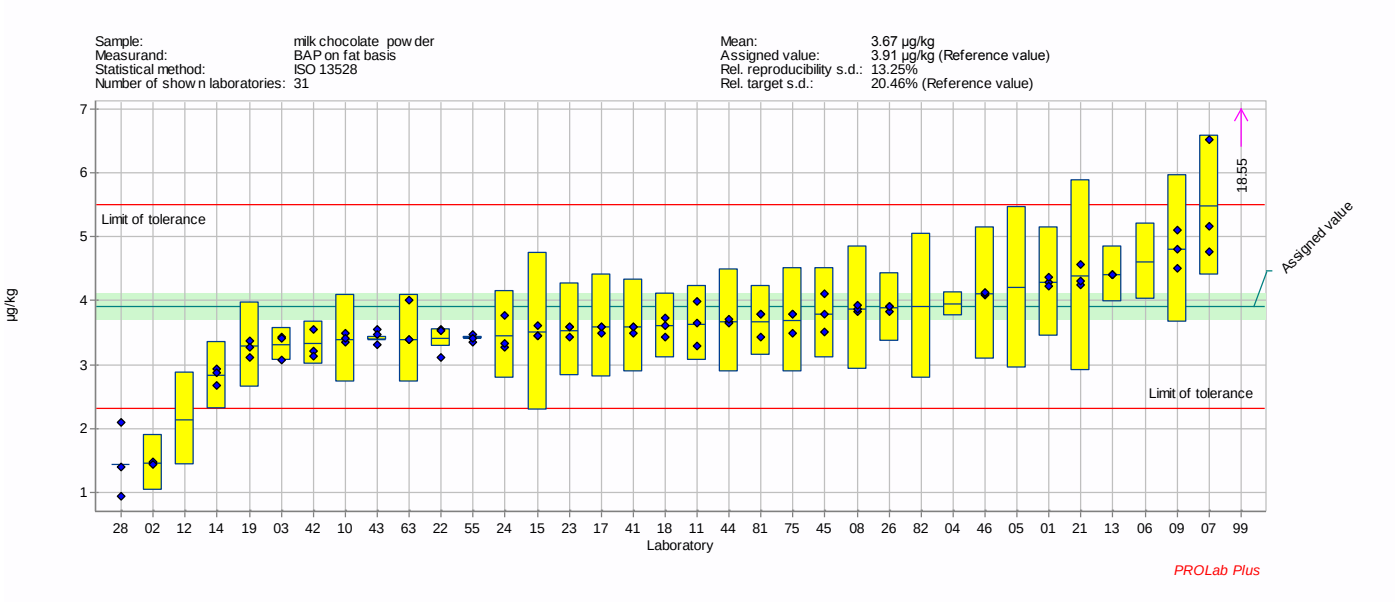
Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA), expressed on fat basis, of the milk chocolate test sample.

Assigned value is 4.66 µg/kg**.** The uncertainty refers to the "final value".

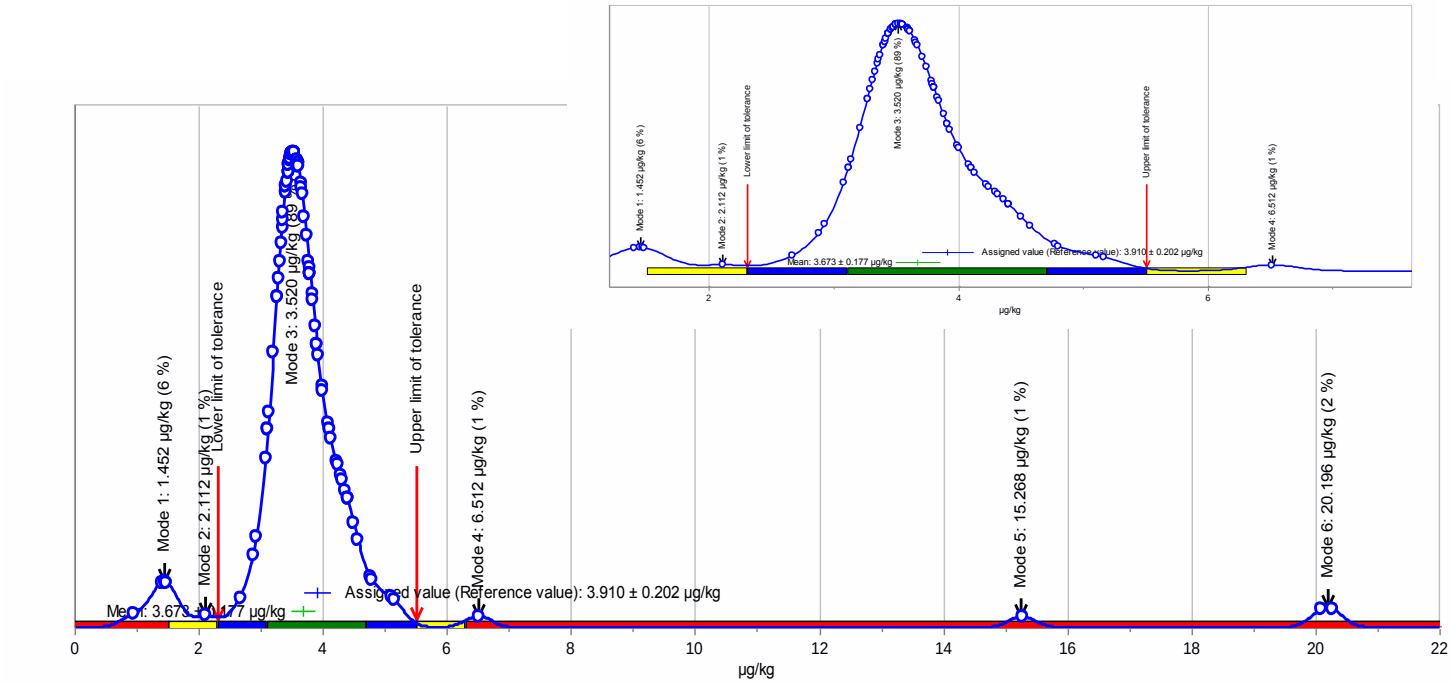
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BAA_FAT	5.72	5.62	5.89	5.744	20	GC-MS/MS
2	BAA_FAT	3.19	3.02	2.85	3.02	35	HPLC-UV/FLD
3	BAA_FAT	4.89	4.87	4.5	4.75	5.6	GC-MS/MS
4	BAA_FAT				4.89	15	GC-MS
5	BAA_FAT				5.63	30	HPLC-FLD
6	BAA_FAT				6.2	21	GC-MS/MS
7	BAA_FAT	6.65	5.71	6.59	6.32	12	GC-MS
8	BAA_FAT	5.02	5.05	5.19	5.09	16	GC-MS
9	BAA_FAT	5.1	5.1	5.1	5.1	21	GC-MS
10	BAA_FAT	4.51	4.47	4.53	4.5	20	GC-MS
11	BAA_FAT	4.92	4.26	4.48	4.55	17	HPLC-FLD
12	BAA_FAT				3.07	40	GC-MS/MS
13	BAA_FAT	5.8	5.7	5.8	5.8	15	GC-HRMS
14	BAA_FAT	3.48	3.82	3.87	3.72	22.3	GC-MS/MS
15	BAA_FAT	6.33	6.28	6.28	6.3	23.8	HPLC-FLD
16	BAA_FAT						
17	BAA_FAT	4.6	4.5	4.6	4.6	23.9	GC-MS
18	BAA_FAT	5.31	5.72	5.75	5.58	13.3	HPLC-FLD
19	BAA_FAT	4.46	4.41	4.57	4.5	20	HPLC-FLD
20	BAA_FAT						
21	BAA_FAT	4.63	4.28	4.68	4.53	26	HPLC-FLD
22	BAA_FAT	4.35	5.12	5.16	4.88	7.3	
23	BAA_FAT	3.03	3.63	3.29	3.31	20.71	HPLC-FLD
24	BAA_FAT	6.36	5.92	3.9	5.39	20	HPLC-FLD
25	BAA_FAT						
26	BAA_FAT	8.04	8.06	8.3	8.13	18	HPLC-FLD
28	BAA_FAT	2.68	1.65	1.46	1.907		HPLC-UV/FLD
29	BAA_FAT						HPLC-FLD
31	BAA_FAT	3.15	3.32	3.51	3.329	11	GC-MS/MS
41	BAA_FAT	4.6	4.6	4.8	4.7	20	GC-MS/MS
42	BAA_FAT	4.51	4.2	4.13	4.28	6.8	GC-MS/MS
43	BAA_FAT	4.44	4.23	4.27	4.3	1.4	HPLC-FLD
44	BAA_FAT	4.73	4.89	4.9	4.84	22	HPLC-FLD
45	BAA_FAT	4.88	4.64	4.56	4.69	6.7	GC-MS
46	BAA_FAT	4.75	4.89	4.94	4.86	25	HPLC-FLD
55	BAA_FAT	7.05	7.09	7.23	7.12	1.6	GC-MS
63	BAA_FAT	4.6	4.4	5.2	4.6	27	GC-MS
75	BAA_FAT	4.8	5.2	4.8	4.9	22	GC-MS/MS
81	BAA_FAT	5.05	4.3	3.8	4.38	40	HPLC-FLD
82	BAA_FAT				4.71	30	
99	BAA_FAT	44.26	19.11	21.52	28.3	3.5	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*a*] pyrene (BAP) content, expressed on fat basis, of the milk chocolate test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the milk chocolate test sample



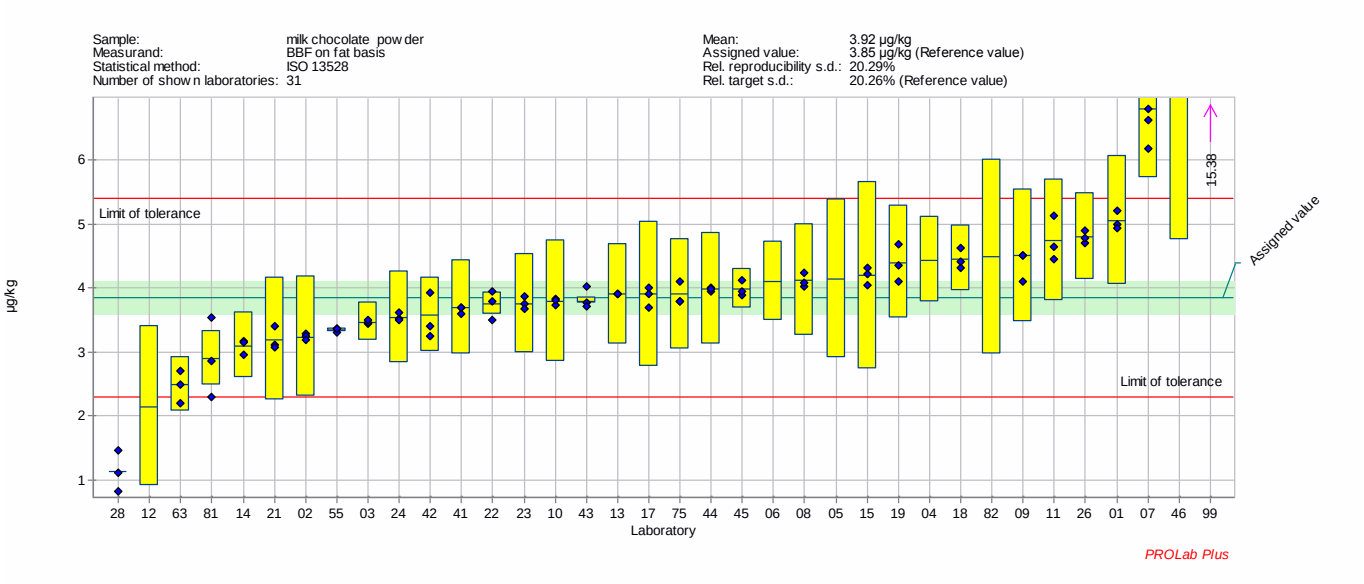
Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP), expressed on fat basis, of the milk chocolate test sample.

Assigned value is 3.91 µg/kg**.** The uncertainty refers to the final value.

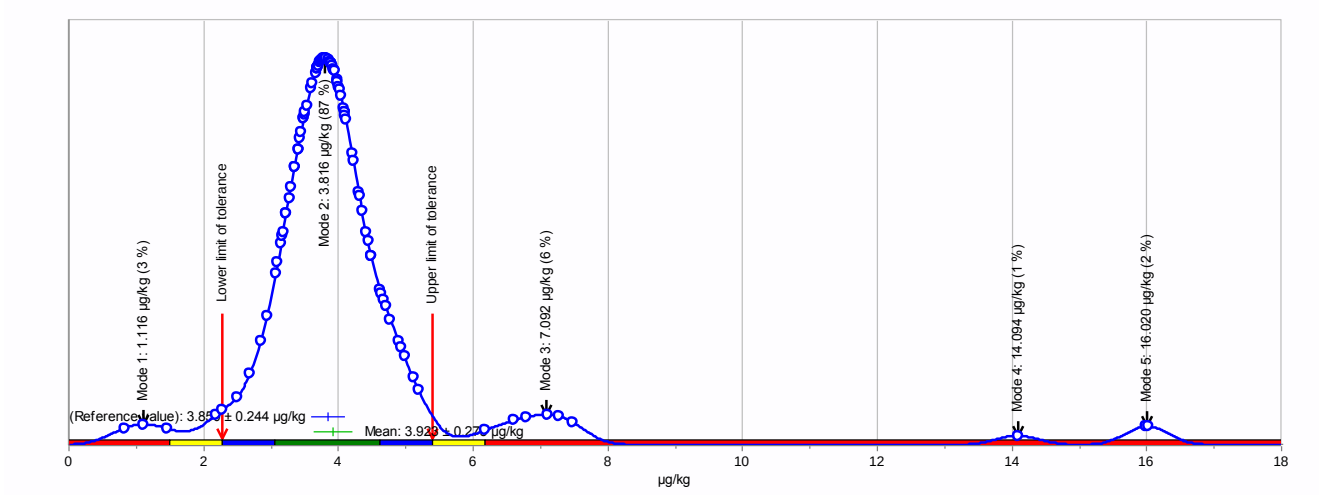
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BAP_FAT	4.29	4.22	4.36	4.291	20	GC-MS/MS
2	BAP_FAT	1.47	1.48	1.45	1.467	30	HPLC-UV/FLD
3	BAP_FAT	3.44	3.08	3.42	3.31	7.8	GC-MS/MS
4	BAP_FAT				3.94	5	GC-MS
5	BAP_FAT				4.2	30	HPLC-FLD
6	BAP_FAT				4.6	13	GC-MS/MS
7	BAP_FAT	5.16	4.77	6.51	5.48	20	GC-MS
8	BAP_FAT	3.83	3.88	3.93	3.88	25	GC-MS
9	BAP_FAT	4.5	5.1	4.8	4.8	24	GC-MS
10	BAP_FAT	3.5	3.36	3.41	3.4	20	GC-MS
11	BAP_FAT	3.29	3.99	3.65	3.64	16	HPLC-FLD
12	BAP_FAT				2.15	34	GC-MS/MS
13	BAP_FAT	4.4	4.4	4.4	4.4	10	GC-HRMS
14	BAP_FAT	2.67	2.93	2.88	2.83	18.8	GC-MS/MS
15	BAP_FAT	3.61	3.46	3.46	3.51	34.9	HPLC-FLD
16	BAP_FAT						
17	BAP_FAT	3.6	3.5	3.6	3.6	22.17	GC-MS
18	BAP_FAT	3.44	3.61	3.74	3.61	14	HPLC-FLD
19	BAP_FAT	3.37	3.12	3.27	3.3	20	HPLC-FLD
20	BAP_FAT						
21	BAP_FAT	4.57	4.24	4.31	4.38	34	HPLC-FLD
22	BAP_FAT	3.12	3.55	3.54	3.41	4.1	
23	BAP_FAT	3.44	3.59	3.59	3.54	20.62	HPLC-FLD
24	BAP_FAT	3.27	3.78	3.33	3.46	20	HPLC-FLD
25	BAP_FAT						
26	BAP_FAT	3.84	3.91	3.91	3.89	14	HPLC-FLD
28	BAP_FAT	2.11	1.4	0.95	1.452		HPLC-UV/FLD
29	BAP_FAT						HPLC-FLD
31	BAP_FAT	< 3.12	< 3.12	< 3.12		13	GC-MS/MS
41	BAP_FAT	3.6	3.5	3.6	3.6	20	GC-MS/MS
42	BAP_FAT	3.55	3.21	3.14	3.33	10.1	GC-MS/MS
43	BAP_FAT	3.55	3.48	3.31	3.4	1	HPLC-FLD
44	BAP_FAT	3.67	3.66	3.71	3.68	22	HPLC-FLD
45	BAP_FAT	4.1	3.79	3.52	3.8	18.8	GC-MS
46	BAP_FAT	4.08	4.1	4.13	4.11	25	HPLC-FLD
55	BAP_FAT	3.47	3.35	3.41	3.41	0.7	GC-MS
63	BAP_FAT	3.4	3.4	4	3.4	20	GC-MS
75	BAP_FAT	3.8	3.8	3.5	3.7	22	GC-MS/MS
81	BAP_FAT	3.8	3.8	3.44	3.68	15	HPLC-FLD
82	BAP_FAT				3.91	29	
99	BAP_FAT	15.27	20.1	20.28	18.55	3.3	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content, expressed on fat basis, of the milk chocolate test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the milk chocolate test sample



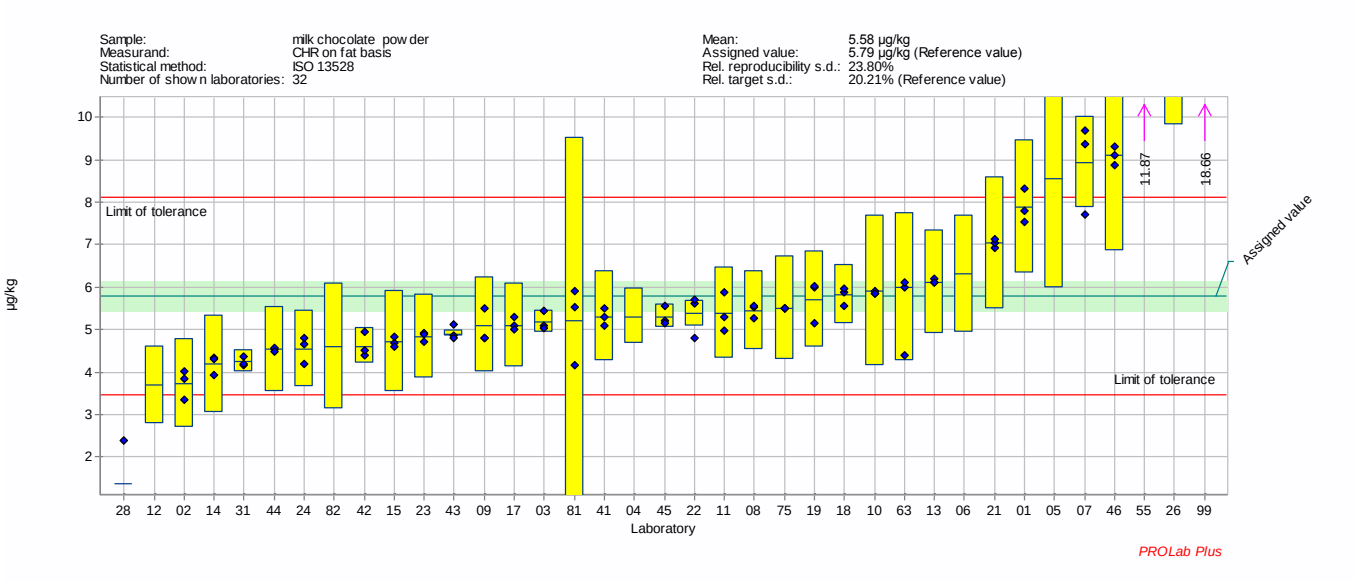
Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF), expressed on fat basis, of the milk chocolate test sample.

Assigned value is 3.85 µg/kg. The uncertainty refers to the final value.

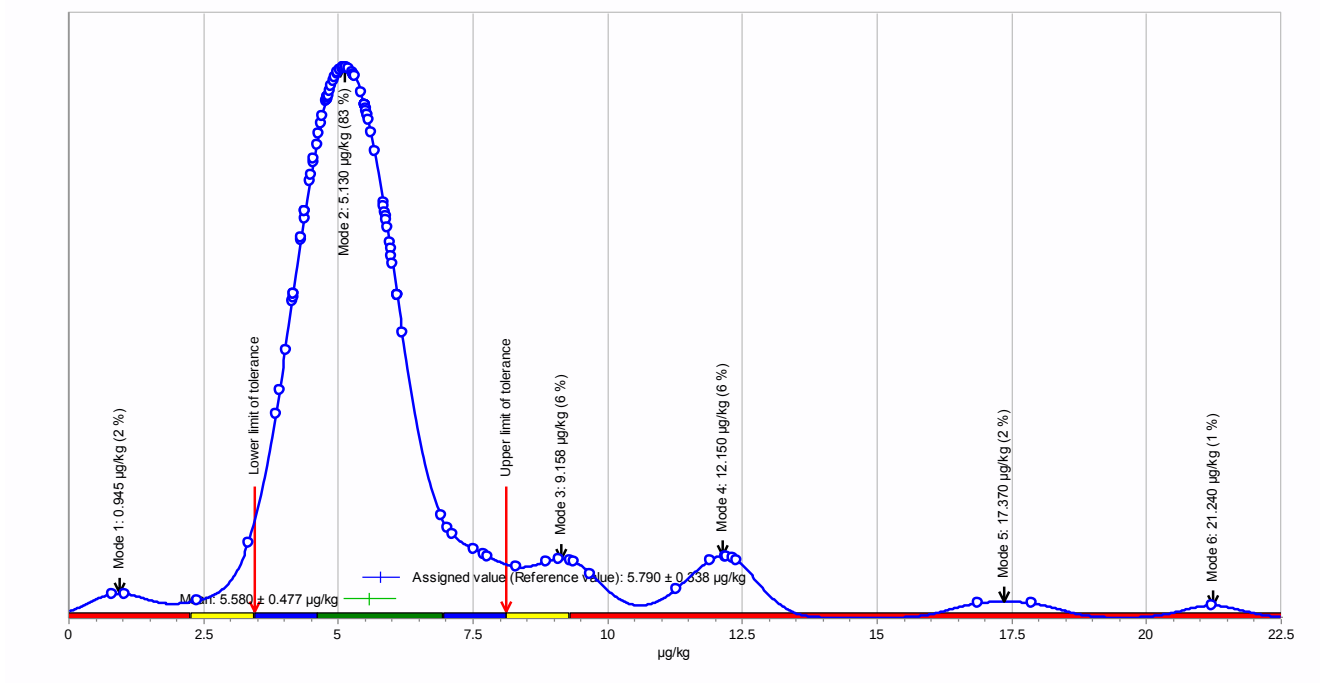
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BBF_FAT	4.99	4.94	5.2	5.05	20	GC-MS/MS
2	BBF_FAT	3.28	3.24	3.19	3.24	29	HPLC-UV/FLD
3	BBF_FAT	3.44	3.46	3.5	3.47	8.6	GC-MS/MS
4	BBF_FAT				4.44	15	GC-MS
5	BBF_FAT				4.14	30	HPLC-FLD
6	BBF_FAT				4.1	15	GC-MS/MS
7	BBF_FAT	6.62	6.18	6.79	6.79	16	GC-MS
8	BBF_FAT	4.03	4.09	4.23	4.12	21	GC-MS
9	BBF_FAT	4.1	4.5	4.5	4.5	23	GC-MS
10	BBF_FAT	3.74	3.83	3.82	3.8	25	GC-MS
11	BBF_FAT	5.12	4.45	4.65	4.74	20	HPLC-FLD
12	BBF_FAT				2.15	58	GC-MS/MS
13	BBF_FAT	3.9	3.9	3.9	3.9	20	GC-HRMS
14	BBF_FAT	2.95	3.18	3.16	3.1	16.5	GC-MS/MS
15	BBF_FAT	4.31	4.21	4.05	4.19	34.8	HPLC-FLD
16	BBF_FAT						
17	BBF_FAT	4	3.7	3.9	3.9	29.08	GC-MS
18	BBF_FAT	4.32	4.63	4.42	4.46	11.5	HPLC-FLD
19	BBF_FAT	4.36	4.68	4.11	4.4	20	HPLC-FLD
20	BBF_FAT						
21	BBF_FAT	3.41	3.11	3.08	3.2	30	HPLC-FLD
22	BBF_FAT	3.51	3.79	3.95	3.75	4.5	
23	BBF_FAT	3.76	3.67	3.86	3.76	20.55	HPLC-FLD
24	BBF_FAT	3.52	3.62	3.5	3.54	20	HPLC-FLD
25	BBF_FAT						
26	BBF_FAT	4.9	4.71	4.78	4.8	14	HPLC-FLD
28	BBF_FAT	1.47	1.11	0.83	1.13		HPLC-UV/FLD
29	BBF_FAT						HPLC-FLD
31	BBF_FAT	< 3.12	< 3.12	< 3.12		8	GC-MS/MS
41	BBF_FAT	3.7	3.6	3.7	3.7	20	GC-MS/MS
42	BBF_FAT	3.92	3.41	3.24	3.58	16.4	GC-MS/MS
43	BBF_FAT	4.02	3.78	3.71	3.8	1.1	HPLC-FLD
44	BBF_FAT	3.94	4	3.99	3.98	22	HPLC-FLD
45	BBF_FAT	4.12	3.89	3.94	3.98	7.7	GC-MS
46	BBF_FAT	7.28	7.49	7.12	7.3	35	HPLC-FLD
55	BBF_FAT	3.36	3.31	3.36	3.34	0.7	GC-MS
63	BBF_FAT	2.5	2.2	2.7	2.5	17	GC-MS
75	BBF_FAT	3.8	4.1	3.8	3.9	22	GC-MS/MS
81	BBF_FAT	3.54	2.86	2.29	2.9	15	HPLC-FLD
82	BBF_FAT				4.48	34	
99	BBF_FAT	14.09	16	16.03	15.38	2	HPLC-FLD

Distribution of individual results of replicate determinations reported for the chrysene (CHR) content, expressed on fat basis, of the milk chocolate test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the milk chocolate test sample



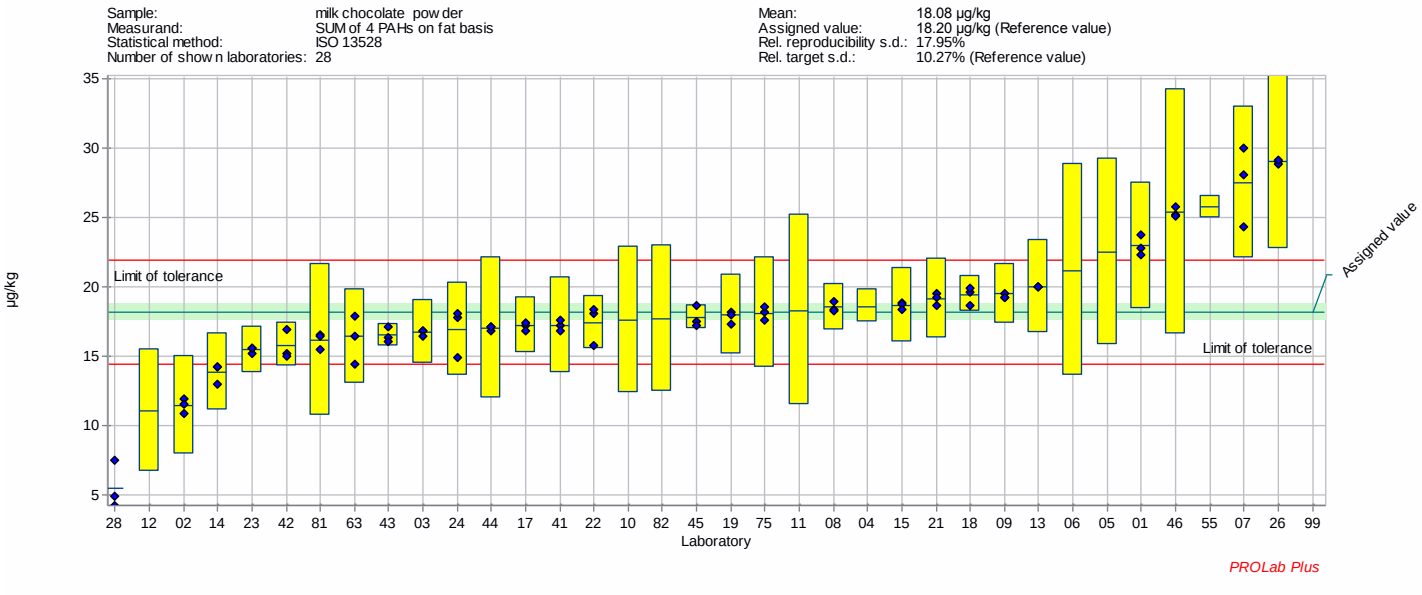
Results, as reported by the participants, for the content, expressed on fat basis, of chrysene (CHR) of the milk chocolate test sample.

Assigned value is 5.79 µg/kg. The uncertainty refers to the final value.

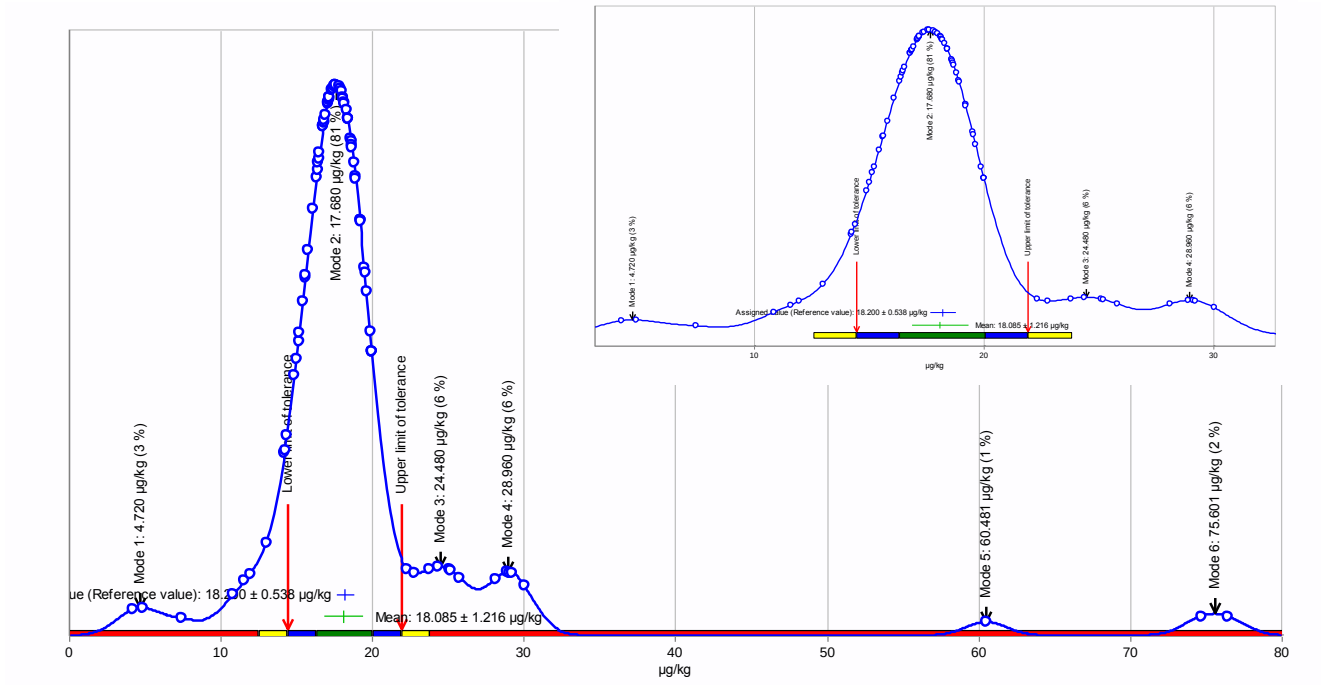
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	CHR_FAT	7.79	7.53	8.32	7.879	20	GC-MS/MS
2	CHR_FAT	4.03	3.85	3.34	3.737	28	HPLC-UV/FLD
3	CHR_FAT	5.08	5.43	5.04	5.18	5.2	GC-MS/MS
4	CHR_FAT				5.31	12.5	GC-MS
5	CHR_FAT				8.54	30	HPLC-FLD
6	CHR_FAT				6.3	22	GC-MS/MS
7	CHR_FAT	9.69	7.72	9.37	8.92	12	GC-MS
8	CHR_FAT	5.52	5.27	5.57	5.45	17	GC-MS
9	CHR_FAT	5.5	4.8	4.8	5.1	22	GC-MS
10	CHR_FAT	5.85	5.92	5.86	5.9	30	GC-MS
11	CHR_FAT	5.88	5.31	4.99	5.39	20	HPLC-FLD
12	CHR_FAT				3.69	25	GC-MS/MS
13	CHR_FAT	6.1	6.2	6.1	6.1	20	GC-HRMS
14	CHR_FAT	3.92	4.33	4.32	4.19	27.4	GC-MS/MS
15	CHR_FAT	4.69	4.82	4.61	4.71	25.2	HPLC-FLD
16	CHR_FAT						
17	CHR_FAT	5.1	5	5.3	5.1	19.29	GC-MS
18	CHR_FAT	5.55	5.89	5.96	5.82	11.8	HPLC-FLD
19	CHR_FAT	5.98	5.15	6.02	5.7	20	HPLC-FLD
20	CHR_FAT						
21	CHR_FAT	6.91	7.04	7.13	7.03	22	HPLC-FLD
22	CHR_FAT	4.81	5.62	5.69	5.37	5.9	
23	CHR_FAT	4.92	4.72	4.88	4.84	20.34	HPLC-FLD
24	CHR_FAT	4.65	4.79	4.18	4.54	20	HPLC-FLD
25	CHR_FAT						
26	CHR_FAT	12.32	12.21	12.2	12.24	20	HPLC-FLD
28	CHR_FAT	2.4	0.82	1.04	1.365		HPLC-UV/FLD
29	CHR_FAT						HPLC-FLD
31	CHR_FAT	4.17	4.18	4.38	4.246	6	GC-MS/MS
41	CHR_FAT	5.3	5.1	5.5	5.3	20	GC-MS/MS
42	CHR_FAT	4.95	4.4	4.51	4.61	9.1	GC-MS/MS
43	CHR_FAT	5.12	4.85	4.81	4.9	1.4	HPLC-FLD
44	CHR_FAT	4.55	4.56	4.49	4.53	22	HPLC-FLD
45	CHR_FAT	5.55	5.21	5.16	5.31	5.1	GC-MS
46	CHR_FAT	9.11	9.3	8.88	9.1	25	HPLC-FLD
55	CHR_FAT	11.91	11.29	12.4	11.87	2.4	GC-MS
63	CHR_FAT	6	4.4	6.1	6	29	GC-MS
75	CHR_FAT	5.5	5.5	5.5	5.5	22	GC-MS/MS
81	CHR_FAT	4.16	5.53	5.9	5.2	83	HPLC-FLD
82	CHR_FAT				4.6	32	
99	CHR_FAT	16.87	17.89	21.23	18.66	3.8	HPLC-FLD

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content, expressed on fat basis, of the milk chocolate test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the milk chocolate test sample



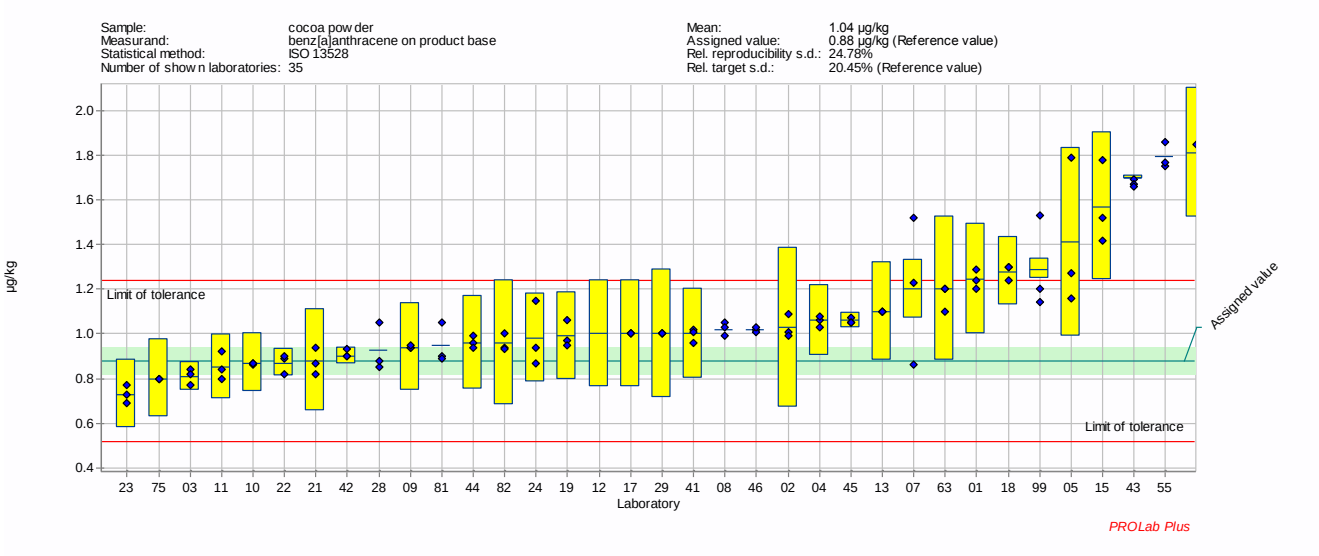
Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH), expressed on fat basis, of the milk chocolate test sample.

Assigned value is 18.2 µg/kg.

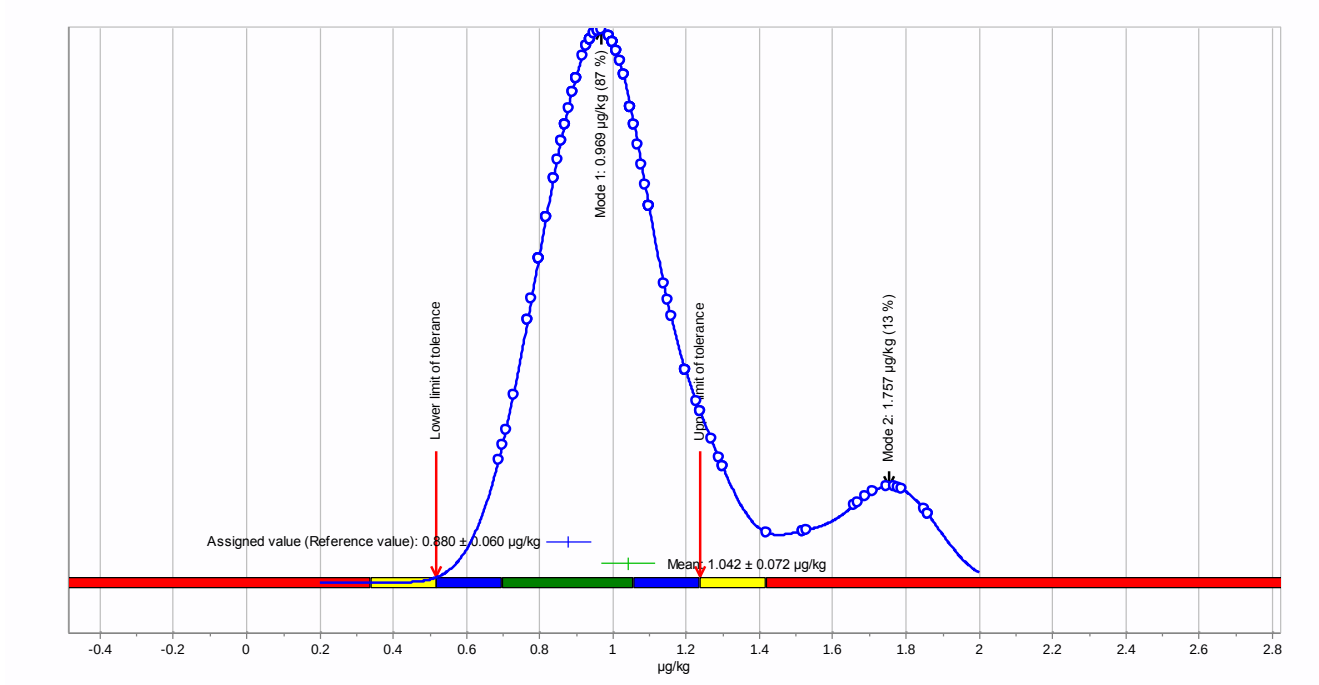
LCode	Measurant	Final value	Rel. exp. uncertainty,	Analytical technique
		µg/kg		
1	SUM_FAT	22.96	20	GC-MS/MS
2	SUM_FAT	11.461	31	HPLC-UV/FLD
3	SUM_FAT	16.71	13.9	GC-MS/MS
4	SUM_FAT	18.58	6.5	GC-MS
5	SUM_FAT	22.5	30	HPLC-FLD
6	SUM_FAT	21.2	36	GC-MS/MS
7	SUM_FAT	27.51	20	GC-MS
8	SUM_FAT	18.54	9	GC-MS
9	SUM_FAT	19.5	11	GC-MS
10	SUM_FAT	17.6	30	GC-MS
11	SUM_FAT	18.32	37.6	HPLC-FLD
12	SUM_FAT	11.07	40	GC-MS/MS
13	SUM_FAT	20	17	GC-HRMS
14	SUM_FAT	13.83	20.1	GC-MS/MS
15	SUM_FAT	18.7	14.4	HPLC-FLD
16	SUM_FAT			
17	SUM_FAT	17.2	11.76	
18	SUM_FAT	19.47	6.5	HPLC-FLD
19	SUM_FAT	18	16	HPLC-FLD
20	SUM_FAT			
21	SUM_FAT	19.14	15	HPLC-FLD
22	SUM_FAT	17.4	11.2	
23	SUM_FAT	15.46	11.05	HPLC-FLD
24	SUM_FAT	16.94	20	HPLC-FLD
25	SUM_FAT			
26	SUM_FAT	29.06	22	HPLC-FLD
28	SUM_FAT	5.475		HPLC-UV/FLD
29	SUM_FAT			HPLC-FLD
31	SUM_FAT		10	GC-MS/MS
41	SUM_FAT	17.2	20	GC-MS/MS
42	SUM_FAT	15.81	10.1	GC-MS/MS
43	SUM_FAT	16.5	4.9	HPLC-FLD
44	SUM_FAT	17.02	30	HPLC-FLD
45	SUM_FAT	17.79	5	GC-MS
46	SUM_FAT	25.4	35	HPLC-FLD
55	SUM_FAT	25.74	3.05	GC-MS
63	SUM_FAT	16.4	21	GC-MS
75	SUM_FAT	18.1	22	GC-MS/MS
81	SUM_FAT	16.16	33.7	HPLC-FLD
82	SUM_FAT	17.7	30	
99	SUM_FAT	70.55	29.9	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content, expressed on product basis, of the cocoa powder test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the cocoa powder test sample

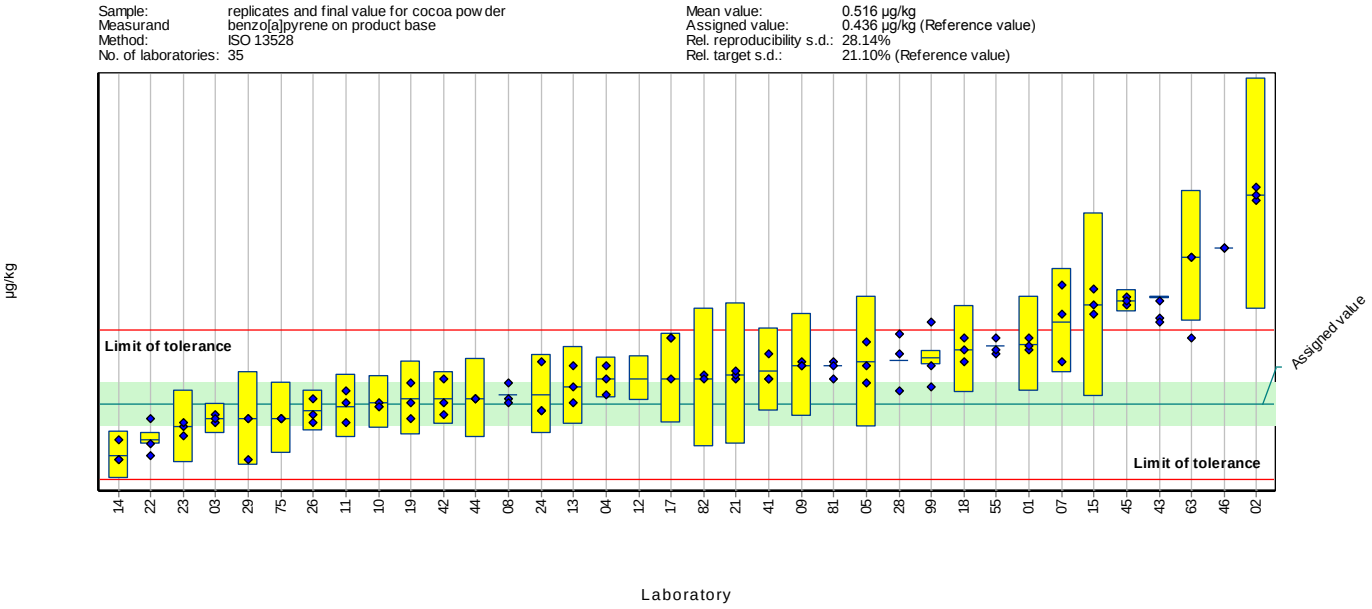


Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA), expressed on product basis, of the cocoa powder test sample
Assigned value is 0.88 µg/kg**.** The uncertainty refers to the "final value".

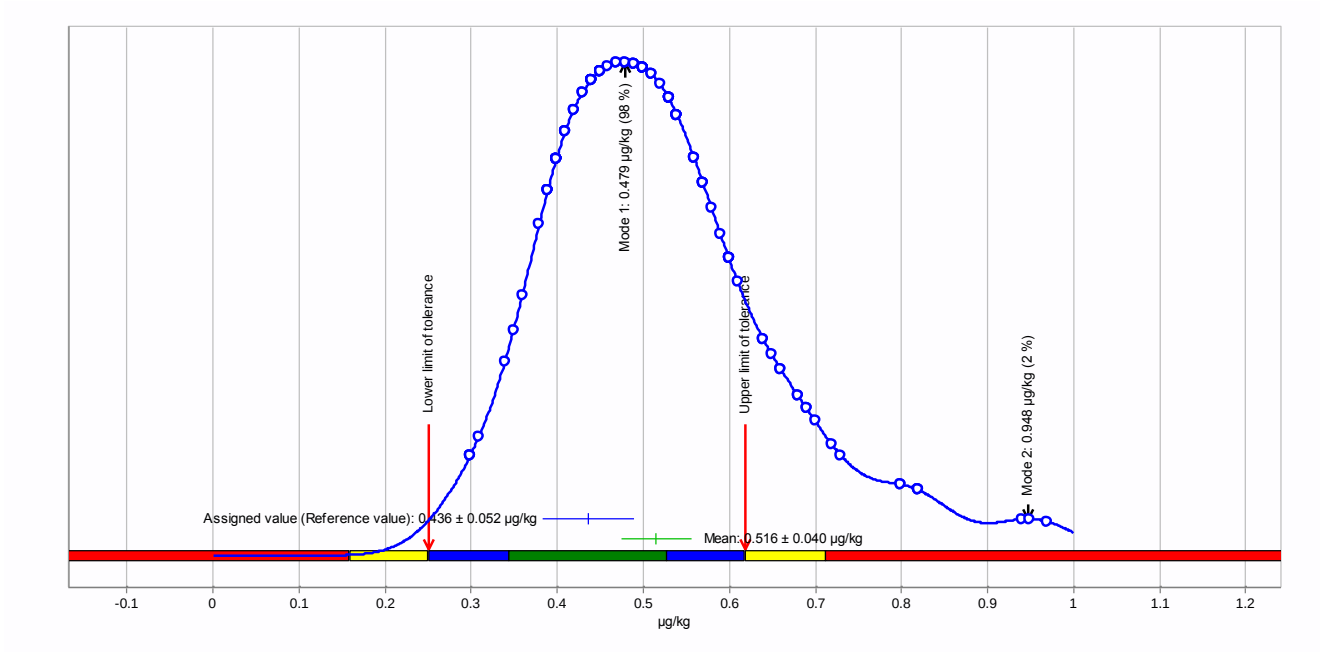
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	BAA	1.29	1.2	1.24	1.244	20	GC-MS/MS
2	BAA	1.01	1.09	0.99	1.028	35	HPLC-UV/FLD
3	BAA	0.84	0.77	0.82	0.81	8	GC-MS/MS
4	BAA	1.06	1.08	1.03	1.06	15	GC-MS
5	BAA	1.79	1.16	1.27	1.41	30	HPLC-FLD
6	BAA						GC-MS/MS
7	BAA	1.52	1.23	0.86	1.2	11	GC-MS
8	BAA	1.05	1.03	0.99	1.02		GC-MS
9	BAA	0.94	0.94	0.95	0.94	21	GC-MS
10	BAA	0.87	0.86	0.87	0.87	15	GC-MS
11	BAA	0.92	0.84	0.8	0.85	17	HPLC-FLD
12	BAA				1	24	GC-MS/MS
13	BAA	1.1	1.1	1.1	1.1	20	GC-HRMS
14	BAA	0.78	0.7	0.71	0.73	22.3	GC-MS/MS
15	BAA	1.78	1.52	1.42	1.57	21.2	HPLC-FLD
16	BAA						
17	BAA	1.0	1.0	1.0	1.0	23.9	GC-MS
18	BAA	1.3	1.24	1.3	1.28	11.8	HPLC-FLD
19	BAA	0.97	0.95	1.06	0.99	20	HPLC-FLD
20	BAA						
21	BAA	0.82	0.87	0.94	0.88	26	HPLC-FLD
22	BAA	0.89	0.82	0.9	0.87	7.3	GC-MS
23	BAA	0.77	0.73	0.69	0.73	21.15	HPLC-FLD
24	BAA	0.87	1.15	0.94	0.98	20.2	HPLC-FLD
25	BAA						
26	BAA	1.85	1.71	1.86	1.81	16	HPLC-FLD
28	BAA	0.85	0.88	1.05	0.928		HPLC-UV/FLD
29	BAA	1.0	1.0	1.0	1.0	29	HPLC-FLD
31	BAA	< 0.90	< 0.90	< 0.90		13	GC-MS/MS
41	BAA	1.02	1.01	0.96	1.0	20	GC-MS/MS
42	BAA	0.9	0.93	0.9	0.9	4.2	GC-MS/MS
43	BAA	1.69	1.67	1.66	1.7	0.5	HPLC-FLD
44	BAA	0.96	0.99	0.94	0.96	22	HPLC-FLD
45	BAA	1.07	1.05	1.05	1.06	3.4	GC-MS
46	BAA	1.02	1.01	1.03	1.02		HPLC-FLD
55	BAA	1.75	1.86	1.77	1.793		GC-MS
63	BAA	1.2	1.2	1.1	1.2	27	GC-MS
75	BAA	0.8	0.8	0.8	0.8	22	GC-MS/MS
81	BAA	1.05	0.9	0.89	0.95		HPLC-FLD
82	BAA	1	0.94	0.93	0.96	29	
99	BAA	1.14	1.2	1.53	1.29	3.5	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*a*] pyrene (BAP) content, expressed on product basis, of the cocoa powder test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the cocoa powder test sample

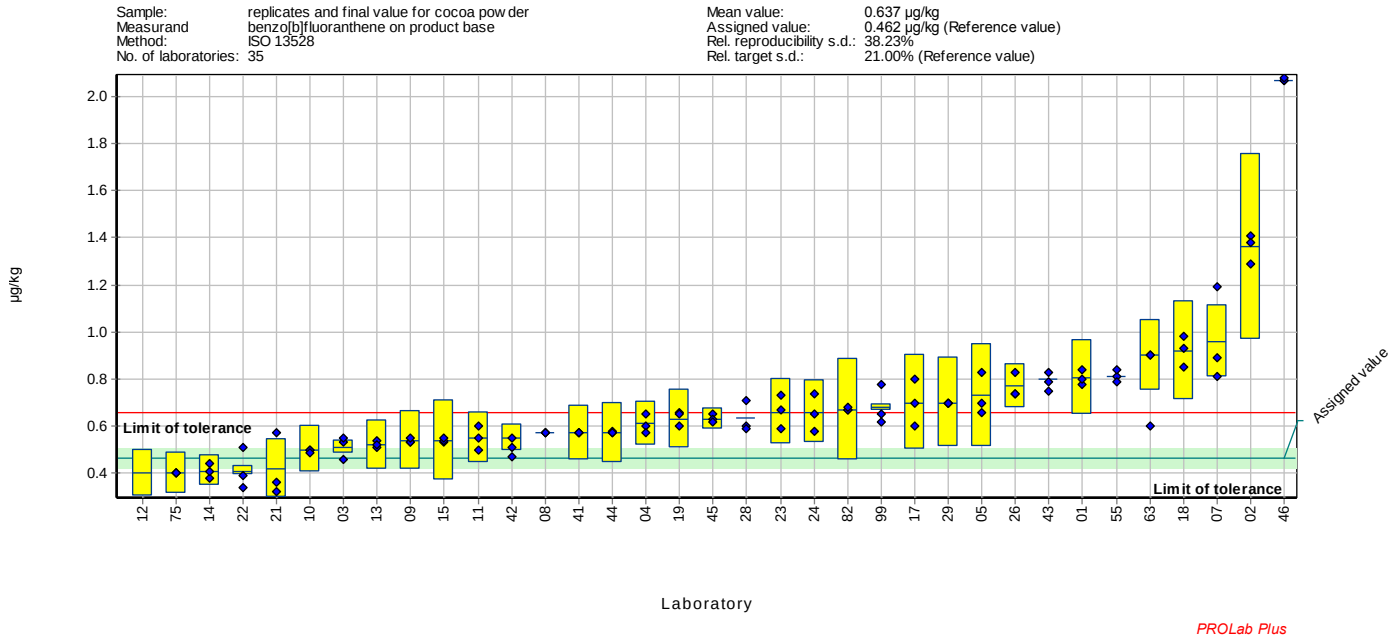


Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP), expressed on product basis, of the cocoa powder test sample
Assigned value is 0.44 µg/kg**.** The uncertainty refers to the final value.

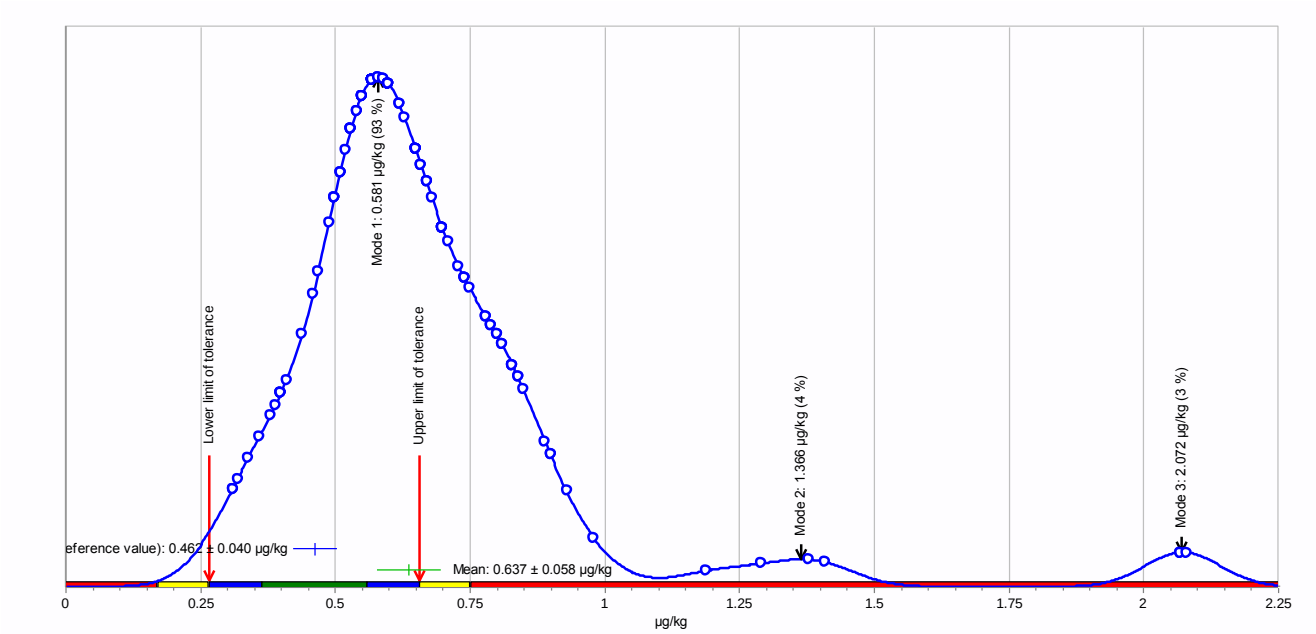
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	BAP	0.6	0.57	0.58	0.583	20	GC-MS/MS
2	BAP	0.97	0.94	0.95	0.953	30	HPLC-UV/FLD
3	BAP	0.39	0.41	0.4	0.4	9.2	GC-MS/MS
4	BAP	0.53	0.5	0.46	0.5	10	GC-MS
5	BAP	0.59	0.53	0.49	0.54	30	HPLC-FLD
6	BAP						GC-MS/MS
7	BAP	0.66	0.73	0.54	0.64	20	GC-MS
8	BAP	0.49	0.45	0.44	0.46		GC-MS
9	BAP	0.54	0.53	0.53	0.53	24	GC-MS
10	BAP	0.43	0.44	0.43	0.44	15	GC-MS
11	BAP	0.47	0.44	0.39	0.43	18	HPLC-FLD
12	BAP				0.5	11	GC-MS/MS
13	BAP	0.53	0.44	0.48	0.48	20	GC-HRMS
14	BAP	0.35	0.3	0.3	0.31	18.8	GC-MS/MS
15	BAP	0.66	0.72	0.68	0.68	33.4	HPLC-FLD
16	BAP						
17	BAP	0.6	0.6	0.5	0.5	22.17	GC-MS
18	BAP	0.57	0.6	0.54	0.57	18.8	HPLC-FLD
19	BAP	0.49	0.44	0.4	0.45	20	HPLC-FLD
20	BAP						
21	BAP	0.5	0.51	0.52	0.51	34	HPLC-FLD
22	BAP	0.4	0.31	0.34	0.35	4.1	GC-MS
23	BAP	0.38	0.39	0.36	0.38	23.99	HPLC-FLD
24	BAP	0.42	0.54	0.42	0.46	21	HPLC-FLD
25	BAP						
26	BAP	0.45	0.41	0.39	0.42	12	HPLC-FLD
28	BAP	0.56	0.47	0.61	0.544	0.096	HPLC-UV/FLD
29	BAP	0.3	0.4	0.4	0.4	29	HPLC-FLD
31	BAP	< 0.90	< 0.90	< 0.90		12	GC-MS/MS
41	BAP	0.5	0.56	0.5	0.52	20	GC-MS/MS
42	BAP	0.5	0.44	0.41	0.45	14.5	GC-MS/MS
43	BAP	0.65	0.64	0.69	0.7	0.2	HPLC-FLD
44	BAP	0.45	0.45	0.45	0.45	22	HPLC-FLD
45	BAP	0.68	0.7	0.69	0.69	3.9	GC-MS
46	BAP	0.82	0.82	0.82	0.822		HPLC-FLD
55	BAP	0.56	0.6	0.57	0.58		GC-MS
63	BAP	0.6	0.8	0.8	0.8	20	GC-MS
75	BAP	0.4	0.4	0.4	0.4	22	GC-MS/MS
81	BAP	0.54	0.5	0.53	0.53		HPLC-FLD
82	BAP	0.51	0.5	< 0.50	0.5	34	
99	BAP	0.64	0.53	0.48	0.55	3.3	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content, expressed on product basis, of the cocoa powder test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the cocoa powder test sample

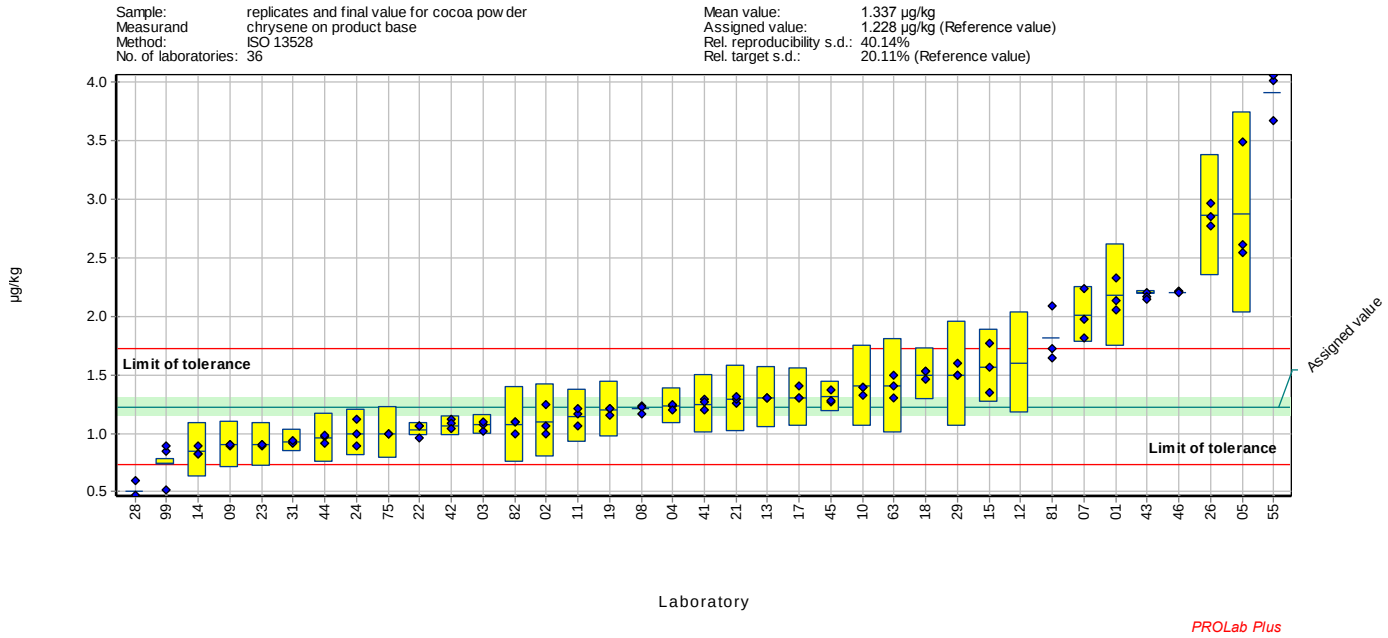


Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF), expressed on product basis, of the cocoa powder test sample
Assigned value is 0.46 µg/kg. The uncertainty refers to the final value.

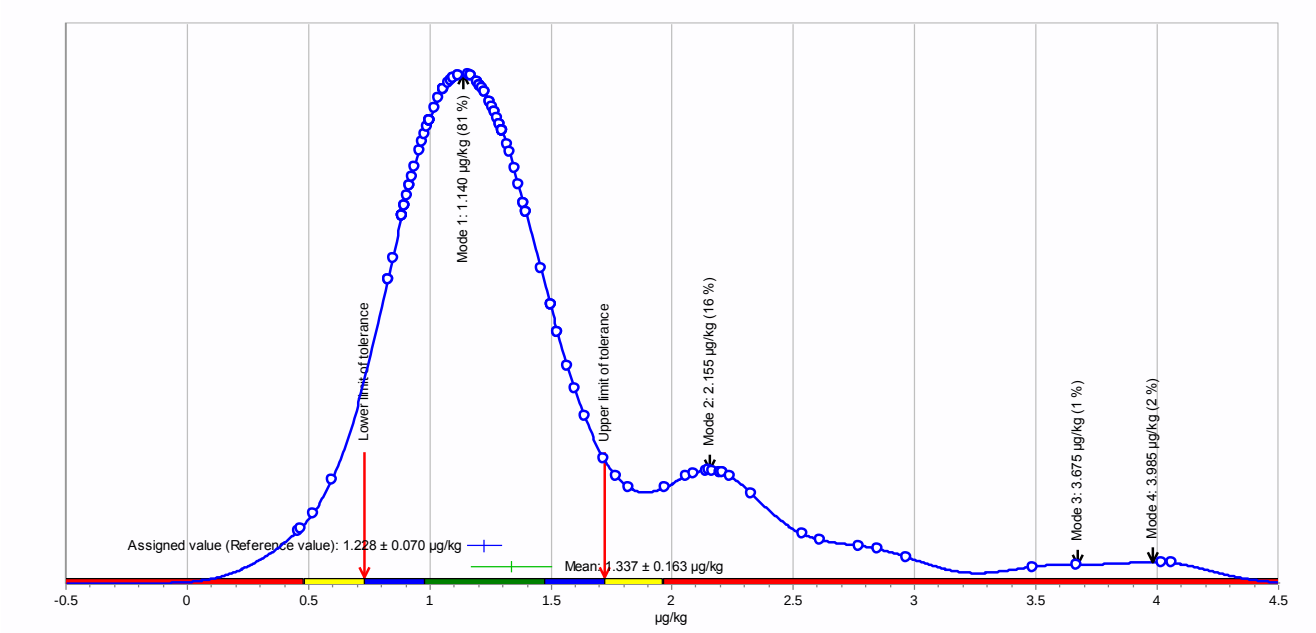
LCode	Measurant	Rep 1	Rep 2	Rep 3	Final value, µg/kg	Uncertainty, %	Analytical technique
1	BBF	0.84	0.78	0.8	0.806	20	GC-MS/MS
2	BBF	1.29	1.41	1.38	1.362	29	HPLC-UV/FLD
3	BBF	0.53	0.46	0.55	0.51	5.8	GC-MS/MS
4	BBF	0.65	0.6	0.57	0.61	15	GC-MS
5	BBF	0.83	0.7	0.66	0.73	30	HPLC-FLD
6	BBF						GC-MS/MS
7	BBF	1.19	0.89	0.81	0.96	16	GC-MS
8	BBF	0.57	0.57	0.57	0.57		GC-MS
9	BBF	0.53	0.53	0.55	0.54	23	GC-MS
10	BBF	0.5	0.5	0.49	0.5	20	GC-MS
11	BBF	0.6	0.55	0.5	0.55	20	HPLC-FLD
12	BBF				0.4	25	GC-MS/MS
13	BBF	0.54	0.51	0.52	0.52	20	GC-HRMS
14	BBF	0.44	0.38	0.41	0.41	16.5	GC-MS/MS
15	BBF	0.53	0.54	0.55	0.54	31.4	HPLC-FLD
16	BBF						
17	BBF	0.6	0.7	0.8	0.7	29.08	GC-MS
18	BBF	0.93	0.98	0.85	0.92	22.8	HPLC-FLD
19	BBF	0.6	0.66	0.65	0.63	20	HPLC-FLD
20	BBF						
21	BBF	0.36	0.32	0.57	0.42	30	HPLC-FLD
22	BBF	0.51	0.34	0.39	0.41	4.5	GC-MS
23	BBF	0.73	0.59	0.67	0.66	21.37	HPLC-FLD
24	BBF	0.74	0.65	0.58	0.66	20.5	HPLC-FLD
25	BBF						
26	BBF	0.74	0.74	0.83	0.77	12	HPLC-FLD
28	BBF	0.6	0.59	0.71	0.633		HPLC-UV/FLD
29	BBF	0.7	0.7	0.7	0.7	27	HPLC-FLD
31	BBF	< 0.90	< 0.90	< 0.90		17	GC-MS/MS
41	BBF	0.57	0.57	0.57	0.57	20	GC-MS/MS
42	BBF	0.55	0.51	0.47	0.55	10.4	GC-MS/MS
43	BBF	0.75	0.79	0.83	0.8	0.2	HPLC-FLD
44	BBF	0.57	0.58	0.57	0.57	22	HPLC-FLD
45	BBF	0.65	0.63	0.62	0.63	7.1	GC-MS
46	BBF	2.07	2.07	2.08	2.07		HPLC-FLD
55	BBF	0.81	0.84	0.79	0.813		GC-MS
63	BBF	0.6	0.9	0.9	0.9	17	GC-MS
75	BBF	0.4	0.4	0.4	0.4	22	GC-MS/MS
81	BBF	0.31	0.4	0.31	0.34		HPLC-FLD
82	BBF	0.67	0.67	0.68	0.67	32	
99	BBF	0.65	0.78	0.62	0.68	2	HPLC-FLD

Distribution of individual results of replicate determinations reported for the chrysene (CHR) content, expressed on product basis, of the cocoa powder test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the cocoa powder test sample



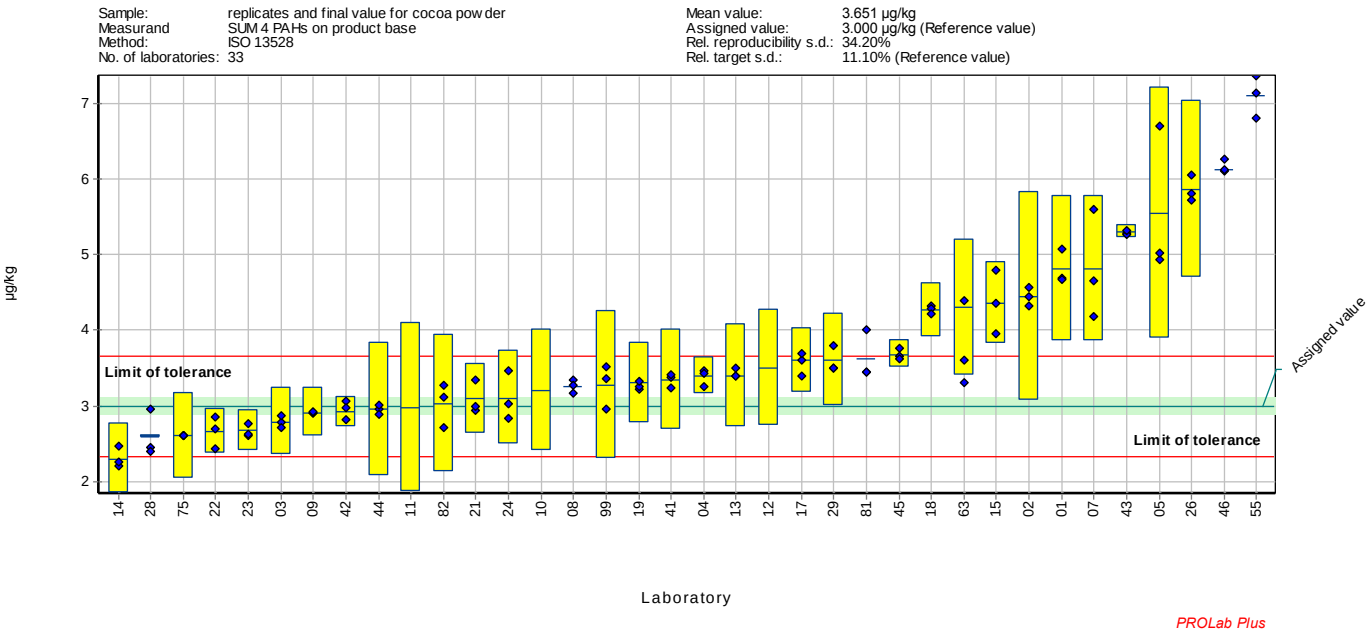
Results, as reported by the participants, for the content of chrysene (CHR), expressed on product basis, of the cocoa powder test sample

Assigned value is 1.23 µg/kg. The uncertainty refers to the final value.

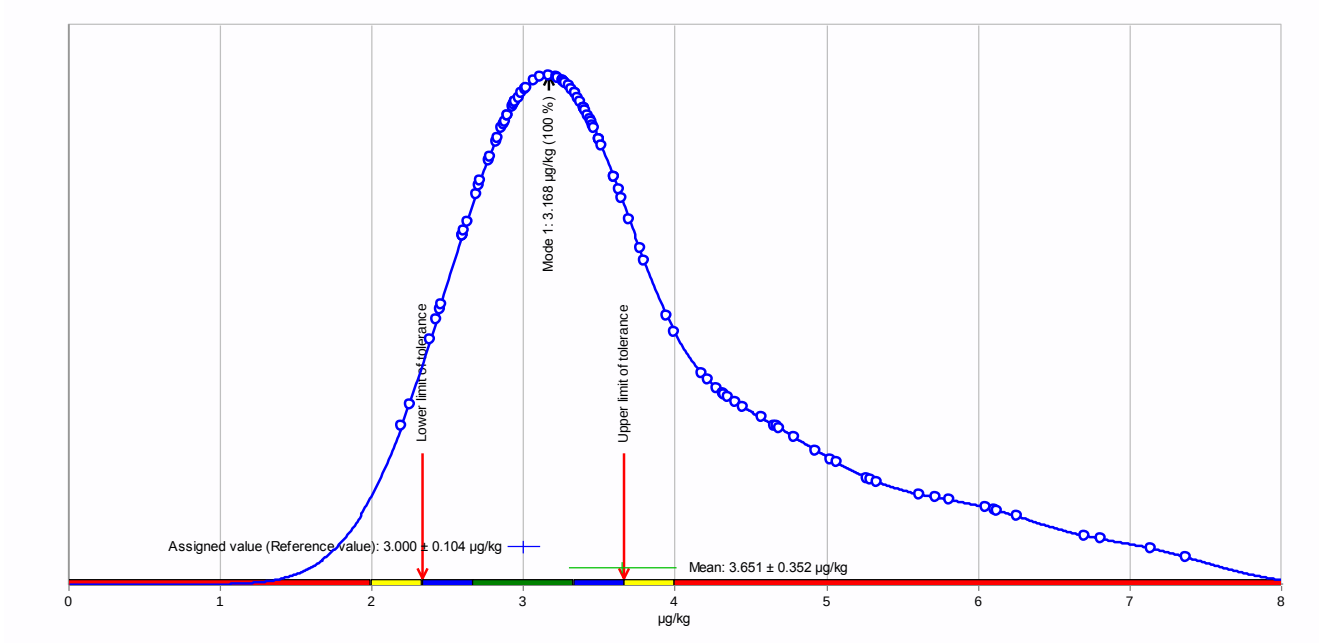
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	CHR	2.33	2.14	2.06	2.176	20	GC-MS/MS
2	CHR	1.06	1	1.25	1.103	28	HPLC-UV/FLD
3	CHR	1.02	1.08	1.1	1.07	8.4	GC-MS/MS
4	CHR	1.23	1.25	1.2	1.23	12.5	GC-MS
5	CHR	3.49	2.54	2.61	2.88	30	HPLC-FLD
6	CHR						GC-MS/MS
7	CHR	2.24	1.82	1.97	2.01	12	GC-MS
8	CHR	1.23	1.22	1.17	1.21		GC-MS
9	CHR	0.89	0.9	0.9	0.9	22	GC-MS
10	CHR	1.39	1.33	1.39	1.4	25	GC-MS
11	CHR	1.17	1.21	1.06	1.14	20	HPLC-FLD
12	CHR				1.6	27	GC-MS/MS
13	CHR	1.3	1.3	1.3	1.3	20	GC-HRMS
14	CHR	0.89	0.83	0.83	0.85	27.4	GC-MS/MS
15	CHR	1.77	1.57	1.35	1.57	19.7	HPLC-FLD
16	CHR						
17	CHR	1.3	1.3	1.4	1.3	19.29	GC-MS
18	CHR	1.53	1.46	1.53	1.5	14.6	HPLC-FLD
19	CHR	1.16	1.21	1.21	1.2	20	HPLC-FLD
20	CHR						
21	CHR	1.26	1.29	1.32	1.29	22	HPLC-FLD
22	CHR	1.06	0.96	1.06	1.03	5.9	GC-MS
23	CHR	0.89	0.9	0.91	0.9	20.76	GC-MS
24	CHR	0.99	1.12	0.89	1	20.2	HPLC-FLD
25	CHR						
26	CHR	2.77	2.85	2.97	2.86	18	HPLC-FLD
28	CHR	0.46	0.47	0.6	0.508		HPLC-UV/FLD
29	CHR	1.5	1.6	1.5	1.5	30	HPLC-FLD
31	CHR	0.93	0.92	0.94	0.932	10	GC-MS/MS
41	CHR	1.29	1.27	1.2	1.25	20	GC-MS/MS
42	CHR	1.12	1.09	1.04	1.06	8.1	GC-MS/MS
43	CHR	2.2	2.17	2.15	2.2	0.7	HPLC-FLD
44	CHR	0.97	0.98	0.92	0.96	22	HPLC-FLD
45	CHR	1.37	1.27	1.28	1.31	10	GC-MS
46	CHR	2.21	2.21	2.2	2.2		HPLC-FLD
55	CHR	4.02	4.06	3.67	3.917		GC-MS
63	CHR	1.4	1.5	1.3	1.4	29	GC-MS
75	CHR	1	1	1	1	22	GC-MS/MS
81	CHR	2.09	1.64	1.72	1.82		HPLC-FLD
82	CHR	1.1	1	1.1	1.07	30	
99	CHR	0.52	0.85	0.89	0.75	3.8	HPLC-FLD

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content, expressed on product basis, of the cocoa powder test sample

blue triangles: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on product basis, of the cocoa powder test sample

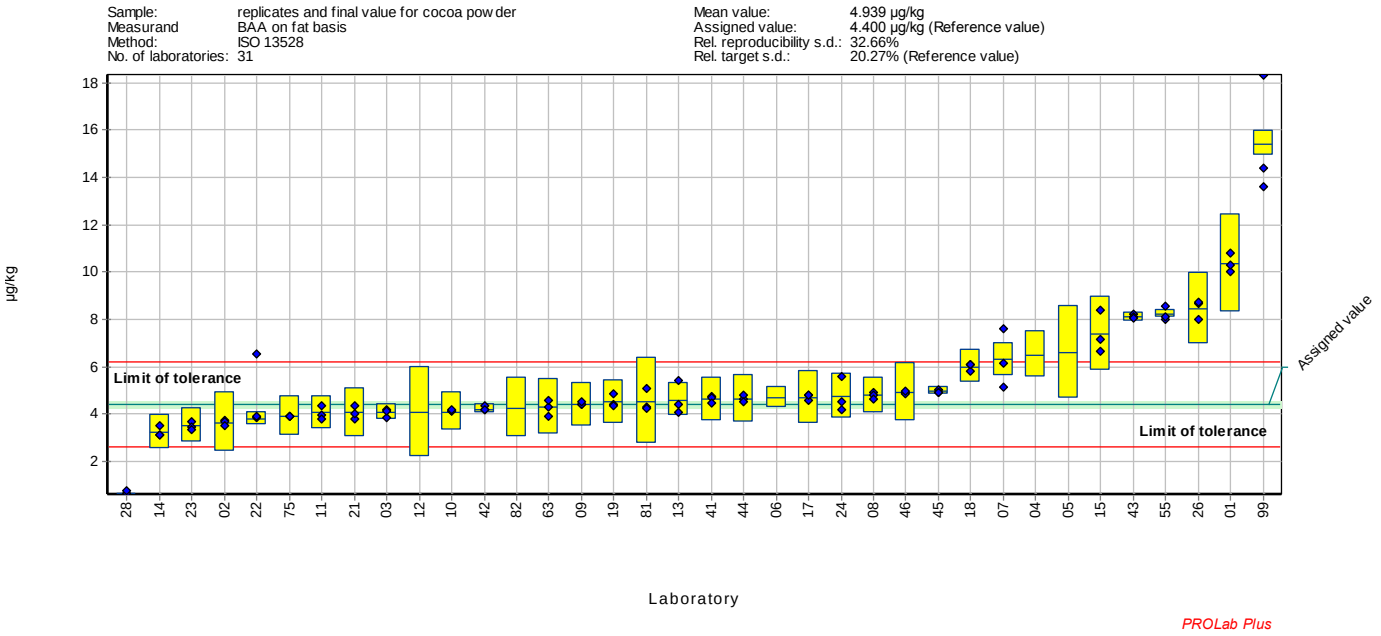


Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH), expressed on product basis, of the cocoa powder test sample
Assigned value is 3.00 µg/kg.

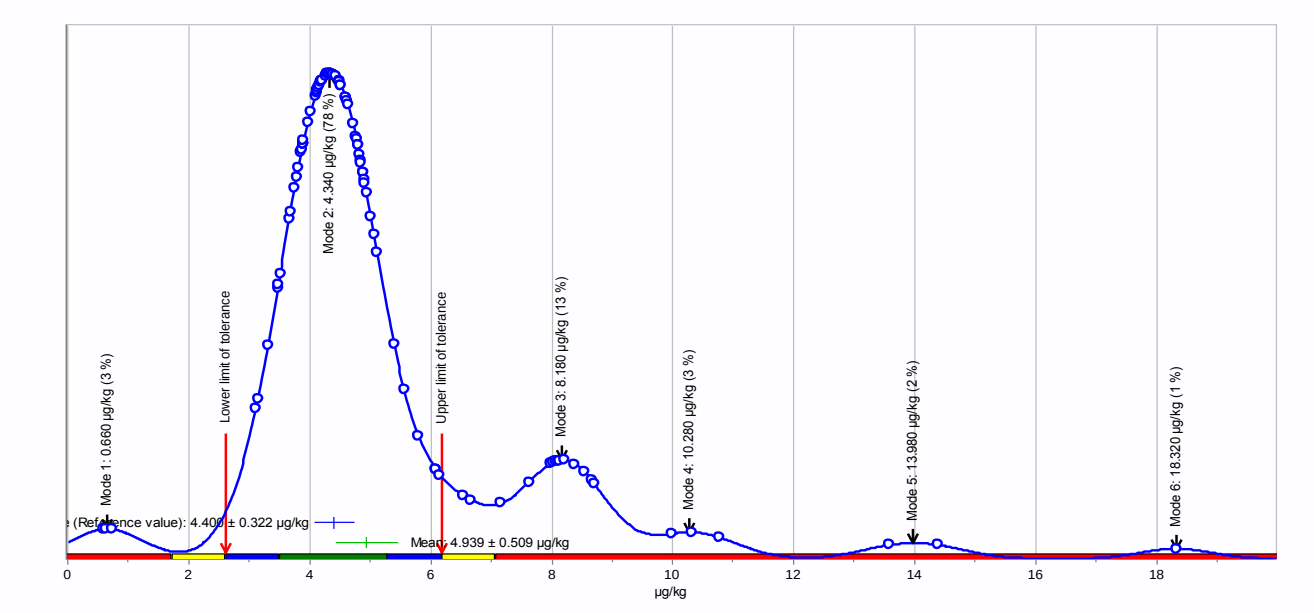
LCode	Measurant	Final value, µg/kg	Uncertainty, %	Analytical technique
1	SUM4PAHS	4.81	20	GC-MS/MS
2	SUM4PAHS	4.445	31	HPLC-UV/FLD
3	SUM4PAHS	2.79	15.9	GC-MS/MS
4	SUM4PAHS	3.39	7.2	GC-MS
5	SUM4PAHS	5.55	30	HPLC-FLD
6	SUM4PAHS			GC-MS/MS
7	SUM4PAHS	4.82	20	GC-MS
8	SUM4PAHS	3.26		GC-MS
9	SUM4PAHS	2.91	11	GC-MS
10	SUM4PAHS	3.2	25	GC-MS
11	SUM4PAHS	2.98	37.6	HPLC-FLD
12	SUM4PAHS	3.5	22	GC-MS/MS
13	SUM4PAHS	3.4	20	GC-HRMS
14	SUM4PAHS	2.3	20.1	GC-MS/MS
15	SUM4PAHS	4.36	12.4	HPLC-FLD
16	SUM4PAHS			
17	SUM4PAHS	3.6	11.85	
18	SUM4PAHS	4.27	8.4	HPLC-FLD
19	SUM4PAHS	3.3	16	HPLC-FLD
20	SUM4PAHS			
21	SUM4PAHS	3.09	15	HPLC-FLD
22	SUM4PAHS	2.66	11.2	
23	SUM4PAHS	2.67	10.37	HPLC-FLD
24	SUM4PAHS	3.1	20	HPLC-FLD
25	SUM4PAHS			
26	SUM4PAHS	5.86	20	HPLC-FLD
28	SUM4PAHS	2.595	0.74	HPLC-UV/FLD
29	SUM4PAHS	3.6	17	HPLC-FLD
31	SUM4PAHS			GC-MS/MS
41	SUM4PAHS	3.34	20	GC-MS/MS
42	SUM4PAHS	2.92	6.9	GC-MS/MS
43	SUM4PAHS	5.3	1.6	HPLC-FLD
44	SUM4PAHS	2.95	30	HPLC-FLD
45	SUM4PAHS	3.68	5	GC-MS
46	SUM4PAHS	6.12		HPLC-FLD
55	SUM4PAHS	7.11		GC-MS
63	SUM4PAHS	4.3	21	GC-MS
75	SUM4PAHS	2.6	22	GC-MS/MS
81	SUM4PAHS	3.63		HPLC-FLD
82	SUM4PAHS	3.03	30	GC-MS
99	SUM4PAHS	3.27	29.9	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content, expressed on fat basis, of the powder test sample

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



Kernel density plot of the reported values for proficiency assessment for the benz[*a*]anthracene (BAA) content, expressed on fat basis, of the cocoa powder test sample

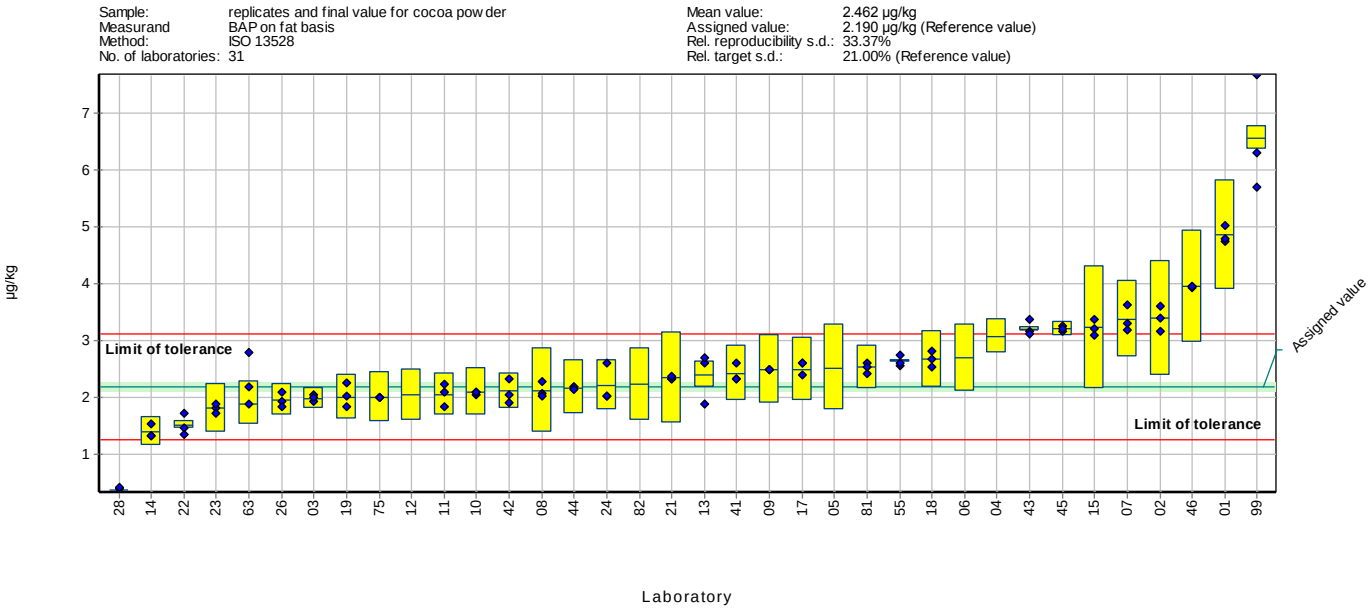


Results, as reported by the participants, for the content of benz[*a*]anthracene (BAA) , expressed on fat basis, of the cocoa powder test sample expressed on fat base.
Assigned value is 4.40 µg/kg**.** The uncertainty refers to the "final value".

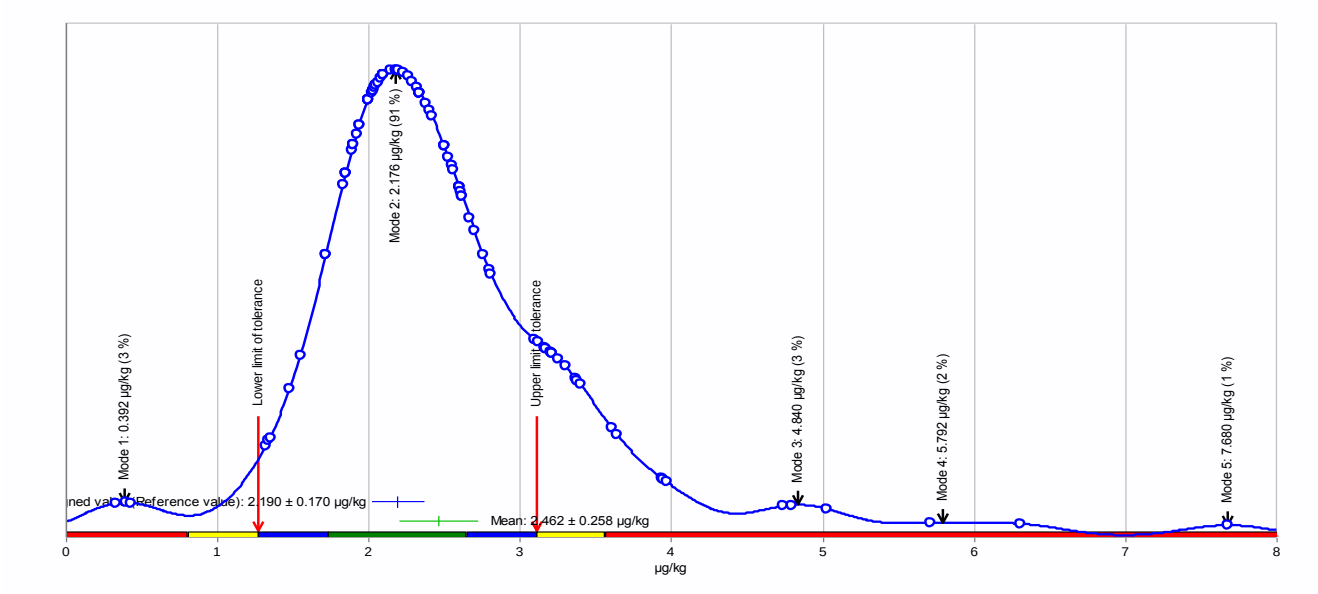
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BAA_FAT	10.78	10	10.31	10.364	20	GC-MS/MS
2	BAA_FAT	3.76	3.67	3.52	3.649	35	HPLC-UV/FLD
3	BAA_FAT	4.2	3.88	4.13	4.07	8.2	GC-MS/MS
4	BAA_FAT				6.5	15	GC-MS
5	BAA_FAT				6.59	30	HPLC-FLD
6	BAA_FAT				4.7	10	GC-MS/MS
7	BAA_FAT	7.63	6.16	5.12	6.3	11	GC-MS
8	BAA_FAT	4.91	4.83	4.64	4.79	16	GC-MS
9	BAA_FAT	4.4	4.4	4.5	4.4	21	GC-MS
10	BAA_FAT	4.15	4.12	4.17	4.1	20	GC-MS
11	BAA_FAT	4.36	3.98	3.82	4.05	17	HPLC-FLD
12	BAA_FAT				4.08	47	GC-MS/MS
13	BAA_FAT	5.4	4.1	4.4	4.6	15	GC-HRMS
14	BAA_FAT	3.49	3.12	3.15	3.25	22.3	GC-MS/MS
15	BAA_FAT	8.39	7.17	6.67	7.41	21.2	HPLC-FLD
16	BAA_FAT						
17	BAA_FAT	4.6	4.8	4.8	4.7	23.9	GC-MS
18	BAA_FAT	6.09	5.81	6.09	6	11.8	HPLC-FLD
19	BAA_FAT	4.44	4.35	4.85	4.5	20	HPLC-FLD
20	BAA_FAT						
21	BAA_FAT	3.79	4.02	4.33	4.05	26	HPLC-FLD
22	BAA_FAT	3.87	6.54	3.91	3.78	7.3	
23	BAA_FAT	3.69	3.48	3.32	3.5	21.15	HPLC-FLD
24	BAA_FAT	4.21	5.57	4.53	4.77	20	HPLC-FLD
25	BAA_FAT						
26	BAA_FAT	8.66	7.99	8.71	8.46	18	HPLC-FLD
28	BAA_FAT	0.6	0.63	0.75	0.661		HPLC-UV/FLD
29	BAA_FAT						HPLC-FLD
31	BAA_FAT	< 4.31	< 4.31	< 4.31		13	GC-MS/MS
41	BAA_FAT	4.77	4.72	4.49	4.63	20	GC-MS/MS
42	BAA_FAT	4.21	4.35	4.21	4.21	4.2	GC-MS/MS
43	BAA_FAT	8.22	8.13	8.08	8.1	2.5	HPLC-FLD
44	BAA_FAT	4.62	4.78	4.53	4.64	22	HPLC-FLD
45	BAA_FAT	5.02	4.92	4.89	4.95	3.4	GC-MS
46	BAA_FAT	4.89	4.86	4.95	4.9	25	HPLC-FLD
55	BAA_FAT	8.03	8.55	8.12	8.23	1.8	GC-MS
63	BAA_FAT	3.9	4.3	4.6	4.3	27	GC-MS
75	BAA_FAT	3.9	3.9	3.9	3.9	22	GC-MS/MS
81	BAA_FAT	5.07	4.32	4.27	4.55	40	HPLC-FLD
82	BAA_FAT				4.27	30	
99	BAA_FAT	13.59	14.39	18.32	15.43	3.5	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*a*] pyrene (BAP) content, expressed on fat basis, of the cocoa powder test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the cocoa powder test sample



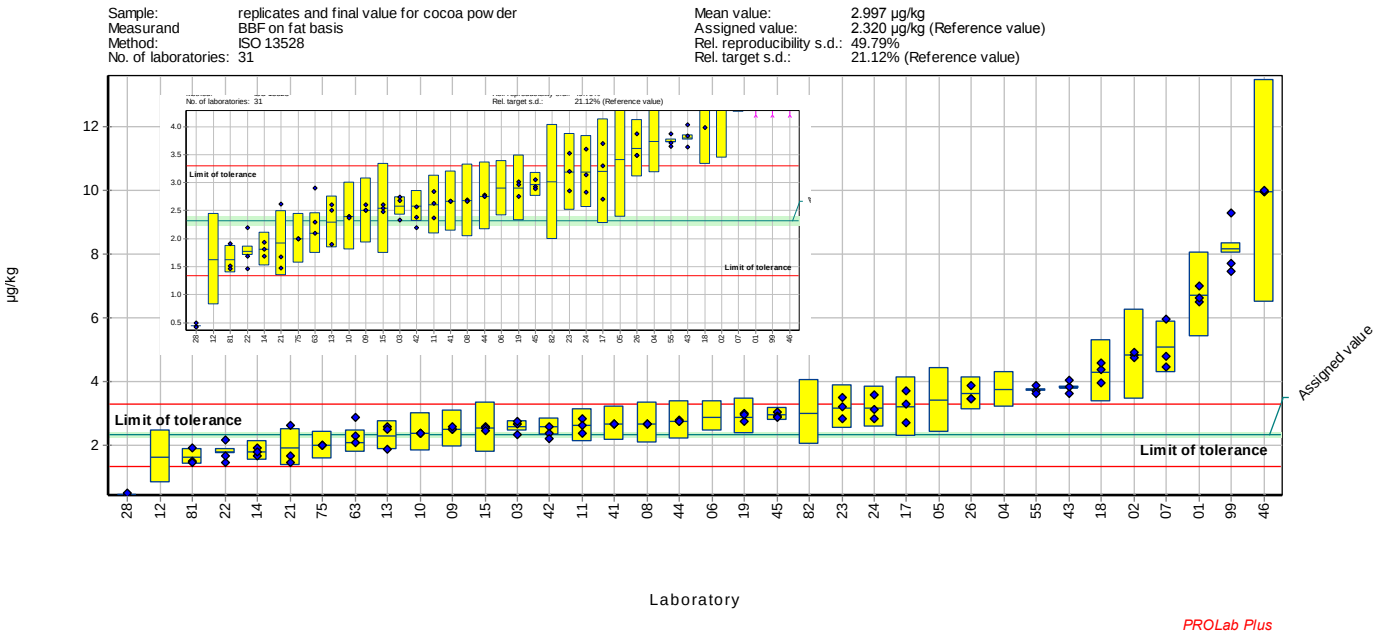
Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP), expressed on fat basis, of the cocoa powder test sample

Assigned value is 2.19µg/kg**.** The uncertainty refers to the final value.

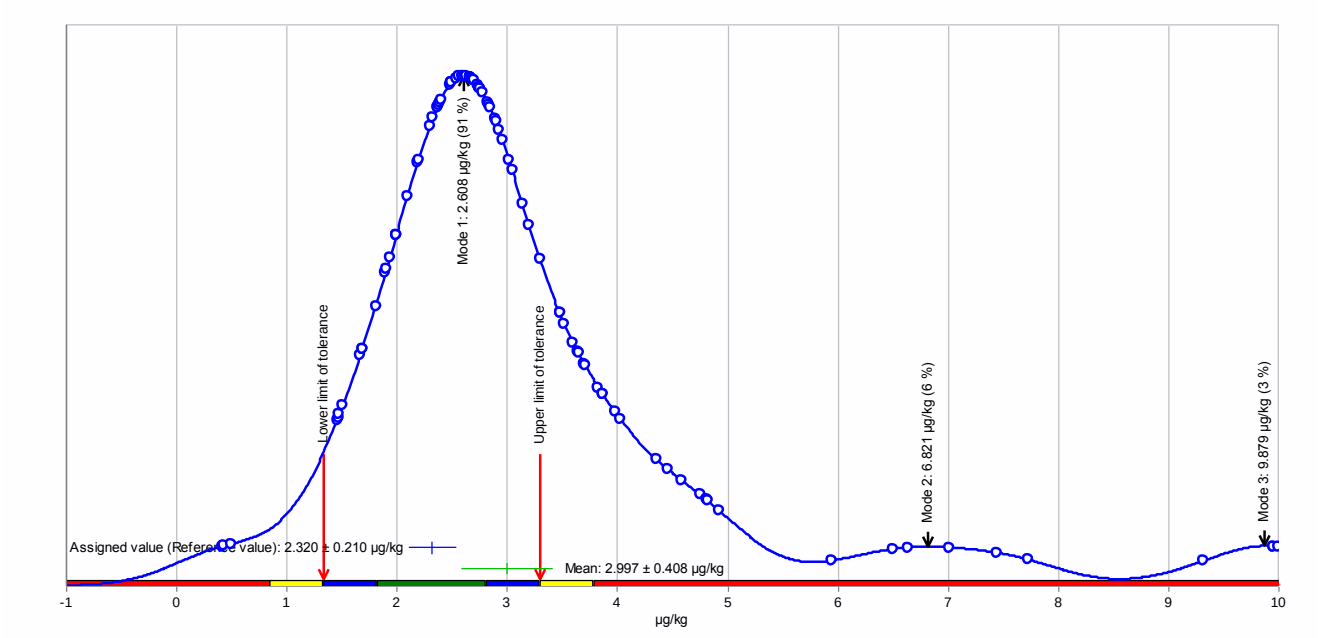
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BAP_FAT	5.03	4.74	4.8	4.856	20	GC-MS/MS
2	BAP_FAT	3.61	3.17	3.4	3.39	30	HPLC-UV/FLD
3	BAP_FAT	1.94	2.04	2	1.99	9.4	GC-MS/MS
4	BAP_FAT				3.07	10	GC-MS
5	BAP_FAT				2.52	30	HPLC-FLD
6	BAP_FAT				2.7	22	GC-MS/MS
7	BAP_FAT	3.3	3.64	3.2	3.38	20	GC-MS
8	BAP_FAT	2.29	2.08	2.03	2.13	35	GC-MS
9	BAP_FAT	2.5	2.5	2.5	2.5	24	GC-MS
10	BAP_FAT	2.05	2.1	2.1	2.1	20	GC-MS
11	BAP_FAT	2.23	2.1	1.85	2.06	18	HPLC-FLD
12	BAP_FAT				2.04	22	GC-MS/MS
13	BAP_FAT	2.6	1.9	2.7	2.4	10	GC-HRMS
14	BAP_FAT	1.55	1.32	1.34	1.4	18.8	GC-MS/MS
15	BAP_FAT	3.21	3.38	3.1	3.23	33.4	HPLC-FLD
16	BAP_FAT						
17	BAP_FAT	2.6	2.6	2.4	2.5	22.17	GC-MS
18	BAP_FAT	2.67	2.81	2.53	2.67	18.8	HPLC-FLD
19	BAP_FAT	2.26	2.03	1.85	2	20	HPLC-FLD
20	BAP_FAT						
21	BAP_FAT	2.32	2.34	2.38	2.35	34	HPLC-FLD
22	BAP_FAT	1.72	1.35	1.48	1.52	4.1	
23	BAP_FAT	1.83	1.89	1.72	1.81	23.99	HPLC-FLD
24	BAP_FAT	2.03	2.61	2.02	2.22	20	HPLC-FLD
25	BAP_FAT						
26	BAP_FAT	2.1	1.94	1.85	1.96	14	HPLC-FLD
28	BAP_FAT	0.4	0.33	0.43	0.388		HPLC-UV/FLD
29	BAP_FAT						HPLC-FLD
31	BAP_FAT	< 4.31	< 4.31	< 4.31		13	GC-MS/MS
41	BAP_FAT	2.34	2.62	2.34	2.43	20	GC-MS/MS
42	BAP_FAT	2.34	2.06	1.92	2.11	14.5	GC-MS/MS
43	BAP_FAT	3.17	3.12	3.37	3.2	1	HPLC-FLD
44	BAP_FAT	2.18	2.19	2.15	2.17	22	HPLC-FLD
45	BAP_FAT	3.16	3.25	3.21	3.21	3.9	GC-MS
46	BAP_FAT	3.97	3.94	3.95	3.95	25	HPLC-FLD
55	BAP_FAT	2.56	2.76	2.62	2.65	0.6	GC-MS
63	BAP_FAT	2.2	1.9	2.8	1.9	20	GC-MS
75	BAP_FAT	2	2	2	2	22	GC-MS/MS
81	BAP_FAT	2.6	2.42	2.55	2.53	15	HPLC-FLD
82	BAP_FAT				2.23	29	
99	BAP_FAT	7.68	6.31	5.71	6.56	3.3	HPLC-FLD

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content, expressed on fat basis, of the cocoa powder test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the cocoa powder test sample

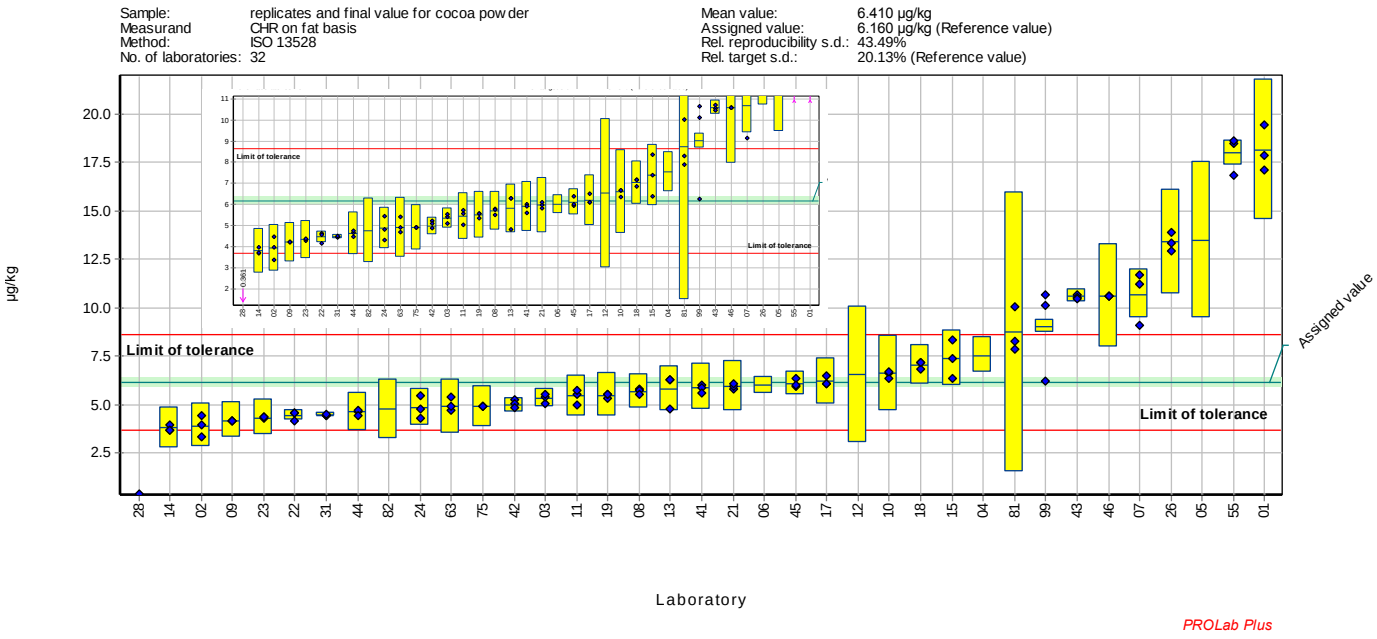


Results, as reported by the participants, for the content of benzo[*b*]fluoranthene (BBF), expressed on fat basis, of the cocoa powder test sample
Assigned value is 2.32 µg/kg. The uncertainty refers to the final value.

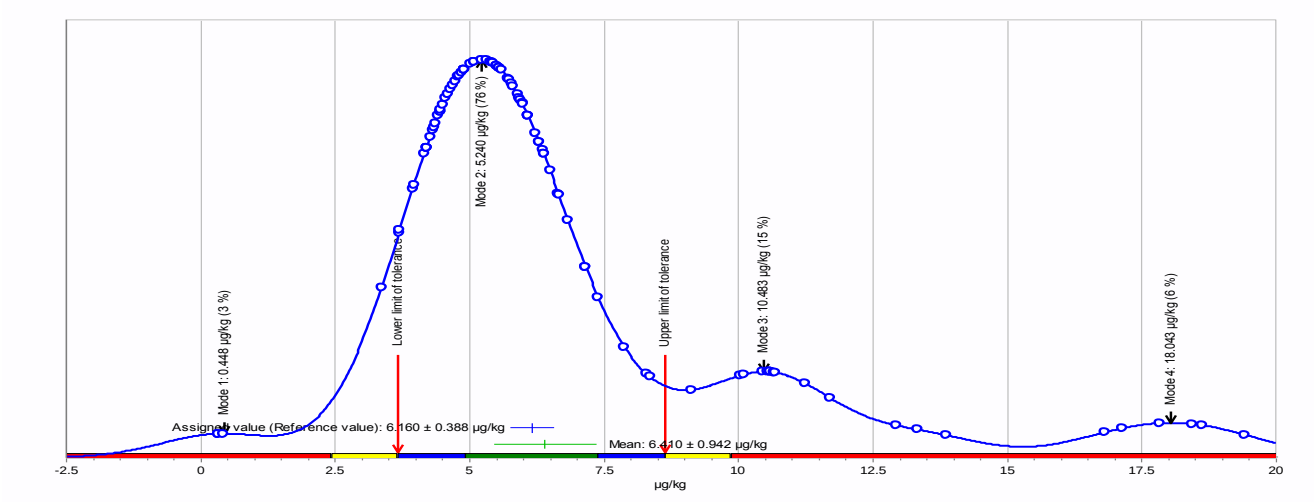
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	BBF_FAT	7.02	6.5	6.64	6.719	20	GC-MS/MS
2	BBF_FAT	4.82	4.75	4.93	4.834	29	HPLC-UV/FLD
3	BBF_FAT	2.68	2.33	2.74	2.58	6.2	GC-MS/MS
4	BBF_FAT				3.74	15	GC-MS
5	BBF_FAT				3.41	30	HPLC-FLD
6	BBF_FAT				2.9	17	GC-MS/MS
7	BBF_FAT	5.95	4.46	4.81	5.07	16	GC-MS
8	BBF_FAT	2.69	2.67	2.67	2.68	24	GC-MS
9	BBF_FAT	2.5	2.5	2.6	2.5	23	GC-MS
10	BBF_FAT	2.4	2.39	2.37	2.4	25	GC-MS
11	BBF_FAT	2.84	2.63	2.37	2.61	20	HPLC-FLD
12	BBF_FAT				1.63	50	GC-MS/MS
13	BBF_FAT	2.6	1.9	2.5	2.3	20	GC-HRMS
14	BBF_FAT	1.94	1.69	1.81	1.81	16.5	GC-MS/MS
15	BBF_FAT	2.6	2.54	2.48	2.54	31.4	HPLC-FLD
16	BBF_FAT						
17	BBF_FAT	2.7	3.3	3.7	3.2	29.08	GC-MS
18	BBF_FAT	4.36	4.59	3.98	4.31	22.8	HPLC-FLD
19	BBF_FAT	2.75	3.02	2.96	2.9	20	HPLC-FLD
20	BBF_FAT						
21	BBF_FAT	1.67	1.48	2.62	1.92	30	HPLC-FLD
22	BBF_FAT	2.19	1.46	1.69	1.78	4.5	
23	BBF_FAT	3.52	2.85	3.2	3.19	21.37	HPLC-FLD
24	BBF_FAT	3.6	3.14	2.83	3.19	20	HPLC-FLD
25	BBF_FAT						
26	BBF_FAT	3.48	3.48	3.87	3.61	14	HPLC-FLD
28	BBF_FAT	0.43	0.42	0.5	0.451		HPLC-UV/FLD
29	BBF_FAT						HPLC-FLD
31	BBF_FAT	< 4.31	< 4.31	< 4.31		13	GC-MS/MS
41	BBF_FAT	2.67	2.67	2.67	2.67	20	GC-MS/MS
42	BBF_FAT	2.57	2.38	2.2	2.58	10.4	GC-MS/MS
43	BBF_FAT	3.64	3.83	4.03	3.8	1.2	HPLC-FLD
44	BBF_FAT	2.76	2.78	2.75	2.76	22	HPLC-FLD
45	BBF_FAT	3.05	2.93	2.89	2.96	7.1	GC-MS
46	BBF_FAT	9.96	9.96	10	9.97	35	HPLC-FLD
55	BBF_FAT	3.71	3.87	3.65	3.74	0.8	GC-MS
63	BBF_FAT	2.3	2.1	2.9	2.1	17	GC-MS
75	BBF_FAT	2	2	2	2	22	GC-MS/MS
81	BBF_FAT	1.51	1.91	1.47	1.63	15	HPLC-FLD
82	BBF_FAT				3.01	34	
99	BBF_FAT	7.73	9.32	7.45	8.17	2	HPLC-FLD

Distribution of individual results of replicate determinations reported for the chrysene (CHR) content, expressed on fat basis, of the cocoa powder test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the cocoa powder test sample



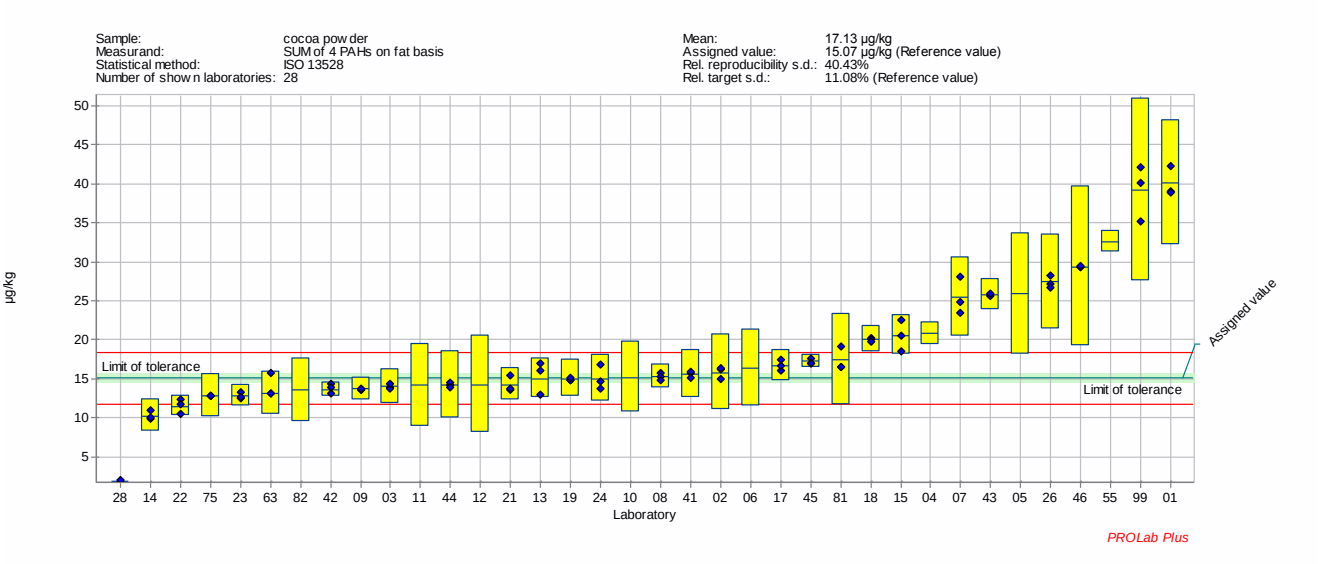
Results, as reported by the participants, for the content of chrysene (CHR), expressed on fat basis, of the cocoa powder test sample

Assigned value is 6.16 µg/kg. The uncertainty refers to the final value.

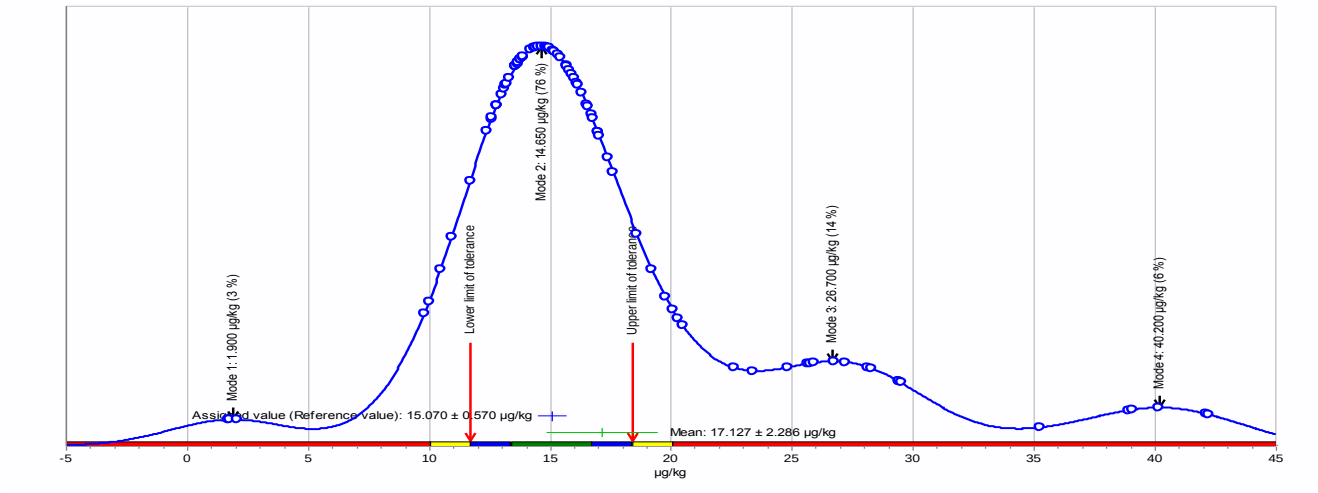
LCode	Measurand	Rep 1	Rep 2	Rep 3	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	µg/kg	µg/kg	µg/kg	%	
1	CHR_FAT	19.41	17.85	17.14	18.133	20	GC-MS/MS
2	CHR_FAT	3.95	3.37	4.46	3.926	28	HPLC-UV/FLD
3	CHR_FAT	5.09	5.42	5.52	5.34	8.6	GC-MS/MS
4	CHR_FAT				7.55	12.5	GC-MS
5	CHR_FAT				13.5	30	HPLC-FLD
6	CHR_FAT				6	7.4	GC-MS/MS
7	CHR_FAT	11.24	9.13	11.71	10.69	12	GC-MS
8	CHR_FAT	5.79	5.74	5.51	5.68	16	GC-MS
9	CHR_FAT	4.2	4.2	4.2	4.2	22	GC-MS
10	CHR_FAT	6.66	6.36	6.67	6.6	30	GC-MS
11	CHR_FAT	5.56	5.73	5.02	5.44	20	HPLC-FLD
12	CHR_FAT				6.53	54	GC-MS/MS
13	CHR_FAT	6.3	4.8	6.3	5.8	20	GC-HRMS
14	CHR_FAT	3.97	3.69	3.71	3.79	27.4	GC-MS/MS
15	CHR_FAT	8.36	7.4	6.39	7.38	19.7	HPLC-FLD
16	CHR_FAT						
17	CHR_FAT	6.1	6.1	6.5	6.2	19.29	GC-MS
18	CHR_FAT	7.17	6.84	7.17	7.03	14.6	HPLC-FLD
19	CHR_FAT	5.33	5.55	5.55	5.5	20	HPLC-FLD
20	CHR_FAT						
21	CHR_FAT	5.82	5.96	6.1	5.96	22	HPLC-FLD
22	CHR_FAT	4.61	4.16	4.57	4.45	5.9	
23	CHR_FAT	4.27	4.34	4.37	4.33	20.76	GC-MS
24	CHR_FAT	4.81	5.45	4.32	4.86	20	HPLC-FLD
25	CHR_FAT						
26	CHR_FAT	12.94	13.34	13.87	13.38	20	HPLC-FLD
28	CHR_FAT	0.33	0.33	0.42	0.361		HPLC-UV/FLD
29	CHR_FAT						HPLC-FLD
31	CHR_FAT	4.47	4.43	4.51	4.472	2	GC-MS/MS
41	CHR_FAT	6	5.9	5.6	5.9	20	GC-MS/MS
42	CHR_FAT	5.23	5.09	4.86	4.96	8.1	GC-MS/MS
43	CHR_FAT	10.7	10.55	10.45	10.6	3.2	HPLC-FLD
44	CHR_FAT	4.66	4.74	4.46	4.62	22	HPLC-FLD
45	CHR_FAT	6.39	5.94	5.99	6.11	10	GC-MS
46	CHR_FAT	10.6	10.6	10.6	10.6	25	HPLC-FLD
55	CHR_FAT	18.45	18.62	16.83	17.97	3.6	GC-MS
63	CHR_FAT	4.7	4.9	5.4	4.9	29	GC-MS
75	CHR_FAT	4.9	4.9	4.9	4.9	22	GC-MS/MS
81	CHR_FAT	10.03	7.89	8.29	8.73	83	HPLC-FLD
82	CHR_FAT				4.76	32	
99	CHR_FAT	6.24	10.12	10.66	9.01	3.8	HPLC-FLD

Distribution of individual results of replicate determinations reported for the sum of the four markers PAHs (SUM4PAH) content, expressed on fat basis, of the cocoa powder test sample

blue diamonds: individual results of replicate determinations, yellow box: reported expanded measurement uncertainty (k=2), blue horizontal line in yellow 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, expressed on fat basis, of the cocoa powder test sample



Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH), expressed on fat basis, of the cocoa powder test sample
Assigned value is 15.07 µg/kg.

LCode	Measurand	Final value	Rel. exp. uncertainty	Analytical technique
		µg/kg	%	
1	SUM_FAT	40.07	20	GC-MS/MS
2	SUM_FAT	15.8	31	HPLC-UV/FLD
3	SUM_FAT	13.98	16.4	GC-MS/MS
4	SUM_FAT	20.8	7.2	GC-MS
5	SUM_FAT	25.9	30	HPLC-FLD
6	SUM_FAT	16.4	30	GC-MS/MS
7	SUM_FAT	25.45	20	GC-MS
8	SUM_FAT	15.28	10	GC-MS
9	SUM_FAT	13.7	11	GC-MS
10	SUM_FAT	15.2	30	GC-MS
11	SUM_FAT	14.16	37.6	HPLC-FLD
12	SUM_FAT	14.28	44	GC-MS/MS
13	SUM_FAT	15	17	GC-HRMS
14	SUM_FAT	10.26	20.1	GC-MS/MS
15	SUM_FAT	20.6	12.4	HPLC-FLD
16	SUM_FAT			
17	SUM_FAT	16.7	11.85	
18	SUM_FAT	20.1	8.4	HPLC-FLD
19	SUM_FAT	15	16	HPLC-FLD
20	SUM_FAT			
21	SUM_FAT	14.28	15	HPLC-FLD
22	SUM_FAT	11.5	11.2	
23	SUM_FAT	12.83	11.05	HPLC-FLD
24	SUM_FAT	15.05	20	HPLC-FLD
25	SUM_FAT			
26	SUM_FAT	27.41	22	HPLC-FLD
28	SUM_FAT	1.848		HPLC-UV/FLD
29	SUM_FAT			HPLC-FLD
31	SUM_FAT		10	GC-MS/MS
41	SUM_FAT	15.6	20	GC-MS/MS
42	SUM_FAT	13.64	6.9	GC-MS/MS
43	SUM_FAT	25.8	7.7	HPLC-FLD
44	SUM_FAT	14.2	30	HPLC-FLD
45	SUM_FAT	17.22	5	GC-MS
46	SUM_FAT	29.4	35	HPLC-FLD
55	SUM_FAT	32.6	4.15	GC-MS
63	SUM_FAT	13.1	21	GC-MS
75	SUM_FAT	12.8	22	GC-MS/MS
81	SUM_FAT	17.44	33.7	HPLC-FLD
82	SUM_FAT	13.54	30	
99	SUM_FAT	39.17	29.9	HPLC-FLD

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doi: 10.2787/071922

ISBN 978-92-79-53877-3