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Laboratoire Central de Surveillance de la Qualité de l'Air

European interlaboratory comparison for the analysis of PAHs in ambient air (2018). Final report.

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Laboratoire National de Métrologie et d'Essais LNE

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"L'expertise au service de la qualité de l'air"

French reference laboratory for air quality monitoring

INERIS – French National Institute for Industrial Environment and Risks

EUROPEAN INTERLABORATORY COMPARISON FOR THE ANALYSIS OF PAHS IN AMBIENT AIR (2018). FINAL REPORT.

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SYNTHESIS IN FRENCH FOR THE REGIONAL AIR QUALITY MONITORING NETWORKS (AASQA)

Dans le cadre de la mise en œuvre des exigences qualité fixées par le ministère chargé de l'environnement, un essai de comparaison inter laboratoires (CIL) analytique a été organisé par le LCSQA (INERIS en collaboration avec le LNE) au premier semestre 2018, pour les laboratoires d'analyse sous-traitants des AASQA (Association Agréée pour la Surveillance de la Qualité de l'Air).

Les inscriptions ont été également ouvertes à des laboratoires européens appliquant les prescriptions des textes normatifs relatifs à l'analyse du Benzo[a]pyrène (B[a]P) et des autres HAP (Hydrocarbures Aromatiques Polycycliques) concernés par la Directive 2004/107/CE ainsi que sur le phénanthrène, le fluoranthène et le benzo[g,h,i]pérylène.

Cet exercice comprenait des matrices de concentrations différentes en HAP afin de prendre en compte les gammes de travail habituelles des laboratoires réalisant l'analyse de filtres issus de prélèvements haut débit ou bas débit. Chaque participant a donc reçu les matériaux suivants :

- 3 poinçons de filtre issus de prélèvements d'air ambiant pour deux d'entre eux, le troisième étant un blanc de laboratoire. Les prélèvements ont été effectués sur filtre en quartz à l'aide d'un préleveur grand volume de type Graseby-Andersen, équipé d'une tête PM_{10}, à un débit de 70 m^3/h. Chaque filtre était découpé avec un emporte-pièce en 20 morceaux de 37 mm de diamètre. Trois filtres notés 18/172774_F1, F2 et F-blanc ont ainsi été envoyés aux participants ;
- 1 matériau de référence certifié (MRC) par l'IRMM (ERM®-CZ100, fine dust PM_{10} like) envoyé en double mais identifiés comme 2 matériaux distincts pour les participants et donc notés 18/172224_MRC1 et MRC2.
- 3 matériaux liquides de référence certifiés (MRC) préparés par le LNE, constitués de trois solutions étalons notées : 18/172774_S1, S2 et S3. Les solutions S1 et S2 étaient identiques.

Finalement, 17 laboratoires européens (dont 13 français) ont participé à cette CIL. Une grande amélioration des résultats a pu être observée par comparaison à ceux obtenus lors des CIL organisées en 2014 et 2015 (Verlhac, 2014, Verlhac and Albinet, 2015). Les dernières recommandations et la rencontre organisée avec les laboratoires sous-traitants des AASQA pour l'analyse des HAP (04/07/2016, https://www.lcsqa.org/system/files/commission/Web_CS-cr-lcsqa_rex_hap_aal_2016-vf.pdf) ont été certainement bénéfiques. Mis à part pour le MRC solide, les incertitudes obtenues, notamment pour le B[a]P, respectent celles qui sont admises par la Directive et la TS XP/CEN 16645 montrant que la dispersion des laboratoires est bien meilleure.

Néanmoins, quelques laboratoires doivent encore améliorer leurs procédures analytiques car ils ont obtenu des mauvais résultats (majoritairement non acceptables c'est-à-dire ayant un $|score\ z| \geq 3$) pour la plupart des matériaux et HAP testés (180430, 180458 et dans une moindre mesure, 18096, pour les solutions certifiées). De plus, les laboratoires 180458 and 180481 n'ont fourni aucun résultat pour le MRC solide et le laboratoire 180429 a seulement fourni des résultats pour le B[a]P pour tous les matériaux de l'essai.

Enfin, sur la base des zêta -scores, les incertitudes de mesure ne sont toujours pas correctement évaluées par la plupart des participants. Les laboratoires français sont donc invités à suivre les recommandations fournies par le LCSQA (Albinet, 2015) afin d'estimer les incertitudes sur l'analyse des HAP.

GLOSSARY

CRM	Certified Reference Material
ILC	InterLaboratory Comparison : ILC is defined and implemented to allow laboratories to assess and demonstrate their performance during a test, NOTE: Three terms may be used: “interlaboratory tests” or “inter-comparison tests” or “aptitude tests,”
LoQ	Limit of Quantification
Test material	matrix of interest containing the targeted compounds by the interlaboratory comparison, potentially added using a spiking solution
B[a]A	Benzo[a]anthracene
B[a]P	Benzo[a]pyrene
B[b]F	Benzo[b]fluoranthene
B[g,h,i]P	Benzo[g,h,i]perylene
B[j]F	Benzo[j]fluoranthene
B[k]F	Benzo[k]fluoranthene
DB[a,h]A	Dibenzo[a,h]anthracene
Flt	Fluoranthene
Ind	Indeno[1,2,3-cd]pyrene
Phen	Phenanthrene
Sum of BF	Sum of Benzo[b,j,k]fluoranthene

DEFINITIONS

CV_r	standard deviation of x measurements divided by the average of those x measurements by % [(Standard deviation / average) by %],
CV_R	reproducibility variation coefficient equal to the standard deviation of the measurements averages divided by the average of the measurements averages by %,
CV_{rep}	mean repeatability variation coefficient, average of the participants CV_r,
Standard deviation	standard deviation of x measurements,
Population standard deviation	standard deviation of the measurement averages,
IC_R	reproducibility confidence interval,
IC_r	repeatability confidence interval,
Average	average of x measurements,
Population average	average of the measurement averages,
Number of decimals	number imposed in the instruction formula,
σ_{pt}	standard deviation for assessing the aptitude (stipulated, perceived or s*: robust standard deviation for evaluating the aptitude obtained using the algorithm A of ISO 13528),
z score	performance criteria provided to each participant making it possible to measure its deviation relative to the assigned value. The assigned value is the robust average,
s*	robust standard deviation obtained using the algorithm A of ISO 13528,
S_L	interlaboratory standard deviation,
S_R	reproducibility standard deviation,
S_r	repeatability standard deviation,
x*	robust average obtained using algorithm A of ISO 13528,
X_{MRC}	reference value resulting from the certificate for the certified reference material.

1. BACKGROUND

The monitoring of polycyclic aromatic hydrocarbons (PAHs) in ambient air is mandatory and regulated according to the European Directive 2004/107/EC Article 9 (European Official Journal, 2004), from the French law of October 21st, 2010 related to the air quality monitoring and public information states that the participation to interlaboratory comparisons (ILC) is mandatory for the laboratories performing chemical analyses for the French regional air quality monitoring associations networks (AASQA).

A new interlaboratory comparison has been organized in 2018 by the French air quality monitoring reference laboratory (LCSQA).

ILC are organized either to check the ability of laboratories to deliver accurate testing results to their customers or to find out whether a certain analytical method performs well and is fit for its intended purposes. Furthermore, this exercise is useful to identify problems connected to the application of the standard procedure EN 15549 (CEN (European Comittee for Standardization), 2008) which has to be applied to the sampling and analysis of B[a]P in ambient air as well as of the technical specification CEN/TS 16445 for the measurement of the benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene (CEN (European Comittee for Standardization), 2014).

This test was first intended for the subcontractor laboratories performing analyses of PAHs in ambient air for the AASQA and for other European laboratories performing this type of analyses.

2. PARTICIPANTS

According to ISO 5725-1 (§ 6.3.3), for each test material, a minimum number of p participants with n measurements such as $p \times n \geq 30$, allows to get a low level of uncertainty on the estimations of standard deviations of repeatability and reproducibility. A minimum of 10 participants is usually required and a maximum of 20 participants would have been ideal in this/our case (limitation due to the number of possible punches made on the field sample filter available).

17 participants took part in the ILC and are listed in the following Table 1. The recommendations of ISO 5725-1 have been followed.

Table 1 : Participants at the PAHs ILC organized in 2018.

Laboratory	Country
ALPA CHIMIES	France
CARSO - LSEHL	France
Conseil Départemental de la Réunion	France
EUROFINS	France
Health Institute Carlos III	Spain
Hygiene Publique En Hainaut Asbl	Belgium
IANESCO Chimie	France
INERIS	France
ITGA - PRYSM	France
LCME	France
LD31	France
LNE	France
Micropolluants Technologie	France
SGS France EHS	France
SynAirGIE	France
TNO-EMSA	Netherlands
Vlaamse Milieumaatschappij (VMM)	Belgium

The instrumentation used by the participants as well as the applied analytical procedures and the obtained results are presented anonymously in this report. A confidential code was assigned to each participant when they registered on-line for their participation to the ILC.

3. ORGANIZATION OF THE INTERLABORATORY COMPARISON

The interlaboratory comparison (ILC) was organized and implemented by the authorized personnel cited in Table 2.

Table 2 : Authorized personnel who implemented the PAHs ILC.

	First and Last Names	ILC Function
INERIS Parc Technologique Alata 60550 VERNEUIL-EN-HALATTE ☎ +33 3.44.55.66.77	Sylvain Bailleul	ILC coordinator
	Robin Aujay	Test material assistant
	José Guarnéri	Webmaster and designer of the statistical processing tool

The ILC was organized as follows:

26th January to 24th February 2018: Participants had to submit the registration form.

5th March 2018: INERIS sent a confidential code, an identifier and a password to each participant.

March 13th, 2018: INERIS sent the different test materials to each participant. Opening of the website for on-line result submissions.

April 13th, 2018 delayed to April 27th, 2018: Deadline for result submissions on the website.

July 18th, 2018: INERIS sent the preliminary report summarizing all calculated z-scores and the results from laboratories.

4. ANALYSES TO BE PERFORMED

Participants should have quantified on each material the following substances:

Benzo[a]pyrene	Benzo[j]fluoranthene*
Benzo[a]anthracene	Benzo[k]fluoranthene*
Phenanthrene	Dibenzo[a,h]anthracene
Fluoranthene	Indeno[1,2,3-cd]pyrene
Benzo[b]fluoranthene*	Benzo[g,h,i]perylene

* *Results for the sum of B[b]F, B[k]F and B[j]F concentrations were accepted.*

Analyses should have been performed according to the methods specified in the standard procedure EN 15549 for the analysis of benzo[a]pyrene (B[a]P) (CEN (European Comittee for Standardization), 2008) and in the technical specification CEN/TS16445 for the measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene (CEN (European Comittee for Standardization), 2014).

The same operator or the same team should have performed all analyses for a given parameter, within a short time period.

5. DESCRIPTIONS OF THE TEST MATERIALS

All the test materials sent to the participants and the number of measurements requested are presented in Table 3.

Table 3 : Test materials sent to the participants.

Matrices	References	Number and type	Number of measurements	Quantity
Ambient air PM_{10} samples (quartz fibre filter punches)	18/172774-F-Blanc 18/172774-F1 18/172774-F2	2 field samples and 1 lab blank filter	4 injections of each sample extract	3 Filter punches of 37 mm ∅
Certified reference material (solid powder)	18/172774-MRC1 18/172774-MRC2	2 (both CRM were the same)	4 injections of one sample extract	About 75 mg
Certified standard solutions (in acetonitrile)	18/172774-S1 18/172774-S2 18/172774-S3	3 (S1 and S2 solutions were the same)	4 injections of each certified standard solution	1.5 ml vial

5.1 Solid Certified Reference Material (CRM)

The ERM® (European Reference Material) CZ100 (fine dust, PM_{10}-like) was used in this ILC as solid CRM. Details on this CRM could be found in the certificate of analysis (Certificate issue date: November 2010: see Appendix 9).

Certified mass fraction values for selected PAHs in ERM®–CZ100 are presented in Table 4.

Table 4 : Certified mass fraction values for selected PAHs in ERM®–CZ100.

Compound	Mass fraction (mg kg^{-1})	Uncertainty (mg kg^{-1}, k=2)
Benzo[a]anthracene	0.91	0.07
Benzo[a]pyrene	0.72	0.05
Benzo[b]fluoranthene	1.42	0.14
Benzo[j]fluoranthene	0.75	0.14
Benzo[k]fluoranthene	0.67	0.06
Sum of Benzofluoranthenes	2.84	0.21
Benzo[g,h,i]perylene	1.76*	Not specified
Dibenzo[a,h]anthracene	0.18	0.04
Fluoranthene	4.67*	Not specified
Indeno[1,2,3-cd]pyrene	1.07	0.10
Phenanthrene	2.23*	Not specified

*: indicative values

5.2 Field sample filter

Natural ambient air aerosol samples were collected using a PM_{10} high volume sampler (Graseby-Andersen working at 70 m^3 h^{-1}) in December 2017 at Verneuil-en-Halatte (France, sub-urban site) and kept under freezing. 20 equivalent punches of 37 mm diameter were performed in the quartz fibre filters (20.3 x 25.4 cm) to be sent to the participants.

5.3 Standard solutions

Three standard solutions (in acetonitrile) were prepared and certified by LNE at different concentration levels defined based on the standard thresholds, sampling flow rates and concentrations observed in ambient air.

For each PAH, individual standard stock solutions were prepared gravimetrically by dissolution of the native compounds in acetonitrile:

- Standard solutions S1 and S2 were prepared gravimetrically by mixing the individual standard stock solutions and dilution in acetonitrile.
- Standard solution 3: standard solution 1 diluted about 33 times, obtained by gravimetrically dilution of the previous standard solution 1 in acetonitrile:

Individual PAH concentrations of standard solutions were determined by implementing ID-GC/MS. C_{13} labelled PAH were used for quantification1.5 ml of standard solutions were placed in amber vials and sent to the participants.

Standard solutions concentrations used in the ILC 2018 are presented in Table 5.

Table 5 : Standard solutions concentrations.

	S1 = S2		S3	
Compound	**ng ml^{-1}**	**Uncertainty U (ng ml^{-1}, k=2)**	**ng ml^{-1}**	**Uncertainty U (ng ml^{-1}, k=2)**
Benzo[a]anthracene	291	12	8.14	0.33
Benzo[a]pyrene	399	20	11.25	0.45
Benzo[b]fluoranthene	552	17	15.53	0.47
Benzo[g,h,i]perylene	399	16	11.32	0.45
Benzo[j]fluoranthene	267	13	7.78	0.39
Benzo[k]fluoranthene	281.4	8.4	7.90	0.24
Dibenzo[a,h]anthracene	89.	12	2.47	0.35
Fluoranthene	769	23	21.69	0.65
Indeno[1,2,3-cd]pyrene	722	14	21.55	0.43
Phenanthrene	1517	30	42.71	0.85

Uncertainty linked to the stability of the standard solution could be considered as negligible. Uncertainties have been evaluated from the uncertainty of measurement and the homogeneity inter- and intra-vials.

6. HOMOGENEITY AND STABILITY OF THE AMBIENT AIR AEROSOL SAMPLES

6.1 Homogeneity of the filters

The homogeneity of the materials has not been checked during this ILC. Homogeneity of the samples collected using Graseby Andersen sampler has been already evaluated and proved during the previous ILCs (e.g.(Verlhac, 2014, Verlhac and Albinet, 2015)).

6.2 Stability of the filters

The stability of filters was checked during all the ILC analytical period. Concurrent analyses were performed on three parallel ambient air filter samples. Punches from the same filter sample were analysed once per week for the entire ILC period of four weeks. The stability of the materials was checked according to the methodology described in the standard method ISO 13528. Only the stability of B[a]P is presented in the figure below (error bars correspond to the analytical uncertainty):

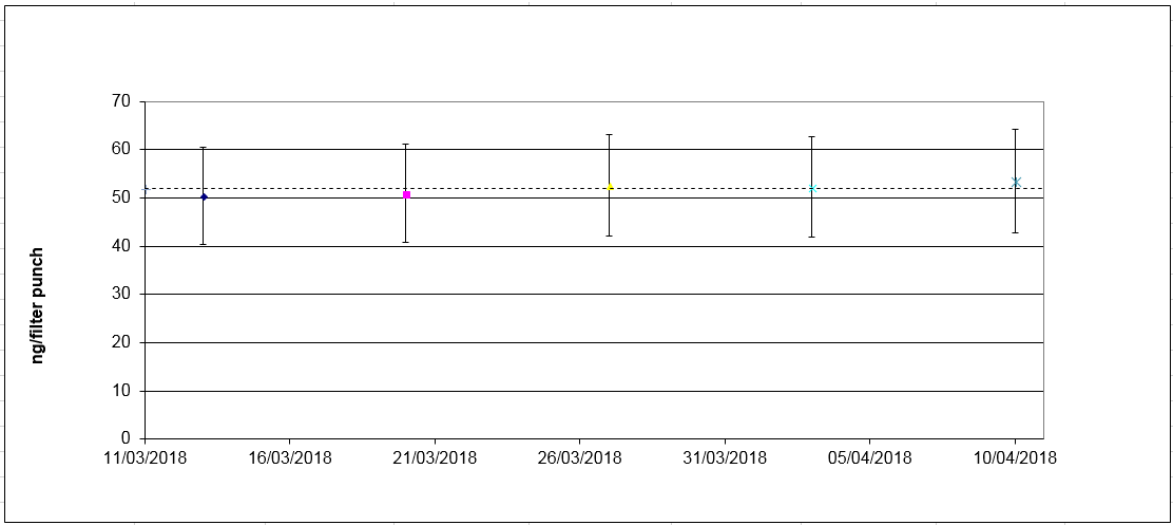

Figure 1 : B[a]P stability

Results obtained from the homogeneity and stability experiments showed that **the field sample filters could be considered as stable and homogeneous for the entire analytical period.**

7. DATA ANALYSIS

Statistical analysis of the results was performed according to the ISO 13528 standard procedure and the following requirements:

- Standard methods 1, 2 and 5 of the ISO 5725 series: “Accuracy (trueness and precision) of measurement methods and results”;
- ISO 13528 standard procedure: “Statistical methods for use in proficiency testing by interlaboratory comparison”;

- X06-050 standard procedure “Statistical application – Study of distribution normality.”

Determination of assigned values was done as follows:

- for the standard solutions and CRM: the assigned value as taken to be equal to the certified value;
- for the field sample filter: the assigned value was taken to be equal to the robust average of the results provided by the participants in the interlaboratory comparison;
- the standard deviation for assessing the aptitude was taken to be equal to the robust standard deviation evaluated using the ISO 13528A algorithm.

Using the robust analysis, calculations of the reference values, confidence intervals and performance statistics are not affected by the analyst’s assessment data.

Evaluation of the performances of the participants was achieved using the Z- and zétascore calculations as described below:

Z score:

Certified value

$$z_i = \frac{\overline{x_i} - X_{CMR}}{\hat{\sigma}}$$

Robust average

$$z_i = \frac{\overline{x_i} - x^*}{\hat{\sigma}}$$

Zeta Score:

$$\zeta = \frac{x - X_{CMR}}{\sqrt{u_x^2 + u_{X_{CMR}}^2}}$$

In addition, for CRM, the robust averages x* were compared to the certified reference values. If the difference between both values is larger than twice the uncertainty on the difference (estimated according EN 13528) ($|x^*-X_{CMR}|>2 \times u|x^*-X_{CMR}|$), a bias is detected.

8. RESULTS OF THE INTERLABORATORY COMPARISON

In the following sections, the results obtained before and after statistical analysis, averages, repeatability standard deviations and uncertainties are presented for each test material. Performance of each laboratory (Z-score) is presented only for B[a]P. Results for the other substances are shown in the appendix. The statistical distribution graphs showing the average and standard deviation values obtained by each laboratory are provided here after.

The following legend is used:

x^*	Robust average obtained using the algorithm A of ISO 13528
x_{CRM}	Certified reference value
x_{pt}	Assigned value to assess the aptitude of the participants equal to x^* or x_{CRM}
σ_{pt}	Standard deviation to assess the aptitude of the participant $\sigma_{pt} = s^*$ (robust standard deviation using the algorithm A of ISO 13528)
x	Participant's average
s_r	Participant's repeatability standard deviation
S_L	Interlaboratory standard deviation
S_R	Reproducibility standard deviation
S_r	Repeatability standard deviation
~~15,93~~	Results discarded from the statistical analysis by the expert [values <LoQ (limit of quantification) or obvious errors (values higher or larger than 10 times form the participant average results) or equal to 0)
score z_i	Performance criteria available to each participant indicating the relative deviation to the assigned value.
NA	Not analyzed
UNS	Uncertainty not submitted
NC	Not calculated (generally for the submitted results equal to LoQ)
	$\lvert Z_i \rvert$ < 2 : Satisfactory score
	2 ≤ $\lvert Z_i \rvert$ < 3 : Score requiring monitoring or preventive action
	$\lvert Z_i \rvert$ ≥ 3 : Unsatisfactory score requiring corrective action (the analytical results are not acceptable)

8.1 MRC1 and MRC2

Results obtained for the analysis of the CRM (ERM®-CZ100) before and after statistical analysis are presented in Table 6 and 7.

Table 6 : 18/172774 – MRC1, raw data and robust analysis of the results.

	Raw data						Robust analysis									
Substances	**Number of laboratories**	**Certified value (mg kg^{-1})**	**x (mg kg^{-1}**	**s (mg kg^{-1}**	**CV_R (%)**	**CV_{rep} (%)**	**x* (mg kg^{-1}**	**s* (mg kg^{-1}**	**σ_{pt}**	**$u_{X\ CRM}$**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2, %)**	**Mean recoveries**
B[a]A	14	0.91	0.94	0.34	36%	3%	0.921	0.284	0.284	0.095	0.283	0.284	0.024	62%	80% [1]	101%
B[a]P	15	0.72	0.66	0.21	32%	3%	0.675	0.182	0.182	0.059	0.181	0.184	0.030	55%	50% [2]	94%
B[b]F	13	1.42	1.63	0.40	25%	3%	1.618	0.437	0.437	0.152	0.436	0.441	0.064	54%	60% [1]	114%
B[g,h,i]P	14	1.76	1.10	0.57	41%	2%	1.473	0.470	0.509	0.157	0.470	0.471	0.030	64%	68% [1]	84%
B[j]F	8	0.75	0.70	0.46	66%	3%	0.725	0.307	0.307	0.136	0.307	0.308	0.027	85%	-	97%
B[k]F	13	0.67	0.64	0.10	16%	3%	0.641	0.099	0.099	0.034	0.098	0.101	0.021	31%	80% [1]	96%
DB[a,h]A	11	0.18	0.21	0.12	59%	3%	0.180	0.101	0.101	0.038	0.101	0.101	0.006	113%	106% [1]	100%
Flt	14	4.67	4.09	1.00	25%	2%	4.238	0.706	0.748	0.236	0.706	0.708	0.062	33%	-	91%
Ind[1,2,3-cd]P	14	1.07	1.01	0.34	34%	3%	1.038	0.291	0.295	0.097	0.291	0.292	0.032	56%	66% [1]	97%
Phen	13	2.23	1.89	0.560	30%	4%	1.944	0.481	0.533	0.167	0.480	0.483	0.052	50%	-	87%
Sum of BF	14	2.84	2.66	0.79	30%	3%	2.650	0.868	0.868	0.290	0.867	0.871	0.084	62%		93%

In red: larger uncertainty from than the maximum one authorised.

[1] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[2] 2004/107/EC European Directive.

Table 7 : 18/172774 – MRC2, raw data and robust analysis the results

	Raw data						Robust analysis									
Substances (mg kg^{-1})	**Number of laboratories**	**Certified value (mg kg^{-1})**	**x (mg kg^{-1}**	**s (mg kg^{-1}**	**CV_R (%)**	**CV_{rep} (%)**	**x* (mg kg^{-1}**	**s* (mg kg^{-1}**	**σ**	**$u_{X\ CRM}$**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2, %)**	**Mean recoveries**
B[a]A	14	0.91	1.00	0.42	42%	3%	0.940	0.308	0.308	0.103	0.940	0.308	0.308	66%	80% [1]	103%
B[a]P	15	0.72	0.68	0.18	28%	3%	0.699	0.145	0.145	0.047	0.699	0.145	0.145	42%	50% [2]	97%
B[b]F	13	1.42	1.65	0.38	23%	3%	1.639	0.399	0.399	0.138	1.639	0.399	0.399	49%	60% [1]	115%
B[g,h,i]P	14	1.76	1.42	0.59	41%	2%	1.497	0.487	0.525	0.163	1.497	0.487	0.525	65%	68% [1]	85%
B[j]F	8	0.75	0.72	0.47	66%	4%	0.741	0.305	0.305	0.135	0.741	0.305	0.305	83%	-	99%
B[k]F	13	0.67	0.65	0.09	14%	3%	0.652	0.072	0.072	0.025	0.652	0.072	0.072	23%	80% [1]	97%
DB[a,h]A	11	0.18	0.20	0.12	59%	2%	0.174	0.088	0.088	0.033	0.174	0.088	0.088	101%	106% [1]	97%
Flt	14	4.67	4.31	1.12	26%	2%	4.428	0.690	0.733	0.231	4.428	0.690	0.733	31%	-	95%
Ind[1,2,3-cd]P	14	1.07	0.99	0.31	31%	3%	1.028	0.227	0.227	0.076	1.028	0.227	0.227	44%	66% [1]	96%
Phen	13	2.23	2.06	0.78	37%	2%	2.060	0.607	0.649	0.211	2.060	0.607	0.649	59%	-	92%
Sum of BF	14	2.84	2.71	0.78	29%	2%	2.699	0.853	0.853	0.285	0.852	0.857	0.091	63%		95%

[1] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[1] 2004/107/EC European Directive.

Results on the analysis of MRC1 and MRC2:

Results obtained for B[a]P are presented hereafter (Table 8 and Figure 3) and the full results including all PAHs are available in the Appendixes 1 and 2.

Overall, Z-score results obtained for MRC 1 and 2 were satisfactory for most of the participants and for all PAHs. Recoveries calculated using the robust average values were satisfactory for all the PAHs (in the range of 0.8 to 1.2 as specified by the EN 15549 and CEN/TS 16645). No bias has been detected between certified reference values and robust averages for all PAHs. No significant differences between results for both materials, which were the same, could be highlighted. In addition, no method effect, due to the extraction or analytical procedures, could be observed.

Only 1 laboratory (180430) had not acceptable results (z-score <-3 or >3) for most of the substances (5 PAHs including B[a]P), and 3 other ones (180402, 180471, 180477) for B[k]F, B[a]A and B[j]F, respectively (Appendix 2). 5 laboratories (18402, 18471, 18476, 18479 and 18486) got warning results for other PAHs than B[a]P.

It is to highlight that 2 laboratories did not provide any results for the analysis of CMR (180458 and 180481) and laboratory 180429 only provided results for B[a]P. Few results, from laboratories 180415, 180471 and 180476, were submitted as equal to the quantification limit, for B[j]F and DB[a,h]A, and were excluded from the statistical analysis. In addition, some laboratories submitted results equal to 0 and their results were discarded from the final data treatment.

The intra-laboratory variability has been evaluated using the Mandel k coherence test. Results showed that intra-laboratory dispersions were higher for laboratories 180402, 180429, 180437 and 180486 for 1 on the 10 studied PAHs; 180476, 180415 and 180470 for 2/10 PAHs; 180471 for 4/10 PAHs; 180430 for 5/10 PAHs; and 180479 6/10 PAHs.

Interestingly, zeta-scores for most of the laboratories and most of the substances were not acceptable or requiring a preventive action. This result shows that uncertainties are not well evaluated by the laboratories especially for 180402, 180430, 180470, and 180476 for which uncertainties on the measurement of B[a]P (but other PAHs too) are probably not well evaluated. Laboratories are invited to follow the guidelines provided by the LCSQA (Albinet, 2015) to define their uncertainties of analysis.

Results obtained from this ILC exercise permitted to evaluate the analytical uncertainties of measurements of the PAHs (Tables 6 and 7). Overall, results obtained for the analysis of this CRM complied with the maximum uncertainties allowed by the 2004/107/EC European Directive and the CEN/TS 16645. **Only 2 values, for B[a]P (55 instead of 50%) and DB[ah,h]A (113 instead of 106%) slightly exceeded the maximum uncertainties allowed.**

Table 8 : B[a]P participants' results on CRM analyses.

	18/172774_MRC1				18/172774_MRC2			
	Benzo[a]pyrene							
Lab ID	x (mg kg^{-1})	s_r (%)	Z-score	Zeta score	x (mg kg^{-1})	s_r (%)	Z-score	Zeta score
180402	0.43	0.0%	-1.59	-4.32	0.45	0.0%	-1.86	-3.86
180405	0.82	0.6%	0.54	0.93	0.74	1.3%	0.16	0.23
180415	0.66	4.3%	-0.32	-0.53	0.65	2.6%	-0.50	-0.68
180429	1.03	5.8%	1.69	UNS	0.89	8.6%	1.17	UNS
180430	0.15	5.4%	-3.13	-22.80	0.15	3.3%	-3.92	-22.70
180437	0.63	3.1%	-0.52	-0.98	0.68	1.7%	-0.28	-0.38
180441	0.82	0.6%	0.54	0.80	0.86	0.6%	0.98	1.12
180453	0.87	1.1%	0.84	1.95	0.82	1.0%	0.69	1.35
180458	NA	NA	NA	NA	NA	NA	NA	NA
180470	0.60	6.2%	-0.66	-3.07	0.70	5.6%	-0.17	-0.58
180471	0.55	6.6%	-0.95	-1.74	0.73	2.6%	0.03	0.04
180476	0.83	5.7%	0.59	2.06	0.86	1.5%	0.93	4.74
180477	0.55	0.9%	-0.92	-2.76	0.56	1.7%	-1.09	-2.56
180479	0.73	7.5%	0.07	0.10	0.74	5.7%	0.12	0.14
180481	NA	NA	NA	NA	NA	NA	NA	NA
180486	0.60	2.9%	-0.67	-1.14	0.62	0.8%	-0.71	-0.92
180496	0.69	0.7%	-0.18	-1.14	0.69	0.7%	-0.22	-1.14

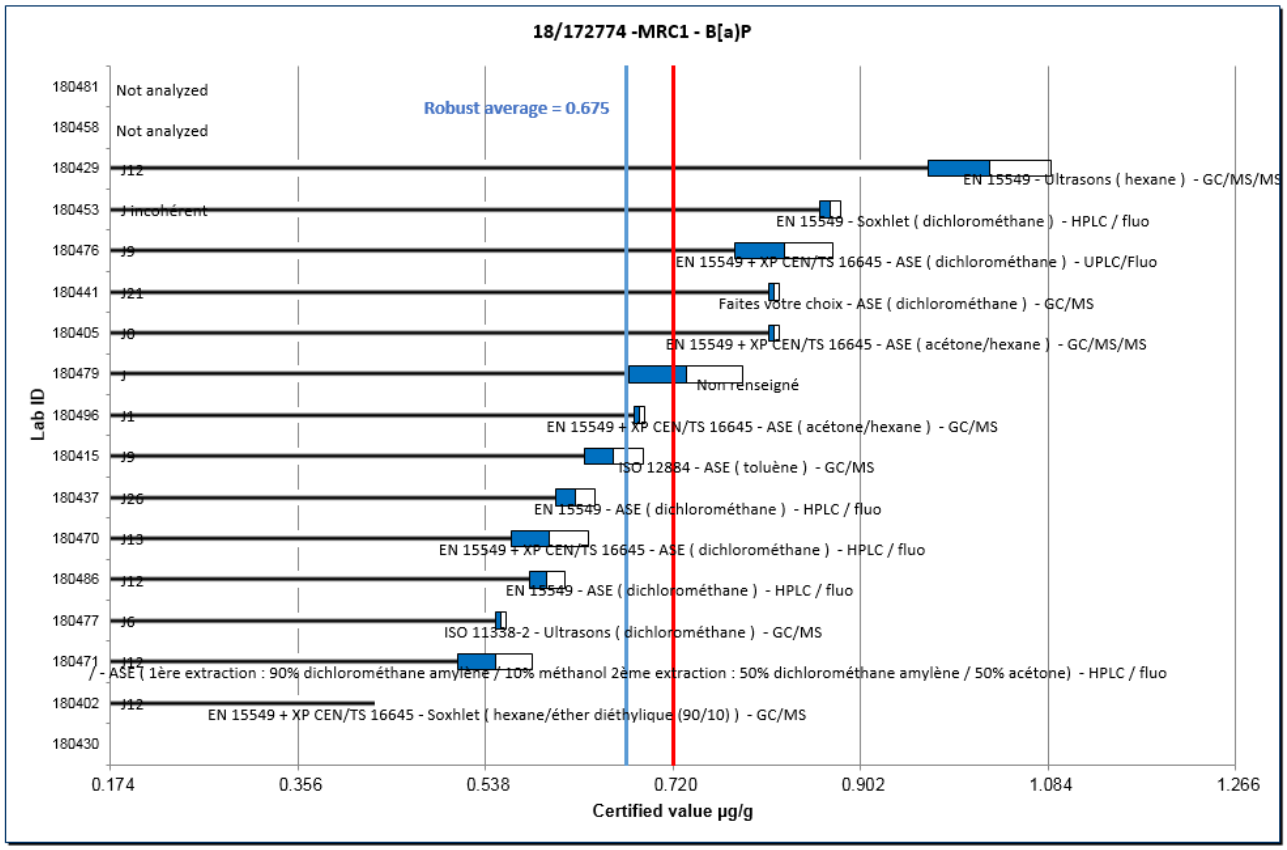

Figure 2: B[a]P participants' dispersion on CRM analysis

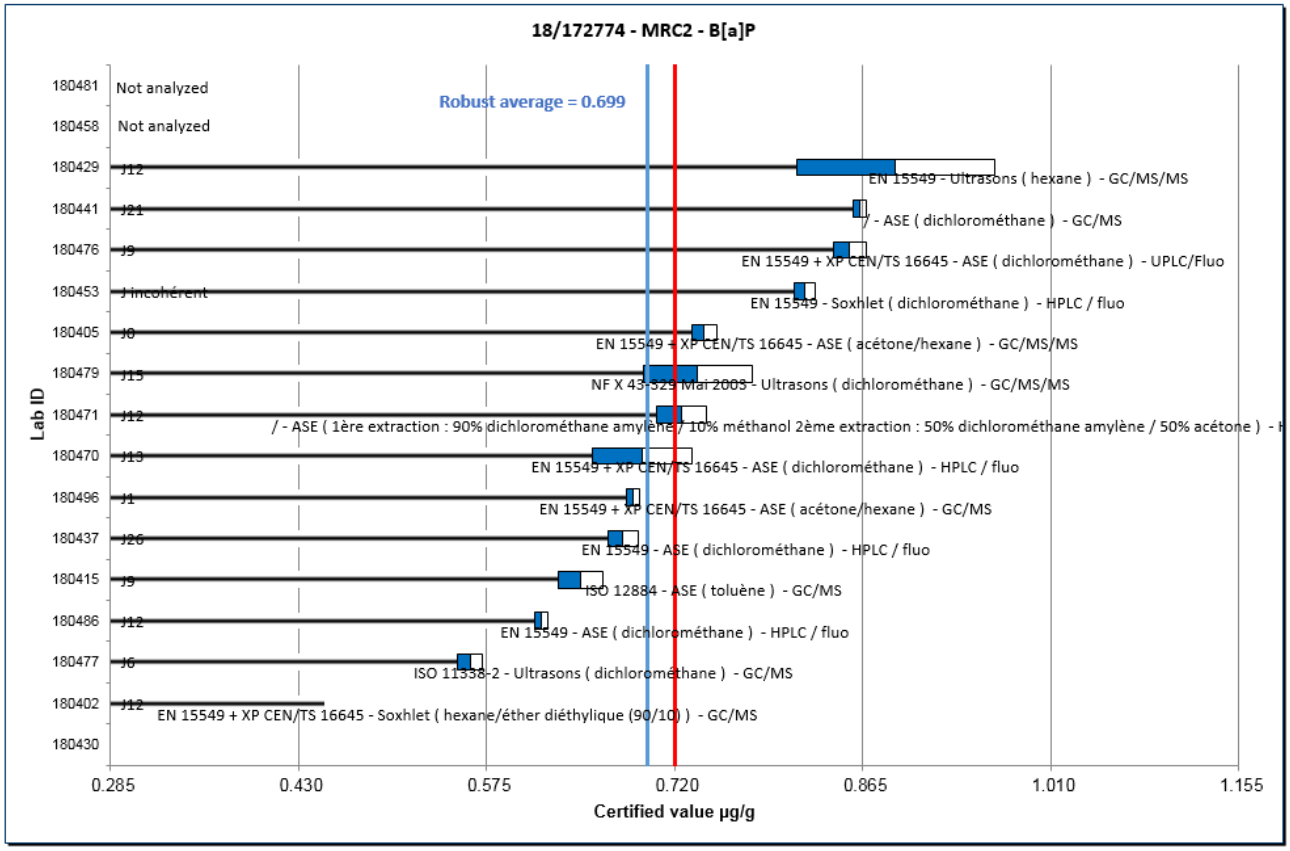

Figure 3 : B[a]P participants' dispersion on CRM analysis.

8.2 Field sample filters

The equivalent atmospheric concentration ranges of the field sample filters provided to the participants are presented in the Table 9 below for high volume samplers (HVS, 30 m^3 h^{-1}) and low volume samplers (LVS, 1 m^3 h^{-1}).

Table 10 : Equivalent concentration ranges of filter 1 and 2

Test materials	Equivalent atmospheric concentration ranges
18/172774_F1	HVS $\Rightarrow$ 0.50 ng m^{-3} / LVS $\Rightarrow$ 15.0 ng m^{-3}
18/172774_F2	HVS $\Rightarrow$ 0.37 ng m^{-3} / LVS $\Rightarrow$ 11.2 ng m^{-3}

Results obtained for the analysis of filter 1 and 2 before and after statistical analysis are presented in Table 11 and Table 12.

Table 11 : 18/172774_F1, raw data and robust analysis of the results.

	Raw data					Robust analysis								
Substances	**Number of laboratories**	**x (ng filter^{-1})**	**s (ng filter^{-1})**	**CV_R (%)**	**CV_{rep} (%)**	**x* (ng filter^{-1})**	**s* (ng filter^{-1})**	**σpt**	**u_{x*}**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2, %)**
B[a]A	16	395.842	297.791	75.2%	3.1%	333.110	90.567	90.567	28.302	90.481	90.827	7.923	55%	80% [3]
B[a]P	17	406.869	260.980	64.1%	2.2%	359.513	52.770	52.770	15.998	52.600	53.275	8.454	30%	50% [4]
B[b]F	15	469.278	315.125	67.2%	3.5%	406.107	129.771	136.362	41.883	129.692	130.006	9.030	64%	60% [1]
B[g,h,i]P	16	277.093	157.052	56.7%	4.3%	273.282	69.459	69.459	21.706	69.296	69.925	9.356	51%	68% [1]
B[j]F	9	210.503	139.677	66.4%	1.8%	251.412	104.365	113.063	43.486	104.340	104.441	4.574	83%	-
B[k]F	15	233.546	229.123	98.1%	3.2%	169.848	35.751	37.567	11.539	35.730	35.815	2.453	42%	80% [1]
DB[a,h]A	15	71.423	261.493	366.1%	11.3%	38.085	14.488	15.224	4.676	14.460	14.567	1.760	76%	106% [1]
Flt	16	261.222	196.940	75.4%	2.7%	218.603	63.598	63.598	19.875	63.552	63.738	4.864	58%	-
Ind[1,2,3-cd]P	16	332.126	204.912	61.7%	3.5%	279.325	72.129	72.129	22.540	71.900	72.813	11.494	52%	66% [1]
Phen	13	249.577	534.011	214.0%	3.2%	101.861	39.338	41.635	13.638	39.284	39.500	4.122	78%	-
Sum of BF	16	842.493	558.745	66.32%	3.15%	779.518	300.907	300.907	94.033	300.780	301.287	17.469	39%	

In red: larger uncertainty from than the maximum one authorised.

[3] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[4] 2004/107/EC European Directive.

Table 12 :18/172774_F2, raw data and robust analysis of the results.

	Raw data					Robust analysis								
Substances (ng filter^{-1})	**Number of laboratories**	**x (ng filter^{-1})**	**s (ng filter^{-1})**	**CV_R (%)**	**CV_{rep} (%)**	**x* (ng filter^{-1})**	**s* (ng filter^{-1})**	**σpt**	**u_{x*}**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2, %)**
B[a]A	16	227.322	195.578	86.0%	3.8%	184.731	55.711	55.711	17.410	55.620	55.985	6.383	61%	80% [5]
B[a]P	17	362.067	406.105	112.2%	4.8%	268.781	59.506	59.506	18.040	59.424	59.750	6.233	44%	50% [6]
B[b]F	15	369.096	346.712	93.9%	5.8%	312.075	93.016	97.741	30.021	92.922	93.294	8.322	60%	60% [1]
B[g,h,i]P	16	233.794	187.374	80.1%	2.2%	221.114	59.937	59.937	18.730	59.869	60.132	5.613	54%	68% [1]
B[j]F	9	173.994	111.770	64.2%	1.3%	212.106	89.263	96.702	37.193	89.252	89.295	2.771	84%	-
B[k]F	15	263.973	382.219	144.8%	7.7%	136.600	38.040	39.972	12.277	38.007	38.141	3.194	56%	80% [1]
DB[a,h]A	14	29.014	12.136	41.8%	3.7%	31.364	10.119	10.669	3.381	10.098	10.182	1.304	65%	106% [1]
Flt	16	196.109	255.671	130.4%	6.6%	135.341	38.256	38.256	11.955	38.192	38.448	4.425	57%	-
Ind[1,2,3-cd]P	16	267.294	197.123	73.7%	2.4%	235.803	68.860	68.860	21.519	68.752	69.169	7.586	59%	66% [1]
Phen	14	142.235	294.997	207.4%	9.8%	65.488	23.627	24.911	7.893	23.575	23.782	3.129	73%	-
Sum of BF	16	754.531	675.533	89.5%	5.7%	617.467	243.958	243.958	76.237	243.875	244.209	12.763	79%	

[5] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[6] 2004/107/EC European Directive.

Results on the analysis of Filters 1, 2 and 3:

Results obtained for B[a]P are presented in Table 12 and Figures 4 and 5 and the full results including all PAHs are available in the Appendixes 3, 4 and 5.

Overall, Z-score results obtained for Filters 1 and 2 were satisfactory for B[a]P except for laboratories 180458, 180481 (2 and 1 results non-acceptable, respectively) and 180402 (warning result for Filter 1). Note that all results submitted for both, Filter 1 and 2, by laboratory 180458 were not acceptable (z-scores >3 or <-3). The samples for this laboratory have been stopped by customs for 5 days and unfortunately, the storage temperature in the cool box exceeded 5°C (up to 25°C). However, this event did not explain the significant differences in the results obtained. In addition, it was difficult to conclude about any systematic error (dilution factor about 10 maybe). Laboratory 180430 obtained also 2 z-scores (B[k]F and sum of benzofluoranthenes) showing the need of corrective actions (z-scores >3 or <-3) Laboratory 180486 had for both filters, non-acceptable results for Ind and warning ones for B[g,h,i]P. Again, laboratory 180429 only provided results for B[a]P. Finally, no method effect, due to the extraction or analytical procedures, could be observed.

Results showed that intra-laboratory dispersions were higher for Laboratories 180430, 180476 and 180486 for 1 on the 10 studied PAHs; 180470 for 1 to 3/10 PAHs; 180471 for 4/10 PAHs; and 180458 for all the 10 PAHs.

Finally, all participants reported results below quantification limit for Filter 3 (blank filter) for all PAHs except 2 laboratories (180458 and 180471) (Appendix 5).

Again, the results obtained from this ILC exercise permitted to evaluate the analytical uncertainties of measurements of the PAHs (Tables 10 and 11). **Except for B[b]F (64 instead of 60%) all results obtained for the analysis of filter samples complied with the maximum uncertainties allowed.**

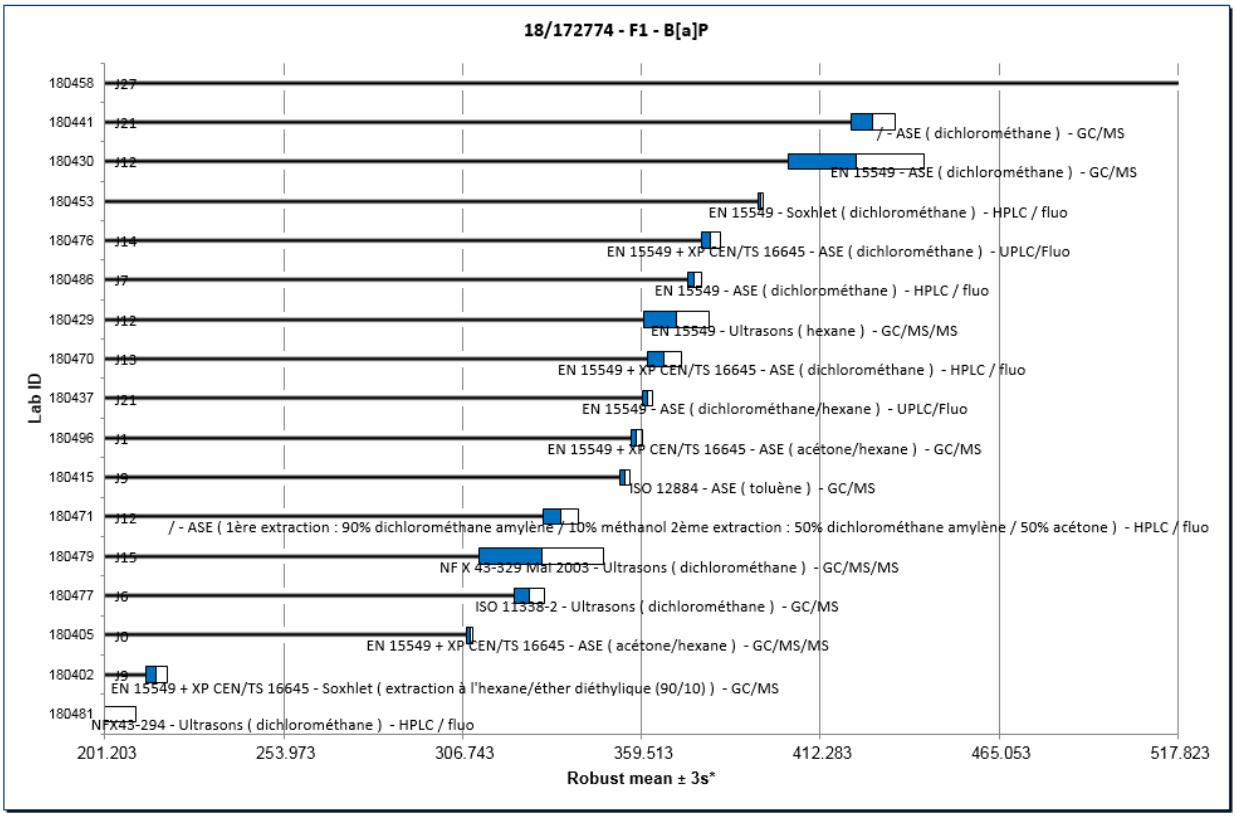

Figure 4 : B[a]P participants' dispersion on filter 1 analysis.

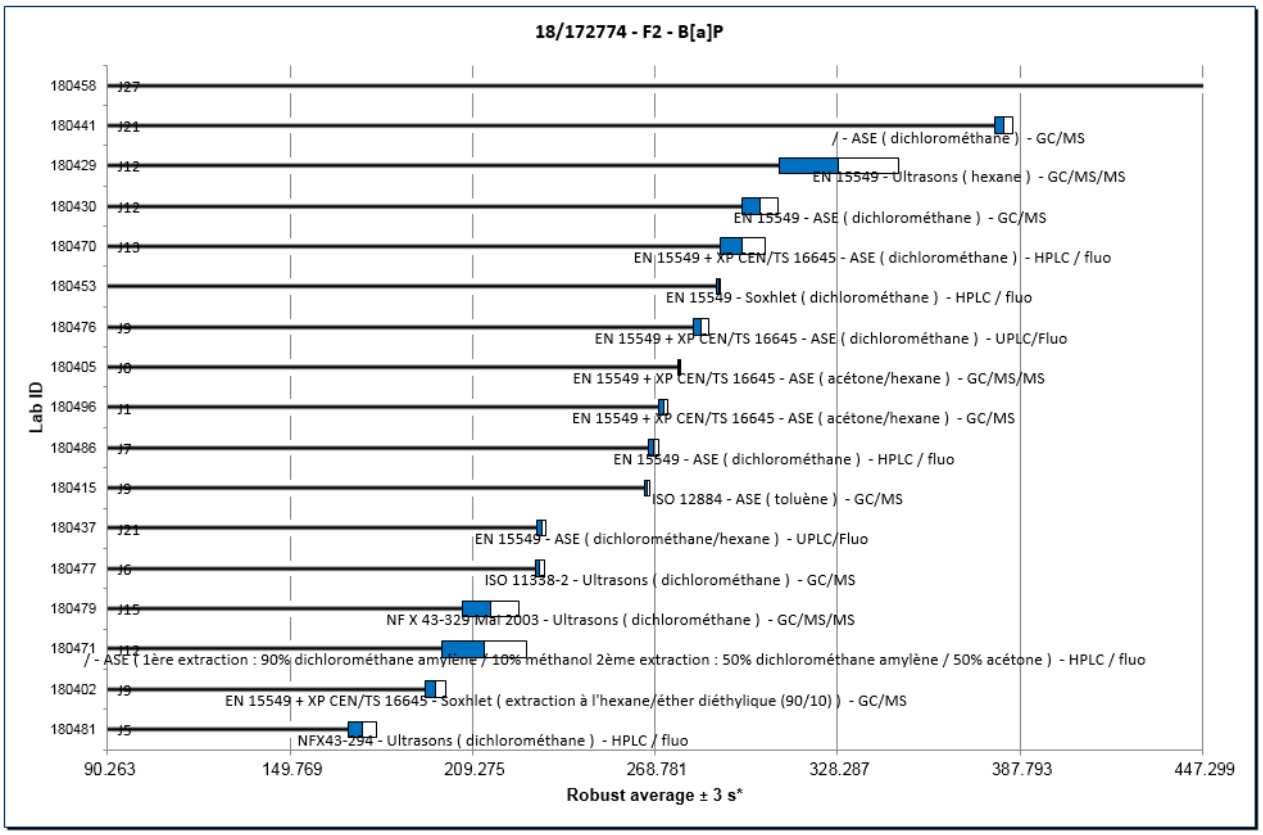

Figure 5 : B[a]P participants' dispersion on filter 2 analysis.

Table 13 : B[a]P participants' results on filter analyses.

Laboratory	Benzo[a]pyrene - Filter 1			Benzo[a]pyrene - Filter 2		
	x (ng filter^{-1})	s_r (%)	Z-score	x (ng filter^{-1})	s_r (%)	Z-score
180402	216.443	1.51%	-2.71	197.308	1.67%	-1.20
180405	308.975	0.32%	-0.96	276.500	0.11%	0.13
180415	354.618	0.43%	-0.09	266.260	0.37%	-0.04
180429	369.925	2.57%	0.20	328.725	5.90%	1.01
180430	422.883	4.76%	1.20	302.950	1.94%	0.57
180437	361.250	0.42%	0.03	231.750	0.65%	-0.62
180441	427.908	1.54%	1.30	382.523	0.80%	1.91
180453	394.725	0.20%	0.67	289.625	0.22%	0.35
180458	1 391.500	7.32%	19.56	1 925.438	51.08%	27.84
180470	366.250	1.36%	0.13	297.250	2.48%	0.48
180471	335.870	1.53%	-0.45	213.243	6.46%	-0.93
180476	380.025	0.75%	0.39	283.775	0.86%	0.25
180477	326.473	1.35%	-0.63	231.263	0.64%	-0.63
180479	330.103	5.56%	-0.56	215.123	4.32%	-0.90
180481	196.500	7.15%	-3.09	173.500	2.68%	-1.60
180486	375.150	0.54%	0.30	268.400	0.60%	-0.01
180496	358.185	0.43%	-0.03	271.510	0.52%	0.05

8.3 Certified solutions

The equivalent atmospheric concentration ranges of the certified solutions provided to the participants are presented in Table 14 for high volume samplers (HVS, 30 m^3 h^{-1}) and low volume samplers (LVS, 1 m^3 h^{-1}).

Table 14 : Equivalent concentration ranges of the certified solutions

Test materials	Atmospheric concentration ranges for B[a]P
18/172774_S1	Equivalent to 0.55 ng m^{-3} for B[a]P using HVS and 16.66 using LVS
18/172774_S2	Equivalent to 0.55 ng m^{-3} for B[a]P using HVS and 16.66 using LVS
18/172774_S3	HVS $\Rightarrow$ 0.02 ng m^{-3} / LVS $\Rightarrow$ 0.47 ng m^{-3}

Results obtained for the analysis of certified solutions 1 to 3 before and after statistical analysis are presented in Table 15, and 16.

Table 15 : 18/172774_S1, raw data and robust analysis results

	Raw data						Robust analysis									
Substances (ng ml^{-1})	**Number of laboratories**	**Certified value**	**x**	**s**	**CV_R (%)**	**CV_{rep} (%)**	**x***	**s***	**σpt**	**$u_{X\ CRM}$**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2)**	**Mean recoveries**
B[a]A	15	290.75	253.424	82.289	32.5%	1.8%	276.501	41.885	41.885	13.518	41.837	42.027	3.989	30%	80% [7]	95%
B[a]P	17	399.39	462.395	386.027	83.5%	4.4%	381.293	61.486	61.486	18.641	61.346	61.905	8.300	32%	50% [8]	95%
B[b]F	15	551.94	797.511	947.391	118.8 %	2.1%	551.053	97.481	97.481	31.462	97.412	97.690	7.364	35%	60% [1]	100%
B[g,h,i]P	16	399.25	508.581	617.222	121.4 %	10.7%	396.708	87.581	87.581	27.369	87.500	87.820	7.498	44%	68% [1]	99%
B[j]F	9	266.55	262.685	174.674	66.5%	1.0%	316.491	137.691	137.691	57.371	137.678	137.731	3.825	87%	-	119%
B[k]F	15	281.43	383.815	338.736	88.3%	2.7%	302.285	90.125	90.125	29.088	90.080	90.261	5.716	60%	80% [1]	107%
DB[a,h]A	15	89.28	195.348	430.499	220.4 %	4.3%	88.490	22.237	22.237	7.177	22.221	22.285	1.679	50%	106% [1]	99%
Flt	16	769.37	901.287	756.436	83.9%	4.5%	741.027	59.867	59.867	18.709	59.696	60.379	9.057	16%	-	96%
Ind[1,2,3-cd]P	16	722.46	793.800	551.590	69.5%	6.9%	656.039	132.209	132.209	41.315	132.016	132.788	14.303	40%	66% [1]	91%
Phen	15	1517.12	1723.553	1027.269	59.6%	6.0%	1504.711	208.920	208.920	67.429	208.476	210.246	27.225	28%	-	99%
Sum of BF	16	1099.92	1378.171	1209.231	87.74 %	1.96%	1115.113	330.020	330.020	103.131	329.954	330.215	13.106	59%		

[7] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[8] 2004/107/EC European Directive.

Table 16 : 18/172774_S2, raw data and robust analysis results

	Raw data						Robust analysis									
Substances (ng ml^{-1})	**Number of laboratories**	**Certified value**	**x**	**s**	**CV_R (%)**	**CV_{rep} (%)**	**x***	**s***	**σpt**	**$u_{X\ CRM}$**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2)**	**Mean recoveries**
B[a]A	14	290.75	334.318	418.697	125.2%	1.8%	277.069	48.978	48.978	16.362	48.940	49.092	3.859	35%	80% [9]	95%
B[a]P	16	399.39	452.516	455.836	100.7%	2.4%	377.430	77.370	77.370	24.178	77.329	77.494	5.056	41%	50% [10]	95%
B[b]F	15	551.94	755.962	790.204	104.5%	2.1%	557.140	116.709	116.709	37.668	116.642	116.910	7.903	42%	60% [1]	101%
B[g,h,i]P	15	399.25	455.471	642.488	141.1%	9.0%	400.315	61.166	61.166	19.741	61.076	61.423	6.519	31%	68% [1]	100%
B[j]F	9	266.55	263.923	177.761	67.4%	1.4%	321.010	149.604	149.604	62.335	149.576	149.688	5.794	93%	-	120%
B[k]F	14	281.43	336.481	303.415	90.2%	1.9%	286.852	66.586	66.586	22.245	66.565	66.649	3.356	46%	80% [1]	102%
DB[a,h]A	15	89.28	146.896	246.810	168.0%	4.9%	92.429	20.815	20.815	6.718	20.743	21.030	3.463	46%	106% [1]	104%
Flt	15	769.37	878.483	906.871	103.2%	2.1%	727.511	57.295	57.295	18.492	56.932	58.372	12.888	16%	-	95%
Ind[1,2,3-cd]P	15	722.46	943.119	1241.043	131.6%	4.4%	678.025	118.992	118.992	38.404	118.872	119.352	10.692	35%	66% [1]	94%
Phen	14	1517.12	1812.868	1703.671	94.0%	4.1%	1517.906	135.203	135.203	45.168	134.985	135.857	15.370	18%	-	100%
Sum of BF	15	1099.92	1158.301	1066.691	92.09%	1.80%	1070.639	283.908	283.908	91.631	283.805	284.220	15.354	53%		

[9] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[10] 2004/107/EC European Directive.

Table 17 : 18/172774_S3, raw data and robust analysis results

	Raw data						Robust analysis									
Substances (ng ml^{-1})	**Number of laboratories**	**Certified value**	**x**	**s**	**CV_R (%)**	**CV_{rep} (%)**	**x***	**s***	**σpt**	**$u_{X\ CRM}$**	**S_L**	**S_R**	**S_r**	**U (k=2, %)**	**Maximum uncertainties allowed (k=2)**	**Mean recoveries**
B[a]A	14	8.14	25.152	67.421	268.06%	3.80%	7.907	2.003	2.003	0.669	1.993	2.034	0.405	51%	80% [11]	97%
B[a]P	15	11.25	28.291	69.776	246.64%	7.08%	11.038	2.244	2.244	0.724	2.186	2.411	1.015	44%	50% [12]	98%
B[b]F	14	15.53	15.970	3.486	21.83%	4.25%	15.331	2.639	2.639	0.882	2.623	2.689	0.596	35%	60% [1]	99%
B[g,h,i]P	15	11.32	23.655	45.210	191.12%	5.50%	11.422	2.262	2.262	0.730	2.226	2.363	0.795	41%	68% [1]	101%
B[j]F	7	7.78	11.534	11.380	98.66%	1.86%	9.638	7.047	7.047	3.330	7.047	7.050	0.213	146%	-	124%
B[k]F	13	7.9	43.953	139.918	318.33%	6.94%	8.296	2.364	2.364	0.820	2.354	2.397	0.452	58%	80% [1]	105%
DB[a,h]A	12	2.47	9.154	13.306	145.35%	6.03%	2.809	0.902	0.902	0.326	0.895	0.924	0.230	66%	106% [1]	114%
Flt	15	21.69	71.483	203.512	284.70%	2.71%	20.626	2.525	2.525	0.815	2.511	2.568	0.540	25%	-	95%
Ind[1,2,3-cd]P	15	21.55	40.238	88.478	219.89%	4.55%	18.598	2.935	2.935	0.947	2.854	3.166	1.371	34%	66% [1]	86%
Phen	14	42.71	113.461	274.274	241.74%	4.78%	42.842	6.504	6.504	2.173	6.432	6.716	1.933	31%	-	100%
Sum of BF	14	31.22	124.965	379.298	303.5%	4.7%	28.202	8.796	8.796	2.938	8.786	8.824	0.818	63%		

[11] CEN/TS 16645: Ambient air — Method for the measurement of benzo[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

[12] 2004/107/EC European Directive.

Results on the analysis of certified solutions 1, 2 and 3:

Results obtained for B[a]P are presented in Table 18 and Figures 6, 7 and 8 and the full results including all PAHs are available in the Appendices 6 to 8.

Z-score results obtained for certified solutions 1 to 3 were satisfactory for most of the participants and PAHs. No significant differences between results for both same solutions, 1 and 2, could be highlighted.

Laboratory 180458 and 180496 had not acceptable or warning results for most of the substances on solutions 1 and 2 and especially B[a]P. These same participants got also bad results on solution 3 for few compounds and laboratory 180430 for all the PAHs. In total, laboratory 180458 obtained 18 z-scores requiring corrective actions and 1 z-score requiring a monitoring action; laboratory 180496, 8 z-scores requiring corrective actions and 7 z-score requiring a monitoring action and laboratory 180430 provided 7 results equal to a limit of quantification and got 10 z-scores requiring corrective actions. The test materials for this last laboratory have been stopped by customs for 5 days and the storage temperature in the cool box exceeded 5°C (up to 25°C). However, this did not explain the significant differences in the results obtained. All these participants have to improve their analytical method to get better and comparable results.

Again, laboratory 180429 only provided results for B[a]P and several results from laboratories 180402, 180405, 180415, 180430 180470, 180476 and 180477, were submitted as equal to the quantification limit or 0 for several PAHs and were excluded from the statistical analysis.

Intra-laboratory dispersions were higher for laboratories 180430, 180437, 180441, 180481 and 180479 for 1 on the 10 studied PAHs; 180470 and 180470 for up to 3/10 PAHs and 180458 up to 9/10 PAHs.

Zeta-scores for many laboratories were not acceptable or requiring a preventive action. This result shows again that uncertainties are not well evaluated by the laboratories especially for 180402, 180430, 180458, 180476, 180481 and 180496 for which uncertainties on the measurement of PAHs are probably not well calculated. Again, laboratories are invited to follow the guidelines provided by the LCSQA (Albinet, 2015) to evaluate their uncertainties of analysis on such substances.

Finally, all results obtained for the analysis of these certified solutions complied with the maximum uncertainties allowed by the 2004/107/EC European Directive and the CEN/TS 16645 for the ambient air particle samples (Tables 14, 15 and 16) showed previously.

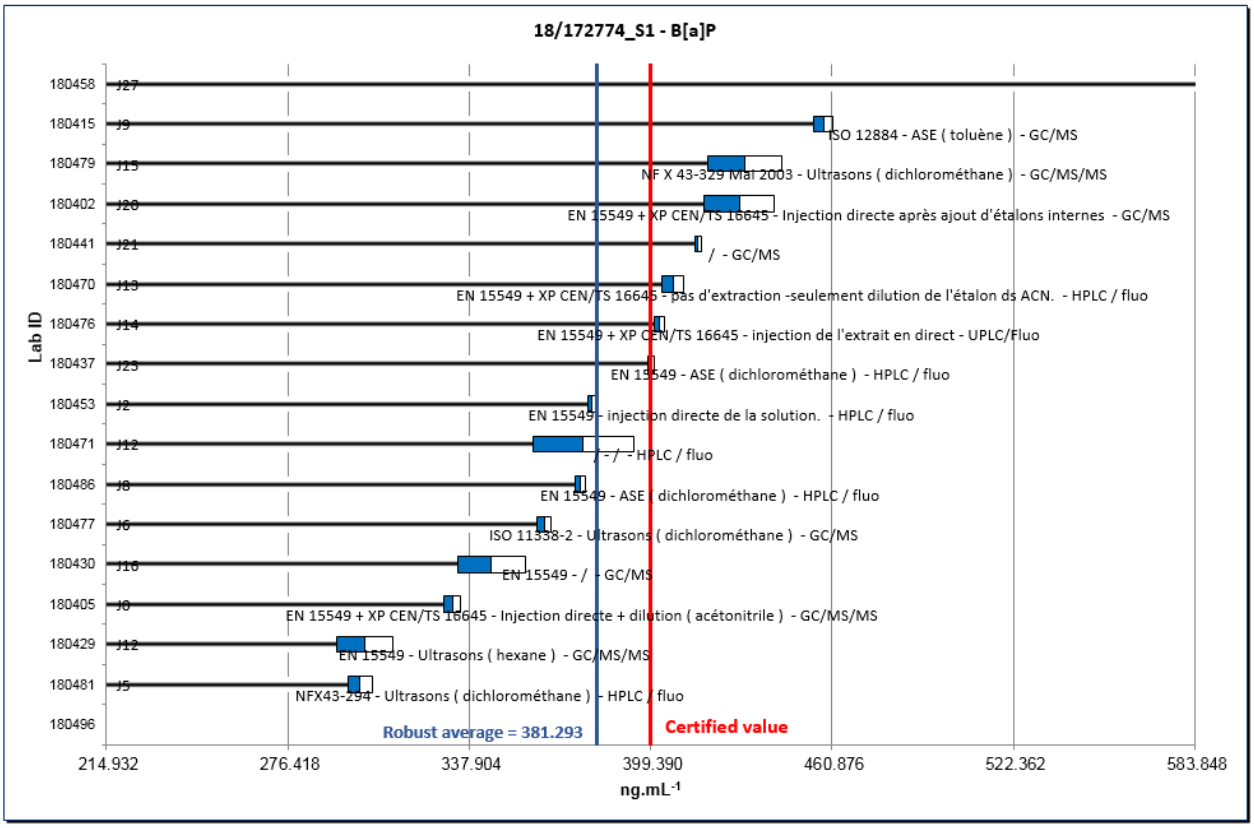

Figure 6 : B[a]P participants' dispersion on S1 analysis.

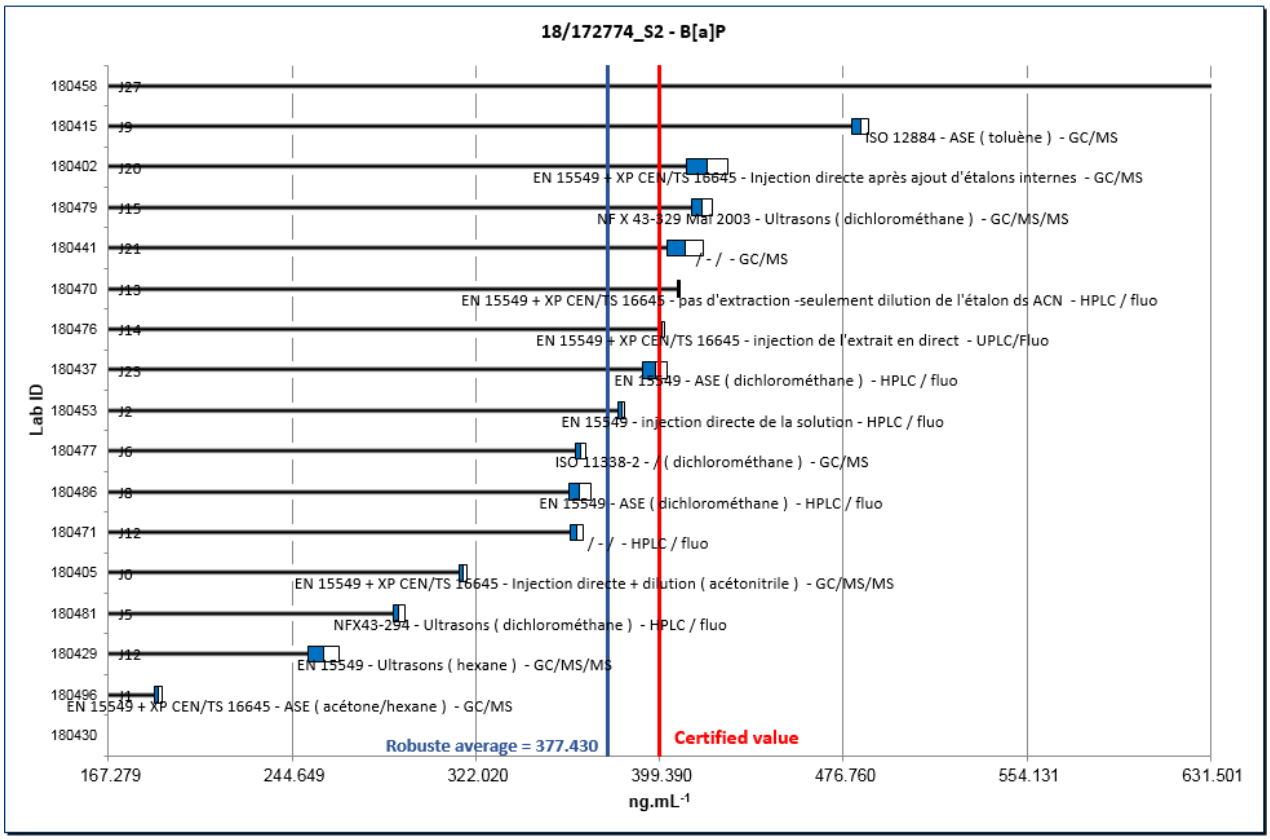

Figure 7 : B[a]P participants' dispersion on S2 analysis0

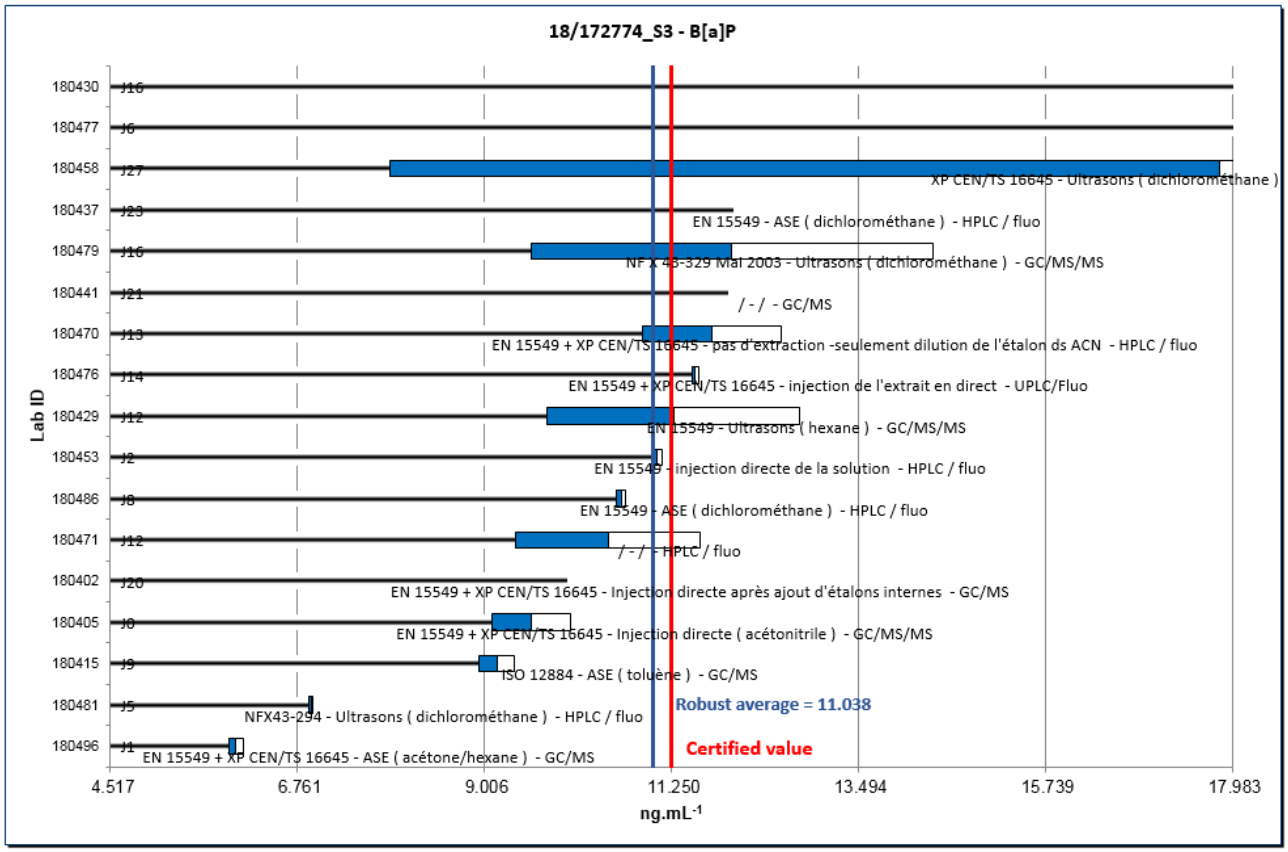

Figure 8 : B[a]P participants' dispersion on S3 analysis.

Table 18 : B[a]P participants' results on standard solution analyses

Laboratory	Benzo[a]pyrene - Solution 1				Benzo[a]pyrene - Solution 2				Benzo[a]pyrene - Solution 3			
	x (ng ml^{-1})	s_r (%)	Z-score	Zeta score	x (ng ml^{-1})	s_r (%)	Z-score	Zeta score	x (ng ml^{-1})	s_r (%)	Z-score	Zeta score
180402	429.475	2.77%	0.49	1.27	419.325	2.09%	0.26	0.86	~~<10.000~~	~~0.00%~~	NC	-2.28
180405	332.175	0.86%	-1.09	-1.57	316.725	0.54%	-1.07	-2.02	9.575	4.93%	-0.75	-1.38
180415	458.000	0.74%	0.95	0.79	484.000	0.74%	1.09	1.08	9.158	2.29%	-0.93	-1.41
180429	302.550	3.20%	-1.57	-9.70	257.875	2.56%	-1.83	UNS	11.278	13.42%	0.01	0.12
180430	345.543	3.36%	-0.88	-4.82	~~<48.400~~	~~0.00%~~	NC	UNS	298.755	3.01%	128.09	85.35
180437	399.500	0.25%	0.00	0.00	397.500	1.26%	-0.02	-0.06	12.000	0.00%	0.33	0.76
180441	415.548	0.31%	0.26	0.76	410.268	1.81%	0.14	0.52	11.930	0.00%	0.30	1.17
180453	379.520	0.34%	-0.32	-1.44	383.455	0.36%	-0.21	-1.15	11.083	0.55%	-0.07	-0.47
180458	1 941.180	50.44%	25.08	1.99	2 175.410	25.36%	22.95	2.33	17.828	55.80%	2.93	1.05
180470	406.928	0.86%	0.12	0.33	407.333	0.10%	0.10	0.35	11.738	7.10%	0.22	0.41
180471	376.625	4.56%	-0.37	-0.81	364.720	0.72%	-0.45	-1.27	10.490	10.55%	-0.34	-0.99
180476	402.273	0.43%	0.05	0.28	400.205	0.32%	0.01	0.08	11.540	0.39%	0.13	1.27
180477	363.358	0.67%	-0.59	-0.96	366.260	0.64%	-0.43	-0.87	~~<20.000~~	~~0.00%~~	NC	4.35
180479	431.300	2.92%	0.52	0.44	417.233	1.06%	0.23	0.26	11.980	20.08%	0.33	0.37
180481	301.000	1.36%	-1.60	-2.35	289.750	0.77%	-1.42	-2.72	6.925	0.30%	-1.93	-4.50
180486	375.600	0.44%	-0.39	-0.36	365.875	1.20%	-0.43	-0.52	10.650	0.54%	-0.27	-0.32
180496	200.135	1.32%	-3.24	-18.52	188.433	0.80%	-2.73	-19.77	6.023	1.43%	-2.33	-20.48

9. CONCLUSIONS

A new ILC for the analysis of PAHs in ambient air was organized in 2018 with seventeen European participants involved. Three liquid certified standard solutions, two PM_{10} field sample filters, one laboratory blank filter and a certified solid reference material have been sent as test materials.

Overall, a great improvement in the results have been observed by comparison to the results obtained for both last ILC organized in 2014 and 2015 (Verlhac, 2014, Verlhac and Albinet, 2015). Except for the solid CMR, all the results obtained complied with the maximum allowed uncertainty, including B[a]P, showing that the dispersion of the laboratories was clearly better.

However, some laboratories have really to improve their analytical procedures because they do not have reliable/acceptable results for most of the tested materials and PAHs (180430, 180458 and in a lesser extent, 18096, only for the certified solutions). In addition, laboratories 180458 and 180481 did not provide any results for the solid CMR and laboratory 180429 only provided results for B[a]P for all materials.

Finally, based on the zeta score the uncertainties of measurement are still not well evaluated by most of the participants. Thus, laboratories are invited to follow the guidelines provided by the LCSQA (Albinet, 2015) to evaluate their uncertainties of analysis for PAHs.

10. REFERENCES

Albinet, A., 2015. Guide méthodologique pour la surveillance des Hydrocarbures Aromatiques Polycycliques (HAP) dans l'air ambiant et dans les dépôts. LCSQA-INERIS: http://www.lcsqa.org/system/files/drc-15-152345-00912a_metrologie_hap_guide_methodologique_hap_2015_vf.pdf.

CEN (European Comittee for Standardization), EN 15549:2008–Air Quality - Standard Method for the Measurement of the Concentration of Benzo[a]pyrene in Air. In CEN: Brussels (Belgium), 2008.

CEN (European Comittee for Standardization), TS-16645: 2014- Ambient air – Method for the measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene et benzo[ghi]perylene. In CEN: Brussels (Belgium), 2014.

European Official Journal, Directive 2004/107/CE of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. In *Official Journal*, 2004; Vol. L23, pp 3-16.

Verlhac, S., 2014. Comparaison interlaboratoires sur l'analyse des HAP dans l'air ambiant. LCSQA: https://www.lcsqa.org/system/files/rapport/drc-14-144350-09750a_lcsqa_cil_hap_final.pdf.

Verlhac, S. and Albinet, A., 2015. European Interlaboratory Comparison for the analysis of PAH in ambient air. LCSQA: http ://www.lcsqa.org/rapport/2015/ineris/european-interlaboratory-comparison-for-the-analysis-of-pah-in-ambient-air.

APPENDICES

Appendix	Title	Number of pages
1	Detailed results on CRM 1	2
2	Detailed results on CRM 2	2
3	Detailed results on filter 1	2
4	Detailed results on filter 2	2
5	Detailed results on blank filter	1
6	Detailed results on solution 1	2
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APPENDIX 1: DETAILED RESULTS ON 18/172774_MRC1 (CRM)

Lab ID	Benzo_a_anthracene				Benzo_a_pyrene				Benzo_b_fluoranthene				Benzo_g,h,i_perylene				Benzo_j_fluoranthene				Benzo_k_fluoranthene			
	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z
180402	0.563	0.005	0.89%	-1.23	0.430	0.000	0.00%	-1.59	1.018	0.010	0.94%	-0.92	0.885	0.017	1.96%	-1.72	0.410	0.008	1.99%	-1.11	0.403	0.005	1.24%	-2.70
180405	1.140	0.000	0.00%	0.81	0.818	0.005	0.61%	0.54	1.828	0.019	1.04%	0.93	1.500	0.018	1.22%	-0.51	NA	NA	NA		0.763	0.010	1.26%	0.93
180415	0.813	0.010	1.18%	-0.34	0.663	0.029	4.34%	-0.32	1.455	0.006	0.40%	0.08	1.728	0.019	1.10%	-0.06	~~0.000~~	~~0.000~~	-	NC	0.718	0.088	12.33%	0.48
180429	NA	NA	NA		1.028	0.060	5.81%	1.69	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	0.360	0.012	3.21%	-1.94	0.150	0.008	5.44%	-3.13	NA	NA	NA		0.150	0.000	0.00%	-3.16	NA	NA	NA		0.625	0.054	8.71%	-0.45
180437	0.890	0.012	1.30%	-0.07	0.625	0.019	3.06%	-0.52	1.405	0.010	0.71%	-0.03	1.375	0.038	2.75%	-0.76	0.630	0.058	9.26%	-0.39	0.603	0.005	0.83%	-0.68
180441	1.035	0.006	0.56%	0.44	0.818	0.005	0.61%	0.54	1.738	0.013	0.72%	0.73	1.843	0.005	0.27%	0.16	0.835	0.019	2.29%	0.28	0.750	0.028	3.77%	0.81
180453	1.185	0.031	2.62%	0.97	0.873	0.010	1.10%	0.84	2.163	0.015	0.69%	1.70	2.125	0.035	1.65%	0.72	1.000	0.008	0.82%	0.81	0.755	0.006	0.76%	0.86
180458	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180470	0.990	0.024	2.47%	0.28	0.600	0.037	6.24%	-0.66	1.343	0.124	9.23%	-0.18	1.718	0.040	2.35%	-0.08	0.668	0.042	6.28%	-0.27	0.630	0.026	4.10%	-0.40
180471	1.213	0.147	12.09%	1.07	0.548	0.036	6.56%	-0.95	1.628	0.172	10.55%	0.47	1.545	0.079	5.08%	-0.42	NA	NA	NA		0.540	0.020	3.70%	-1.31
180476	1.755	0.051	2.89%	2.98	0.828	0.047	5.70%	0.59	1.790	0.066	3.68%	0.85	1.628	0.022	1.36%	-0.26	1.670	0.022	1.29%	3.00	0.645	0.006	0.90%	-0.25
180477	0.715	0.013	1.81%	-0.69	0.553	0.005	0.90%	-0.92	1.293	0.010	0.74%	-0.29	1.338	0.010	0.72%	-0.83	NA	NA	NA		0.610	0.000	0.00%	-0.61
180479	0.960	0.154	16.00%	0.18	0.733	0.055	7.51%	0.07	2.363	0.099	4.20%	2.16	1.855	0.042	2.27%	0.19	NA	NA	NA		~~<0.7~~	~~0.022~~	~~3.09%~~	NC
180481	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180486	0.740	0.008	1.10%	-0.60	0.598	0.017	2.86%	-0.67	1.138	0.079	6.94%	-0.65	0.345	0.019	5.55%	-2.78	0.413	0.010	2.32%	-1.10	0.540	0.012	2.14%	-1.31
180496	0.813	0.010	1.18%	-0.34	0.688	0.005	0.73%	-0.18	1.970	0.027	1.37%	1.26	1.553	0.017	1.10%	-0.41	0.658	0.005	0.76%	-0.30	0.663	0.015	2.26%	-0.08

Lab ID	Dibenzo_a,h_anthracene				Fluoranthene				Indeno_1,2,3_c,d_pyrene				Phenanthrene				Sum_BF			
	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z
180402	0.185	0.006	3.12%	0.05	3.373	0.033	0.98%	-1.74	0.783	0.010	1.22%	-0.97	1.295	0.017	1.34%	-1.75	1.830	0.016	0.89%	-1.16
180405	0.270	0.000	0.00%	0.89	3.950	0.008	0.21%	-0.96	1.265	0.006	0.46%	0.66	1.820	0.008	0.45%	-0.77	2.590	0.016	0.63%	-0.29
180415	0.208	0.010	4.61%	0.27	4.340	0.014	0.33%	-0.44	1.003	0.039	3.94%	-0.23	1.960	0.014	0.72%	-0.51	2.173	0.092	4.22%	-0.77
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180430	0.020	0.000	0.00%	-1.58	1.160	0.018	1.57%	-4.69	0.133	0.005	3.77%	-3.17	0.473	0.049	10.28%	-3.30	1.520	0.101	6.62%	-1.52
180437	NA	NA	NA		4.100	0.045	1.11%	-0.76	0.890	0.024	2.75%	-0.61	1.915	0.019	1.00%	-0.59	2.638	0.049	1.87%	-0.23
180441	0.175	0.006	3.30%	-0.05	5.083	0.080	1.57%	0.55	1.208	0.022	1.84%	0.47	2.355	0.006	0.25%	0.23	3.323	0.038	1.14%	0.56
180453	0.185	0.006	3.12%	0.05	5.138	0.024	0.46%	0.63	1.385	0.031	2.24%	1.07	2.648	0.010	0.36%	0.78	3.918	0.015	0.38%	1.24
180458	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180470	~~<0.2~~	~~0.000~~	~~0.00%~~	NC	4.670	0.078	1.67%	0.00	1.185	0.061	5.18%	0.39	2.430	0.307	12.65%	0.38	2.640	0.129	4.89%	-0.23
180471	0.033	0.005	15.38%	-1.46	4.105	0.190	4.63%	-0.76	0.778	0.021	2.65%	-0.99	2.248	0.127	5.67%	0.03	2.168	0.184	8.47%	-0.77
180476	~~<0.5~~	~~0.000~~	~~0.00%~~	NC	4.540	0.071	1.56%	-0.17	1.293	0.019	1.46%	0.75	2.163	0.067	3.08%	-0.13	4.105	0.070	1.69%	1.46
180477	0.270	0.000	0.00%	0.89	4.325	0.030	0.69%	-0.46	0.740	0.008	1.10%	-1.12	1.770	0.008	0.46%	-0.86	1.903	0.010	0.50%	-1.08
180479	0.310	0.014	4.56%	1.28	4.805	0.311	6.48%	0.18	1.018	0.056	5.46%	-0.18	1.853	0.186	10.03%	-0.71	3.063	0.111	3.63%	0.26
180481	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180486	0.158	0.005	3.17%	-0.22	3.300	0.036	1.08%	-1.83	1.400	0.042	3.03%	1.12	1.598	0.017	1.07%	-1.19	2.090	0.075	3.60%	-0.86
180496	0.155	0.006	3.72%	-0.25	4.420	0.014	0.32%	-0.33	0.988	0.017	1.73%	-0.28	NA	NA	NA	NA	3.290	0.016	0.50%	0.52

Lab ID.	z scores										
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3 _c,d_pyrene	Phenanthrene	Sum_BF
180402	-1.23	-1.59	-0.92	-1.72	-1.11	-2.70	0.05	-1.74	-0.97	-1.75	-1.16
180405	0.81	0.54	0.93	-0.51	NA	0.93	0.89	-0.96	0.66	-0.77	-0.29
180415	-0.34	-0.32	0.08	-0.06	~~NC~~	0.48	0.27	-0.44	-0.23	-0.51	-0.77
180429	NA	1.69	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	-1.94	-3.13	NA	-3.16	NA	-0.45	-1.58	-4.69	-3.17	-3.30	-1.52
180437	-0.07	-0.52	-0.03	-0.76	-0.39	-0.68	NA	-0.76	-0.61	-0.59	-0.23
180441	0.44	0.54	0.73	0.16	0.28	0.81	-0.05	0.55	0.47	0.23	0.56
180453	0.97	0.84	1.70	0.72	0.81	0.86	0.05	0.63	1.07	0.78	1.24
180458	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180470	0.28	-0.66	-0.18	-0.08	-0.27	-0.40	~~NC~~	0.00	0.39	0.38	-0.23
180471	1.07	-0.95	0.47	-0.42	NA	-1.31	-1.46	-0.76	-0.99	0.03	-0.77
180476	2.98	0.59	0.85	-0.26	3.00	-0.25	~~NC~~	-0.17	0.75	-0.13	1.46
180477	-0.69	-0.92	-0.29	-0.83	NA	-0.61	0.89	-0.46	-1.12	-0.86	-1.08
180479	0.18	0.07	2.16	0.19	NA	~~NC~~	1.28	0.18	-0.18	-0.71	0.26
180481	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180486	-0.60	-0.67	-0.65	-2.78	-1.10	-1.31	-0.22	-1.83	1.12	-1.19	-0.86
180496	-0.34	-0.18	1.26	-0.41	-0.30	-0.08	-0.25	-0.33	-0.28	NA	0.52

Lab ID.	Zeta Score (ζ)									
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3_ c,d_pyrene	Phenanthrene
180402	-3.70	-4.32	-2.46	-3.48	-4.14	-4.08	0.12	-2.25	-2.02	-2.59
180405	1.93	0.93	1.44	-1.06	NA	0.78	2.68	-1.55	1.18	-1.27
180415	-0.43	-0.53	0.13	-0.12	~~UNS~~	0.32	1.17	-0.41	-0.63	-0.75
180429	NA	UNS	NA	NA	NA	NA	NA	NA	NA	NA
180430	-15.71	-22.80	NA	-8.26	NA	-1.49	-8.00	-14.33	-18.75	-7.64
180437	-0.14	-0.98	-0.07	-1.36	-0.92	-0.71	NA	-0.86	-1.10	-0.86
180441	1.20	0.80	3.64	0.42	0.88	0.88	-0.18	1.23	1.86	0.51
180453	2.88	1.95	5.76	1.45	2.44	1.33	0.23	1.32	3.69	1.57
180458	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180470	1.16	-3.07	-0.84	-0.21	-1.10	-1.02	UNS	0.00	1.77	0.60
180471	3.47	-1.74	0.78	-0.74	NA	-1.40	-7.12	-1.23	-1.62	0.04
180476	13.12	2.06	3.84	-0.67	12.70	-0.82	UNS	-0.51	4.15	-0.29
180477	-2.45	-2.76	-0.87	-1.79	NA	-0.88	2.68	-0.69	-3.70	-1.58
180479	0.23	0.10	2.53	0.25	NA	~~NA~~	1.79	0.15	-0.28	-1.13
180481	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180486	-1.27	-1.14	-1.34	-6.93	-3.36	-1.31	-0.66	-2.18	1.32	-1.75
180496	-2.53	-1.14	6.43	-1.06	-0.52	-0.23	-1.25	-0.90	-1.53	NA

APPENDIX 2: DETAILED RESULTS ON 18/172774_MRC2 (CRM)

Lab ID.	Benzo a anthracene				Benzo a pyrene				Benzo b fluoranthene				Benzo g,h,i perylene				Benzo j fluoranthene				Benzo k fluoranthene			
	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z
180402	0.580	0.000	0.00%	-1.07	0.450	0.000	0.00%	-1.86	1.048	0.010	0.91%	-0.93	0.878	0.005	0.57%	-1.68	0.418	0.005	1.20%	-1.09	0.415	0.006	1.39%	-3.52
180405	1.058	0.005	0.47%	0.48	0.743	0.010	1.29%	0.16	1.388	0.010	0.69%	-0.08	1.265	0.006	0.46%	-0.94	NA	NA	NA		0.628	0.015	2.39%	-0.59
180415	0.775	0.010	1.29%	-0.44	0.648	0.017	2.64%	-0.50	1.470	0.014	0.96%	0.13	1.698	0.021	1.21%	-0.12	~~0.000~~	~~0.000~~	-	~~NC~~	0.665	0.048	7.21%	-0.07
180429	NA	NA	NA		0.890	0.076	8.56%	1.17	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	0.340	0.008	2.40%	-1.85	0.153	0.005	3.28%	-3.92	NA	NA	NA		0.130	0.000	0.00%	-3.11	NA	NA	NA		0.618	0.022	3.59%	-0.73
180437	0.970	0.000	0.00%	0.19	0.680	0.012	1.70%	-0.28	1.535	0.010	0.65%	0.29	1.545	0.089	5.75%	-0.41	0.710	0.037	5.14%	-0.13	0.655	0.010	1.53%	-0.21
180441	1.100	0.012	1.05%	0.62	0.863	0.005	0.58%	0.98	1.840	0.012	0.63%	1.05	1.995	0.006	0.29%	0.45	0.873	0.021	2.36%	0.40	0.798	0.032	4.01%	1.76
180453	1.070	0.018	1.71%	0.52	0.820	0.008	1.00%	0.69	1.965	0.006	0.29%	1.36	1.890	0.037	1.98%	0.25	0.968	0.005	0.52%	0.71	0.700	0.000	0.00%	0.41
180458	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180470	1.070	0.029	2.75%	0.52	0.695	0.039	5.57%	-0.17	1.533	0.084	5.47%	0.28	1.848	0.030	1.62%	0.17	0.705	0.081	11.44%	-0.15	0.678	0.021	3.04%	0.10
180471	1.903	0.088	4.61%	3.22	0.725	0.019	2.64%	0.03	1.998	0.159	7.94%	1.45	1.770	0.056	3.16%	0.02	NA	NA	NA		0.730	0.038	5.25%	0.83
180476	1.803	0.037	2.04%	2.90	0.855	0.013	1.51%	0.93	1.765	0.097	5.52%	0.86	1.715	0.025	1.47%	-0.09	1.713	0.051	2.95%	3.15	0.678	0.010	1.41%	0.10
180477	0.725	0.006	0.80%	-0.60	0.563	0.010	1.70%	-1.09	1.303	0.005	0.38%	-0.29	1.343	0.017	1.27%	-0.80	NA	NA	NA		0.605	0.013	2.13%	-0.90
180479	0.945	0.144	15.22%	0.11	0.738	0.042	5.69%	0.12	2.395	0.182	7.61%	2.44	1.918	0.046	2.42%	0.30	NA	NA	NA		~~0.705~~	~~0.017~~	~~2.46%~~	NC
180481	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180486	0.770	0.014	1.84%	-0.45	0.618	0.005	0.81%	-0.71	1.255	0.090	7.14%	-0.41	0.340	0.032	9.30%	-2.71	0.400	0.029	7.36%	-1.15	0.530	0.008	1.54%	-1.93
180496	0.820	0.008	1.00%	-0.29	0.688	0.005	0.73%	-0.22	1.978	0.013	0.64%	1.40	1.558	0.013	0.81%	-0.39	0.660	0.000	0.00%	-0.29	0.668	0.010	1.43%	-0.03

Lab ID.	Dibenzo a,h anthracene				Fluoranthene				Indeno 1,2,3 c,d pyrene				Phenanthrene				Sum BF			
	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z	x (µg/g)	s_r (µg/g)	s_r en %	score z
180402	0.185	0.006	3.12%	0.06	3.965	0.035	0.89%	-0.96	0.793	0.010	1.21%	-1.22	1.400	0.036	2.54%	-1.28	1.880	0.008	0.43%	-1.13
180405	0.185	0.006	3.12%	0.06	3.925	0.010	0.25%	-1.02	0.993	0.015	1.51%	-0.34	1.805	0.006	0.32%	-0.65	2.015	0.021	1.03%	-0.97
180415	0.198	0.017	8.65%	0.20	4.405	0.010	0.23%	-0.36	0.978	0.017	1.75%	-0.41	1.998	0.005	0.25%	-0.36	2.135	0.045	2.11%	-0.83
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180430	0.020	0.000	0.00%	-1.81	1.118	0.010	0.86%	-4.85	0.110	0.000	0.00%	-4.23	0.448	0.015	3.35%	-2.74	1.593	0.017	1.07%	-1.46
180437	NA	NA	NA		4.398	0.100	2.28%	-0.37	1.035	0.010	0.97%	-0.15	2.000	0.037	1.83%	-0.35	2.900	0.038	1.32%	0.07
180441	0.180	0.000	0.00%	0.00	5.425	0.021	0.38%	1.03	1.333	0.026	1.97%	1.16	2.590	0.008	0.32%	0.55	3.510	0.059	1.68%	0.79
180453	0.183	0.005	2.74%	0.03	4.723	0.015	0.32%	0.07	1.253	0.013	1.00%	0.80	2.425	0.006	0.24%	0.30	3.633	0.005	0.14%	0.93
180458	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180470	~~<0.2~~	~~0.000~~	~~0.00%~~	NC	4.735	0.104	2.20%	0.09	1.180	0.054	4.54%	0.48	2.828	0.175	6.18%	0.92	2.915	0.164	5.63%	0.09
180471	0.050	0.000	0.00%	-1.47	6.133	0.264	4.30%	2.00	0.965	0.024	2.47%	-0.46	3.688	0.173	4.69%	2.24	2.728	0.165	6.03%	-0.13
180476	~~<0.5~~	~~0.000~~	~~0.00%~~	NC	4.778	0.102	2.14%	0.15	1.323	0.029	2.17%	1.11	2.075	0.010	0.48%	-0.24	4.155	0.125	3.00%	1.54
180477	0.270	0.000	0.00%	1.02	4.278	0.046	1.07%	-0.54	0.740	0.008	1.10%	-1.45	1.775	0.013	0.73%	-0.70	1.908	0.017	0.90%	-1.09
180479	0.328	0.017	5.21%	1.67	4.575	0.813	17.76%	-0.13	1.078	0.043	4.04%	0.03	2.140	0.203	9.48%	-0.14	3.100	0.168	5.40%	0.30
180481	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180486	0.168	0.005	2.99%	-0.14	3.498	0.024	0.68%	-1.60	1.060	0.148	13.93%	-0.04	1.630	0.018	1.12%	-0.92	2.185	0.083	3.78%	-0.77
180496	0.153	0.005	3.28%	-0.31	4.433	0.017	0.39%	-0.32	0.980	0.000	0.00%	-0.40	NA	NA	NA	NA	3.305	0.006	0.17%	0.55

Lab ID.	Z scores										
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3_ c,d_pyrene	Phenanthrene	Sum_BF
180402	-1.07	-1.86	-0.93	-1.68	-1.09	-3.52	0.06	-0.96	-1.22	-1.28	-1.13
180405	0.48	0.16	-0.08	-0.94	NA	-0.59	0.06	-1.02	-0.34	-0.65	-0.97
180415	-0.44	-0.50	0.13	-0.12	~~NC~~	-0.07	0.20	-0.36	-0.41	-0.36	-0.83
180429	NA	1.17	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	-1.85	-3.92	NA	-3.11	NA	-0.73	-1.81	-4.85	-4.23	-2.74	-1.46
180437	0.19	-0.28	0.29	-0.41	-0.13	-0.21	NA	-0.37	-0.15	-0.35	0.07
180441	0.62	0.98	1.05	0.45	0.40	1.76	0.00	1.03	1.16	0.55	0.79
180453	0.52	0.69	1.36	0.25	0.71	0.41	0.03	0.07	0.80	0.30	0.93
180458	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180470	0.52	-0.17	0.28	0.17	-0.15	0.10	~~NC~~	0.09	0.48	0.92	0.09
180471	3.22	0.03	1.45	0.02	NA	0.83	-1.47	2.00	-0.46	2.24	-0.13
180476	2.90	0.93	0.86	-0.09	3.15	0.10	~~NC~~	0.15	1.11	-0.24	1.54
180477	-0.60	-1.09	-0.29	-0.80	NA	-0.90	1.02	-0.54	-1.45	-0.70	-1.09
180479	0.11	0.12	2.44	0.30	NA	~~NC~~	1.67	-0.13	0.03	-0.14	0.30
180481	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180486	-0.45	-0.71	-0.41	-2.71	-1.15	-1.93	-0.14	-1.60	-0.04	-0.92	-0.77
180496	-0.29	-0.22	1.40	-0.39	-0.29	-0.03	-0.31	-0.32	-0.40	NA	0.55

Lab ID	Zeta Score (ζ)									
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3_ c,d_pyrene	Phenanthrene
180402	-3.42	-3.86	-2.23	-3.52	-4.03	-3.79	0.12	-1.07	-1.93	-2.19
180405	1.32	0.23	-0.15	-2.13	NA	-0.43	0.18	-1.61	-0.58	-1.32
180415	-0.63	-0.68	0.18	-0.24	UNS	-0.04	0.75	-0.33	-0.88	-0.64
180429	NA	UNS	NA	NA	NA	NA	NA	NA	NA	NA
180430	-16.28	-22.70	NA	-8.36	NA	-1.75	-8.00	-14.50	-19.20	-7.75
180437	0.40	-0.38	0.48	-0.71	-0.28	-0.15	NA	-0.39	-0.19	-0.61
180441	1.72	1.12	4.71	1.18	1.24	1.32	0.00	2.18	3.36	1.46
180453	1.83	1.35	4.52	0.54	2.16	0.50	0.11	0.15	2.28	0.75
180458	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180470	2.19	-0.58	1.14	0.42	-0.60	0.19	UNS	0.15	1.70	1.64
180471	7.64	0.04	1.79	0.03	NA	0.49	-6.00	2.32	-0.48	2.13
180476	17.85	4.74	2.84	-0.23	11.15	0.24	UNS	0.40	4.32	-0.67
180477	-2.30	-2.56	-0.79	-1.76	NA	-0.96	2.68	-0.80	-3.70	-1.57
180479	0.16	0.14	2.58	0.40	NA	~~NA~~	1.93	-0.11	0.04	-0.25
180481	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180486	-1.01	-0.92	-0.72	-6.97	-3.54	-1.44	-0.35	-1.78	-0.05	-1.64
180496	-2.33	-1.14	6.51	-1.03	-0.50	-0.08	-1.37	-0.85	-1.68	NA

APPENDIX 3: DETAILED RESULTS ON 18/172774_F1 (FILTER 1)

Lab ID.	Benzo_a_anthracene				Benzo_a_pyrene				Benzo_b_fluoranthene				Benzo_g,h,i_perylene				Benzo_j_fluoranthene				Benzo_k_fluoranthene			
	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z
180402	202.590	0.622	0.31%	-1.44	216.443	3.260	1.51%	-2.71	248.208	5.994	2.41%	-1.16	140.660	3.588	2.55%	-1.91	145.435	2.453	1.69%	-0.94	100.565	1.693	1.68%	-1.84
180405	299.800	1.551	0.52%	-0.37	308.975	0.974	0.32%	-0.96	304.150	2.452	0.81%	-0.75	203.550	1.863	0.92%	-1.00	NA	NA	NA		180.425	1.605	0.89%	0.28
180415	310.760	0.938	0.30%	-0.25	354.618	1.530	0.43%	-0.09	358.483	1.445	0.40%	-0.35	301.875	0.518	0.17%	0.41	~~0.000~~	~~0.000~~	-	NC	168.973	2.163	1.28%	-0.02
180429	NA	NA	NA		369.925	9.525	2.57%	0.20	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	489.390	15.278	3.12%	1.73	422.883	20.122	4.76%	1.20	NA	NA	NA		250.270	36.730	14.68%	-0.33	NA	NA	NA		1 017.720	25.604	2.52%	22.57
180437	327.000	2.000	0.61%	-0.07	361.250	1.500	0.42%	0.03	367.750	4.924	1.34%	-0.28	260.250	13.574	5.22%	-0.19	196.750	2.062	1.05%	-0.48	168.750	0.500	0.30%	-0.03
180441	363.610	5.695	1.57%	0.34	427.908	6.576	1.54%	1.30	440.908	1.302	0.30%	0.26	340.880	2.892	0.85%	0.97	273.673	1.953	0.71%	0.20	202.888	1.469	0.72%	0.88
180453	352.045	1.864	0.53%	0.21	394.725	0.806	0.20%	0.67	474.113	1.638	0.35%	0.50	325.075	1.424	0.44%	0.75	392.105	1.426	0.36%	1.24	165.595	0.302	0.18%	-0.11
180458	1 474.750	378.796	25.69%	12.61	1 391.500	101.877	7.32%	19.56	1 548.325	369.563	23.87%	8.38	821.700	170.978	20.81%	7.90	~~0.000~~	~~0.000~~	-	NC	514.865	155.912	30.28%	9.18
180470	312.250	7.932	2.54%	-0.23	366.250	4.992	1.36%	0.13	368.500	20.793	5.64%	-0.28	312.500	8.347	2.67%	0.56	232.500	14.799	6.37%	-0.17	161.500	3.697	2.29%	-0.22
180471	346.958	5.432	1.57%	0.15	335.870	5.136	1.53%	-0.45	356.863	8.995	2.52%	-0.36	303.360	5.127	1.69%	0.43	NA	NA	NA		138.418	1.365	0.99%	-0.84
180476	457.708	19.142	4.18%	1.38	380.025	2.858	0.75%	0.39	457.188	5.187	1.13%	0.37	313.390	5.844	1.86%	0.58	460.783	5.107	1.11%	1.85	174.720	1.549	0.89%	0.13
180477	302.353	2.424	0.80%	-0.34	326.473	4.410	1.35%	-0.63	361.153	2.742	0.76%	-0.33	264.685	2.003	0.76%	-0.12	NA	NA	NA		164.380	2.090	1.27%	-0.15
180479	315.455	17.777	5.64%	-0.19	330.103	18.350	5.56%	-0.56	570.713	39.413	6.91%	1.21	267.933	20.308	7.58%	-0.08	NA	NA	NA		~~147.540~~	~~6.174~~	~~4.18%~~	~~NC~~
180481	174.750	0.957	0.55%	-1.75	196.500	14.059	7.15%	-3.09	240.500	6.028	2.51%	-1.21	204.750	9.639	4.71%	-0.99	239.500	6.658	2.78%	-0.11	87.725	0.785	0.89%	-2.19
180486	324.375	2.597	0.80%	-0.10	375.150	2.007	0.54%	0.30	350.550	11.095	3.17%	-0.41	86.575	3.762	4.34%	-2.69	182.500	3.592	1.97%	-0.61	165.300	1.894	1.15%	-0.12
180496	279.675	2.397	0.86%	-0.59	358.185	1.544	0.43%	-0.03	591.765	2.654	0.45%	1.36	308.335	0.935	0.30%	0.50	192.285	0.665	0.35%	-0.52	177.380	1.827	1.03%	0.20

Lab ID.	Dibenzo a,h anthracene				Fluoranthene				Indeno 1,2,3 c,d pyrene				Phenanthrene				Sum BF			
	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z
180402	36.645	1.117	3.05%	-0.09	150.510	2.144	1.42%	-1.07	186.215	4.203	2.26%	-1.29	64.573	0.280	0.43%	-0.90	494.208	9.450	1.91%	-0.95
180405	34.650	0.926	2.67%	-0.23	148.550	0.551	0.37%	-1.10	219.050	2.838	1.30%	-0.84	73.450	0.904	1.23%	-0.68	484.575	2.150	0.44%	-0.98
180415	42.270	1.177	2.78%	0.27	200.198	1.003	0.50%	-0.29	250.475	0.716	0.29%	-0.40	98.280	0.249	0.25%	-0.09	527.455	1.575	0.30%	-0.84
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	~~0.000~~	~~0.000~~	-	NC
180430	48.970	5.670	11.58%	0.72	266.460	7.701	2.89%	0.75	305.190	36.064	11.82%	0.36	119.285	5.887	4.94%	0.42	2 248.665	78.966	3.51%	4.88
180437	NA	NA	NA		172.250	0.957	0.56%	-0.73	280.750	8.461	3.01%	0.02	232.750	7.365	3.16%	3.14	733.250	5.315	0.72%	-0.15
180441	43.075	1.059	2.46%	0.33	233.673	1.402	0.60%	0.24	325.188	4.412	1.36%	0.64	95.990	2.887	3.01%	-0.14	917.468	1.277	0.14%	0.46
180453	19.605	1.618	8.25%	-1.21	200.135	1.274	0.64%	-0.29	329.178	1.306	0.40%	0.69	146.420	0.926	0.63%	1.07	1 031.813	2.945	0.29%	0.84
180458	1 048.350	1 190.273	113.54%	66.36	972.150	178.029	18.31%	11.85	1 002.400	118.029	11.77%	10.02	~~2 098.000~~	~~188.154~~	~~8.97%~~	47.94	2 063.190	524.810	25.44%	4.27
180470	17.700	0.898	5.07%	-1.34	318.250	6.238	1.96%	1.57	290.000	13.089	4.51%	0.15	NA	NA	NA	NA	762.500	30.116	3.95%	-0.06
180471	20.753	0.796	3.84%	-1.14	178.075	2.571	1.44%	-0.64	232.303	6.205	2.67%	-0.65	158.435	4.742	2.99%	1.36	495.280	8.217	1.66%	-0.94
180476	48.180	1.993	4.14%	0.66	202.228	3.216	1.59%	-0.26	345.758	8.179	2.37%	0.92	97.743	1.743	1.78%	-0.10	1 092.690	9.655	0.88%	1.04
180477	37.560	0.599	1.59%	-0.03	212.943	3.267	1.53%	-0.09	212.180	2.145	1.01%	-0.93	94.338	1.317	1.40%	-0.18	525.533	4.712	0.90%	-0.84
180479	52.590	2.509	4.77%	0.95	199.535	14.297	7.16%	-0.30	226.210	15.724	6.95%	-0.74	80.993	7.317	9.03%	-0.50	718.253	38.486	5.36%	-0.20
180481	24.025	0.403	1.68%	-0.92	333.500	3.512	1.05%	1.81	210.000	5.944	2.83%	-0.96	55.250	0.370	0.67%	-1.12	567.725	12.895	2.27%	-0.70
180486	46.425	1.500	3.23%	0.55	224.000	5.746	2.57%	0.08	617.450	19.626	3.18%	4.69	78.575	4.410	5.61%	-0.56	698.350	16.107	2.31%	-0.27
180496	39.008	0.389	1.00%	0.06	167.095	2.210	1.32%	-0.81	281.670	1.102	0.39%	0.03	NA	NA	NA	NA	961.430	3.313	0.34%	0.60

Lab ID	Z scores										
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h _anthracene	Fluoranthene	Indeno_1,2,3 _c,d_pyrene	Phenanthrene	Sum_BF
180402	-1.44	-2.71	-1.16	-1.91	-0.94	-1.84	-0.09	-1.07	-1.29	-0.90	-0.95
180405	-0.37	-0.96	-0.75	-1.00	NA	0.28	-0.23	-1.10	-0.84	-0.68	-0.98
180415	-0.25	-0.09	-0.35	0.41	~~NC~~	-0.02	0.27	-0.29	-0.40	-0.09	-0.84
180429	NA	0.20	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	1.73	1.20	NA	-0.33	NA	22.57	0.72	0.75	0.36	0.42	4.88
180437	-0.07	0.03	-0.28	-0.19	-0.48	-0.03	NA	-0.73	0.02	3.14	-0.15
180441	0.34	1.30	0.26	0.97	0.20	0.88	0.33	0.24	0.64	-0.14	0.46
180453	0.21	0.67	0.50	0.75	1.24	-0.11	-1.21	-0.29	0.69	1.07	0.84
180458	12.61	19.56	8.38	7.90	~~NC~~	9.18	66.36	11.85	10.02	~~47.94~~	4.27
180470	-0.23	0.13	-0.28	0.56	-0.17	-0.22	-1.34	1.57	0.15	NA	-0.06
180471	0.15	-0.45	-0.36	0.43	NA	-0.84	-1.14	-0.64	-0.65	1.36	-0.94
180476	1.38	0.39	0.37	0.58	1.85	0.13	0.66	-0.26	0.92	-0.10	1.04
180477	-0.34	-0.63	-0.33	-0.12	NA	-0.15	-0.03	-0.09	-0.93	-0.18	-0.84
180479	-0.19	-0.56	1.21	-0.08	NA	~~NC~~	0.95	-0.30	-0.74	-0.50	-0.20
180481	-1.75	-3.09	-1.21	-0.99	-0.11	-2.19	-0.92	1.81	-0.96	-1.12	-0.70
180486	-0.10	0.30	-0.41	-2.69	-0.61	-0.12	0.55	0.08	4.69	-0.56	-0.27
180496	-0.59	-0.03	1.36	0.50	-0.52	0.20	0.06	-0.81	0.03	NA	0.60

APPENDIX 4: DETAILED RESULTS ON 18/172774_F2 (FILTER 2)

Lab ID.	Benzo_a_anthracene				Benzo_a_pyrene				Benzo_b_fluoranthene				Benzo_g,h,i_perylene				Benzo_j_fluoranthene				Benzo_k_fluoranthene			
	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z
180402	136.420	1.623	1.19%	-0.87	197.308	3.297	1.67%	-1.20	228.003	2.238	0.98%	-0.86	143.303	1.248	0.87%	-1.30	134.190	2.071	1.54%	-0.81	95.370	2.027	2.13%	-1.03
180405	201.575	0.640	0.32%	0.30	276.500	0.316	0.11%	0.13	285.325	3.940	1.38%	-0.27	194.850	1.025	0.53%	-0.44	NA	NA	NA		157.225	1.992	1.27%	0.52
180415	168.738	0.938	0.56%	-0.29	266.260	0.991	0.37%	-0.04	273.373	0.504	0.18%	-0.40	230.473	0.779	0.34%	0.16	~~0.000~~	~~0.000~~	-	~~NC~~	130.483	1.387	1.06%	-0.15
180429	NA	NA	NA		328.725	19.404	5.90%	1.01	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	276.975	6.458	2.33%	1.66	302.950	5.877	1.94%	0.57	NA	NA	NA		219.173	8.264	3.77%	-0.03	NA	NA	NA		1 063.240	28.707	2.70%	23.18
180437	156.250	0.957	0.61%	-0.51	231.750	1.500	0.65%	-0.62	247.750	2.630	1.06%	-0.66	182.500	3.000	1.64%	-0.64	131.750	1.258	0.96%	-0.83	114.000	0.816	0.72%	-0.57
180441	240.278	5.580	2.32%	1.00	382.523	3.056	0.80%	1.91	402.205	1.294	0.32%	0.92	318.785	2.435	0.76%	1.63	253.568	1.351	0.53%	0.43	187.548	2.866	1.53%	1.27
180453	186.050	0.624	0.34%	0.02	289.625	0.626	0.22%	0.35	360.030	1.305	0.36%	0.49	262.898	1.613	0.61%	0.70	298.478	1.139	0.38%	0.89	130.255	0.307	0.24%	-0.16
180458	941.065	263.945	28.05%	13.58	1 925.438	983.530	51.08%	27.84	1 615.167	898.154	55.61%	13.33	922.500	23.335	2.53%	11.70	~~0.000~~	~~0.000~~	-	~~NC~~	1 394.375	1 268.908	91.00%	31.47
180470	178.500	6.557	3.67%	-0.11	297.250	7.365	2.48%	0.48	309.250	11.758	3.80%	-0.03	284.750	21.282	7.47%	1.06	200.000	5.944	2.97%	-0.13	138.250	4.500	3.25%	0.04
180471	142.553	10.068	7.06%	-0.76	213.243	13.782	6.46%	-0.93	235.435	15.032	6.38%	-0.78	206.160	11.306	5.48%	-0.25	NA	NA	NA		94.913	6.502	6.85%	-1.04
180476	257.885	10.130	3.93%	1.31	283.775	2.434	0.86%	0.25	341.330	3.831	1.12%	0.30	239.558	3.011	1.26%	0.31	350.975	1.839	0.52%	1.44	137.123	1.067	0.78%	0.01
180477	156.535	0.411	0.26%	-0.51	231.263	1.485	0.64%	-0.63	262.150	2.337	0.89%	-0.51	196.008	4.313	2.20%	-0.42	NA	NA	NA		123.045	0.522	0.42%	-0.34
180479	152.478	9.552	6.26%	-0.58	215.123	9.295	4.32%	-0.90	388.933	31.477	8.09%	0.79	183.653	5.798	3.16%	-0.63	NA	NA	NA		~~104.268~~	~~9.876~~	~~9.47%~~	NC
180481	108.750	0.957	0.88%	-1.36	173.500	4.655	2.68%	-1.60	215.750	8.180	3.79%	-0.99	199.000	2.828	1.42%	-0.37	250.000	1.826	0.73%	0.39	93.250	0.700	0.75%	-1.08
180486	170.150	3.154	1.85%	-0.26	268.400	1.610	0.60%	-0.01	228.400	5.352	2.34%	-0.86	59.200	1.637	2.77%	-2.70	147.550	4.455	3.02%	-0.67	125.375	1.676	1.34%	-0.28
180496	162.945	2.026	1.24%	-0.39	271.510	1.409	0.52%	0.05	454.858	4.008	0.88%	1.46	242.253	1.471	0.61%	0.35	147.423	1.053	0.71%	-0.67	134.843	0.648	0.48%	-0.04

Lab ID.	Dibenzo_a,h_anthracene				Fluoranthene				Indeno_1,2,3_c,d_pyrene				Phenanthrene				Sum_BF			
	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z	x (ng/filtre)	sr (ng/filter)	s_r en %	score z
180402	37.748	0.401	1.06%	0.60	111.573	1.275	1.14%	-0.62	187.078	1.605	0.86%	-0.71	45.528	0.303	0.67%	-0.80	457.563	5.914	1.29%	-0.66
180405	32.875	0.222	0.67%	0.14	124.775	0.754	0.60%	-0.28	215.600	1.499	0.70%	-0.29	54.575	0.704	1.29%	-0.44	442.550	5.357	1.21%	-0.72
180415	33.075	1.833	5.54%	0.16	127.533	0.191	0.15%	-0.20	200.600	1.830	0.91%	-0.51	57.455	0.241	0.42%	-0.32	403.855	1.318	0.33%	-0.88
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	~~0.000~~	~~0.000~~	-	~~NC~~
180430	44.695	2.327	5.21%	1.25	177.685	4.257	2.40%	1.11	286.413	13.758	4.80%	0.73	62.473	4.673	7.48%	-0.12	2 308.608	49.630	2.15%	6.93
180437	NA	NA	NA		97.750	2.062	2.11%	-0.98	194.000	5.888	3.03%	-0.61	111.500	1.291	1.16%	1.85	493.500	3.109	0.63%	-0.51
180441	39.810	0.254	0.64%	0.79	188.908	1.687	0.89%	1.40	318.418	7.519	2.36%	1.20	81.955	1.766	2.16%	0.66	843.320	4.995	0.59%	0.93
180453	18.550	0.517	2.79%	-1.20	130.138	0.503	0.39%	-0.14	264.135	0.985	0.37%	0.41	84.493	0.735	0.87%	0.76	788.763	0.968	0.12%	0.70
180458	~~0.000~~	~~0.000~~	-	~~NC~~	1 146.988	741.201	64.62%	26.44	919.500	27.577	3.00%	9.93	1 164.813	1 041.067	89.38%	44.13	2 605.750	1 673.698	64.23%	8.15
180470	14.175	2.133	15.05%	-1.61	210.750	4.272	2.03%	1.97	233.250	9.179	3.94%	-0.04	NA	NA	NA	NA	647.500	12.396	1.91%	0.12
180471	14.303	1.124	7.86%	-1.60	98.890	6.097	6.17%	-0.95	172.740	13.643	7.90%	-0.92	47.118	6.529	13.86%	-0.74	330.348	21.524	6.52%	-1.18
180476	36.695	1.924	5.24%	0.50	129.468	3.173	2.45%	-0.15	273.788	6.197	2.26%	0.55	64.070	0.755	1.18%	-0.06	829.428	6.317	0.76%	0.87
180477	27.880	0.347	1.24%	-0.33	137.260	1.716	1.25%	0.05	164.070	1.655	1.01%	-1.04	62.655	1.033	1.65%	-0.11	385.195	2.443	0.63%	-0.95
180479	39.790	0.918	2.31%	0.79	104.745	11.342	10.83%	-0.80	157.843	3.891	2.47%	-1.13	46.958	4.654	9.91%	-0.74	493.200	40.894	8.29%	-0.51
180481	33.250	0.603	1.81%	0.18	104.375	8.788	8.42%	-0.81	200.000	5.354	2.68%	-0.52	75.600	2.903	3.84%	0.41	559.000	6.775	1.21%	-0.24
180486	31.075	0.618	1.99%	-0.03	130.575	2.100	1.61%	-0.12	588.650	4.872	0.83%	5.12	32.100	1.178	3.67%	-1.34	501.325	5.339	1.07%	-0.48
180496	31.283	0.241	0.77%	-0.01	116.338	0.945	0.81%	-0.50	226.725	2.194	0.97%	-0.13	NA	NA	NA	NA	737.123	5.274	0.72%	0.49

Lab ID.	Z scores										
	Benzo_a_anthracene	Benzo_a_pyrene	Benzo_b_fluoranthene	Benzo_g,h,i_perylene	Benzo_j_fluoranthene	Benzo_k_fluoranthene	Dibenzo_a,h_anthracene	Fluoranthene	Indeno_1,2,3_c,d_pyrene	Phenanthrene	Sum_BF
180402	-0.87	-1.20	-0.86	-1.30	-0.81	-1.03	0.60	-0.62	-0.71	-0.80	-0.66
180405	0.30	0.13	-0.27	-0.44	NA	0.52	0.14	-0.28	-0.29	-0.44	-0.72
180415	-0.29	-0.04	-0.40	0.16	~~NC~~	-0.15	0.16	-0.20	-0.51	-0.32	-0.88
180429	NA	1.01	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	1.66	0.57	NA	-0.03	NA	23.18	1.25	1.11	0.73	-0.12	6.93
180437	-0.51	-0.62	-0.66	-0.64	-0.83	-0.57	NA	-0.98	-0.61	1.85	-0.51
180441	1.00	1.91	0.92	1.63	0.43	1.27	0.79	1.40	1.20	0.66	0.93
180453	0.02	0.35	0.49	0.70	0.89	-0.16	-1.20	-0.14	0.41	0.76	0.70
180458	13.58	27.84	13.33	11.70	~~NC~~	31.47	~~NC~~	26.44	9.93	44.13	8.15
180470	-0.11	0.48	-0.03	1.06	-0.13	0.04	-1.61	1.97	-0.04	NA	0.12
180471	-0.76	-0.93	-0.78	-0.25	NA	-1.04	-1.60	-0.95	-0.92	-0.74	-1.18
180476	1.31	0.25	0.30	0.31	1.44	0.01	0.50	-0.15	0.55	-0.06	0.87
180477	-0.51	-0.63	-0.51	-0.42	NA	-0.34	-0.33	0.05	-1.04	-0.11	-0.95
180479	-0.58	-0.90	0.79	-0.63	NA	~~NC~~	0.79	-0.80	-1.13	-0.74	-0.51
180481	-1.36	-1.60	-0.99	-0.37	0.39	-1.08	0.18	-0.81	-0.52	0.41	-0.24
180486	-0.26	-0.01	-0.86	-2.70	-0.67	-0.28	-0.03	-0.12	5.12	-1.34	-0.48
180496	-0.39	0.05	1.46	0.35	-0.67	-0.04	-0.01	-0.50	-0.13	NA	0.49

APPENDIX 5: DETAILED RESULTS ON 18/172774_F-BLANK

Lab ID.	Benzo_a_anthracene			Benzo_a_pyrene			Benzo_b_fluoranthene			Benzo_g,h,i_perylene			Benzo_j_fluoranthene		
	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %
180402	<2.5	-	-	<5	-	-	<5	-	-	<5	-	-	<5	-	-
180405	<5	-	-	<1	-	-	<5	-	-	<5	-	-	NA	NA	NA
180415	<1	-	-	<1	-	-	<1	-	-	<1	-	-	0.000	-	-
180429	NA	NA	NA	<5	-	-	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	<12.06	-	-	<14.52	-	-	NA	NA	NA	10.830	-	-	NA	NA	NA
180437	<2	-	-	<1	-	-	<2	-	-	<2	-	-	<2	-	-
180441	<4	-	-	<8	-	-	<8	-	-	<9	-	-	<8	-	-
180453	<10	-	-	<3	-	-	<10	-	-	<10	-	-	<10	-	-
180458	28.000	56.000	200.00%	28.750	55.518	193.11%	0.000	-	-	0.000	-	-	0.000	-	-
180470	<2	-	-	<1	-	-	<5	-	-	<5	-	-	97.000	5.715	5.89%
180471	0.148	0.033	22.40%	0.163	0.013	7.74%	0.205	0.075	36.61%	0.900	0.136	15.15%	NA	NA	NA
180476	<25	-	-	<25	-	-	<25	-	-	<25	-	-	<25	-	-
180477	<20	-	-	<20	-	-	<20	-	-	<20	-	-	<20	-	-
180479	<2	-	-	<2	-	-	<2	-	-	<2	-	-	NA	NA	NA
180481	<5	-	-	<5	-	-	<30	-	-	<10	-	-	<10	-	-
180486	<1	-	-	<1	-	-	<1	-	-	<1	-	-	<1	-	-
180496	<0.42	-	-	<0.71	-	-	<0.53	-	-	<0.48	-	-	NA	NA	NA

Lab ID.	Benzo_k_fluoranthene			Dibenzo_a,h_anthracene			Fluoranthene			Indeno_1,2,3_c,d_pyrene			Phenanthrene		
	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %	x (ng/filtre)	sr (ng/filter)	s_r en %
180402	<5	-	-	<2	-	-	<2.5	-	-	<5	-	-	<2.5	-	-
180405	<5	-	-	<5	-	-	<5	-	-	<5	-	-	<5	-	-
180415	<1	-	-	<1	-	-	<1	-	-	<1	-	-	<1	-	-
180429	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	<13.89	-	-	10.620	-	-	<22.68	-	-	<12.6	-	-	<10.68	-	-
180437	<2	-	-	NA	NA	NA	<2	-	-	<2	-	-	<2	-	-
180441	<8	-	-	<9	-	-	<4	-	-	<10	-	-	<8	-	-
180453	<10	-	-	<3	-	-	<10	-	-	<10	-	-	<10	-	-
180458	0.000	-	-	0.000	-	-	38.750	77.500	200.00%	10.000	20.000	200.00%	81.500	95.378	117.03%
180470	<1	-	-	<5	-	-	<15	-	-	<5	-	-	<25	-	-
180471	0.110	0.022	19.64%	<0.03	-	-	0.183	0.043	23.83%	<0.13	-	-	0.628	0.120	19.14%
180476	<25	-	-	<25	-	-	<25	-	-	<25	-	-	<25	-	-
180477	<20	-	-	<20	-	-	<20	-	-	<20	-	-	<20	-	-
180479	<2	-	-	<2	-	-	2.453	0.458	18.67%	<2	-	-	3.830	2.474	64.59%
180481	<10	-	-	<10	-	-	<10	-	-	<10	-	-	<5	-	-
180486	<1	-	-	<1	-	-	<1	-	-	<1	-	-	<1	-	-
180496	<0.65	-	-	<0.77	-	-	<0.46	-	-	<0.22	-	-	NA	NA	NA

APPENDIX 6: DETAILED RESULTS ON 18/172774_S1 (SOLUTION 1)

Lab ID	Benzo_a_anthracene				Benzo_a_pyrene				Benzo_b_fluoranthene				Benzo_g,h,i_perylene				Benzo_j_fluoranthene				Benzo_k_fluoranthene			
	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z
180402	319.400	2.811	0.88%	0.68	429.475	11.916	2.77%	0.49	635.075	2.207	0.35%	0.85	712.550	12.920	1.81%	3.58	394.225	3.884	0.99%	0.93	436.025	12.003	2.75%	1.72
180405	259.600	1.339	0.52%	-0.74	332.175	2.869	0.86%	-1.09	432.425	9.344	2.16%	-1.23	355.675	1.891	0.53%	-0.50	NA	NA	NA		343.275	6.997	2.04%	0.69
180415	295.750	0.957	0.32%	0.12	458.000	3.367	0.74%	0.95	621.500	5.972	0.96%	0.71	408.000	0.816	0.20%	0.10	~~0.000~~	~~0.000~~	~~Pb. Moy.=0~~	NC	267.250	1.500	0.56%	-0.16
180429	NA	NA	NA		302.550	9.680	3.20%	-1.57	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	307.918	25.314	8.22%	0.41	345.543	11.603	3.36%	-0.88	NA	NA	NA		202.025	5.473	2.71%	-2.25	NA	NA	NA		565.988	7.415	1.31%	3.16
180437	292.750	0.500	0.17%	0.05	399.500	1.000	0.25%	0.00	545.000	5.774	1.06%	-0.07	395.250	0.500	0.13%	-0.05	288.500	3.416	1.18%	0.16	283.000	0.816	0.29%	0.02
180441	317.575	0.967	0.30%	0.64	415.548	1.282	0.31%	0.26	560.905	5.184	0.92%	0.09	398.748	1.000	0.25%	-0.01	288.935	5.791	2.00%	0.16	286.360	9.706	3.39%	0.05
180453	279.790	0.615	0.22%	-0.26	379.520	1.307	0.34%	-0.32	547.775	1.733	0.32%	-0.04	432.188	1.114	0.26%	0.38	269.520	0.813	0.30%	0.02	279.090	0.525	0.19%	-0.03
180458	262.500	8.869	3.38%	-0.67	1 941.180	979.064	50.44%	25.08	4 197.800	738.878	17.60%	37.40	2 820.640	4 251.552	150.73%	27.65	~~0.000~~	~~0.000~~	~~Pb. Moy.=0~~	NC	1 607.950	275.015	17.10%	14.72
180470	284.693	5.053	1.77%	-0.14	406.928	3.509	0.86%	0.12	545.540	6.093	1.12%	-0.07	439.278	7.898	1.80%	0.46	274.563	7.350	2.68%	0.06	276.958	3.257	1.18%	-0.05
180471	175.390	3.660	2.09%	-2.75	376.625	17.166	4.56%	-0.37	517.530	8.959	1.73%	-0.35	415.228	24.507	5.90%	0.18	NA	NA	NA		250.708	3.551	1.42%	-0.34
180476	~~<5~~	~~0.000~~	~~0.00%~~	NC	402.273	1.729	0.43%	0.05	566.093	0.894	0.16%	0.15	405.885	5.303	1.31%	0.08	564.150	1.214	0.22%	2.16	298.345	0.704	0.24%	0.19
180477	267.238	1.788	0.67%	-0.56	363.358	2.440	0.67%	-0.59	524.000	2.572	0.49%	-0.29	386.080	2.066	0.54%	-0.15	NA	NA	NA		272.848	2.271	0.83%	-0.10
180479	327.178	22.824	6.98%	0.87	431.300	12.594	2.92%	0.52	893.628	17.231	1.93%	3.51	449.118	14.546	3.24%	0.57	NA	NA	NA		~~312.170~~	~~29.051~~	~~9.31%~~	~~NC~~
180481	223.500	2.380	1.07%	-1.61	301.000	4.082	1.36%	-1.60	431.250	4.924	1.14%	-1.24	286.250	1.708	0.60%	-1.29	462.500	2.082	0.45%	1.42	219.000	0.816	0.37%	-0.69
180486	282.275	1.841	0.65%	-0.20	375.600	1.663	0.44%	-0.39	524.575	2.249	0.43%	-0.28	388.800	1.954	0.50%	-0.12	201.575	1.352	0.67%	-0.47	279.375	0.793	0.28%	-0.02
180496	154.223	2.420	1.57%	-3.26	200.135	2.635	1.32%	-3.24	419.575	6.105	1.46%	-1.36	219.600	0.901	0.41%	-2.05	145.573	1.115	0.77%	-0.88	162.708	2.181	1.34%	-1.32

Lab ID	Dibenzo_a,h_anthracene				Fluoranthene				Indeno_1,2,3_c,d_pyrene				Phenanthrene				Sum_BF			
	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/litre)	s_r (µg/litre)	s_r en %	score z
180402	116.125	0.873	0.75%	1.21	752.875	3.974	0.53%	-0.28	1 306.425	18.841	1.44%	4.42	1 780.900	24.905	1.40%	1.26	1 465.325	8.287	0.57%	1.11
180405	71.375	0.685	0.96%	-0.81	632.600	1.030	0.16%	-2.28	619.550	4.814	0.78%	-0.78	1 102.825	20.245	1.84%	-1.98	775.700	10.633	1.37%	-0.98
180415	109.500	0.577	0.53%	0.91	789.750	1.500	0.19%	0.34	663.750	3.862	0.58%	-0.44	1 547.250	3.304	0.21%	0.14	888.750	6.898	0.78%	-0.64
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180430	53.290	2.892	5.43%	-1.62	768.500	13.330	1.73%	-0.01	423.170	15.616	3.69%	-2.26	1 014.505	38.771	3.82%	-2.41	1 623.470	40.267	2.48%	1.59
180437	99.250	0.957	0.96%	0.45	745.000	5.774	0.77%	-0.41	702.500	9.574	1.36%	-0.15	1 532.500	5.000	0.33%	0.07	1 116.500	6.952	0.62%	0.05
180441	92.105	1.404	1.52%	0.13	773.435	9.178	1.19%	0.07	723.490	9.339	1.29%	0.01	1 529.563	3.927	0.26%	0.06	1 136.200	18.889	1.66%	0.11
180453	89.180	0.218	0.24%	0.00	731.558	2.253	0.31%	-0.63	720.700	2.223	0.31%	-0.01	1 537.510	1.112	0.07%	0.10	1 096.385	0.971	0.09%	-0.01
180458	~~1 807.950~~	~~777.954~~	~~43.03%~~	77.29	3 714.000	2 028.188	54.61%	49.19	2 721.450	2 409.339	88.53%	15.12	5 366.050	3 439.453	64.10%	18.42	5 805.750	941.097	16.21%	14.26
180470	83.873	3.784	4.51%	-0.24	753.230	9.476	1.26%	-0.27	691.033	9.817	1.42%	-0.24	1 489.790	19.901	1.34%	-0.13	1 097.060	2.618	0.24%	-0.01
180471	90.455	2.265	2.50%	0.05	736.965	3.701	0.50%	-0.54	686.413	28.880	4.21%	-0.27	1 658.830	52.580	3.17%	0.68	768.238	12.401	1.61%	-1.01
180476	92.785	0.281	0.30%	0.16	777.933	1.994	0.26%	0.14	724.865	3.110	0.43%	0.02	1 576.795	7.977	0.51%	0.29	1 428.588	2.437	0.17%	1.00
180477	97.400	1.118	1.15%	0.37	726.348	6.129	0.84%	-0.72	556.753	3.414	0.61%	-1.25	1 449.700	7.409	0.51%	-0.32	796.848	3.562	0.45%	-0.92
180479	118.183	4.640	3.93%	1.30	795.550	56.292	7.08%	0.44	634.515	22.119	3.49%	-0.67	1 530.678	180.276	11.78%	0.06	1 205.798	42.749	3.55%	0.32
180481	65.700	0.258	0.39%	-1.06	598.000	13.166	2.20%	-2.86	531.000	2.582	0.49%	-1.45	1 246.000	1.633	0.13%	-1.30	1 112.750	5.500	0.49%	0.04
180486	91.150	0.597	0.66%	0.08	720.775	2.901	0.40%	-0.81	617.900	13.311	2.15%	-0.79	1 490.400	10.900	0.73%	-0.13	1 005.525	3.638	0.36%	-0.29
180496	47.243	0.944	2.00%	-1.89	404.073	0.714	0.18%	-6.10	377.295	1.205	0.32%	-2.61	NA	NA	NA	NA	727.855	5.587	0.77%	-1.13

Lab ID.	Z scores										
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h _anthracene	Fluoranthene	Indeno_1,2,3 _c,d_pyrene	Phenanthrene	Sum_BF
180402	0.68	0.49	0.85	3.58	0.93	1.72	1.21	-0.28	4.42	1.26	1.11
180405	-0.74	-1.09	-1.23	-0.50	NA	0.69	-0.81	-2.28	-0.78	-1.98	-0.98
180415	0.12	0.95	0.71	0.10	~~NC~~	-0.16	0.91	0.34	-0.44	0.14	-0.64
180429	NA	-1.57	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	0.41	-0.88	NA	-2.25	NA	3.16	-1.62	-0.01	-2.26	-2.41	1.59
180437	0.05	0.00	-0.07	-0.05	0.16	0.02	0.45	-0.41	-0.15	0.07	0.05
180441	0.64	0.26	0.09	-0.01	0.16	0.05	0.13	0.07	0.01	0.06	0.11
180453	-0.26	-0.32	-0.04	0.38	0.02	-0.03	0.00	-0.63	-0.01	0.10	-0.01
180458	-0.67	25.08	37.40	27.65	~~NC~~	14.72	~~77.29~~	49.19	15.12	18.42	14.26
180470	-0.14	0.12	-0.07	0.46	0.06	-0.05	-0.24	-0.27	-0.24	-0.13	-0.01
180471	-2.75	-0.37	-0.35	0.18	NA	-0.34	0.05	-0.54	-0.27	0.68	-1.01
180476	~~NC~~	0.05	0.15	0.08	2.16	0.19	0.16	0.14	0.02	0.29	1.00
180477	-0.56	-0.59	-0.29	-0.15	NA	-0.10	0.37	-0.72	-1.25	-0.32	-0.92
180479	0.87	0.52	3.51	0.57	NA	~~NC~~	1.30	0.44	-0.67	0.06	0.32
180481	-1.61	-1.60	-1.24	-1.29	1.42	-0.69	-1.06	-2.86	-1.45	-1.30	0.04
180486	-0.20	-0.39	-0.28	-0.12	-0.47	-0.02	0.08	-0.81	-0.79	-0.13	-0.29
180496	-3.26	-3.24	-1.36	-2.05	-0.88	-1.32	-1.89	-6.10	-2.61	NA	-1.13

Lab ID.	Zeta Score (ζ)									
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3_ c,d_pyrene	Phenanthrene
180402	1.69	1.27	2.53	8.58	6.14	6.96	3.15	-0.42	8.89	2.92
180405	-1.17	-1.57	-1.83	-1.20	NA	1.20	-1.89	-2.13	-1.32	-2.99
180415	0.06	0.79	0.60	0.20	UNS	-0.26	2.23	0.15	-0.93	0.14
180429	NA	UNS	NA	NA	NA	NA	NA	NA	NA	NA
180430	1.51	-4.82	NA	-24.34	NA	42.32	-5.76	-0.05	-27.29	-9.77
180437	0.07	0.00	-0.14	-0.11	0.71	0.06	0.72	-0.32	-0.26	0.11
180441	1.46	0.76	0.64	-0.04	1.30	0.40	0.39	0.21	0.06	0.36
180453	-1.20	-1.44	-0.26	2.45	0.31	-0.29	-0.02	-1.75	-0.09	0.49
180458	-0.43	1.99	2.17	2.86	UNS	2.06	~~2.38~~	2.27	1.84	1.79
180470	-0.34	0.33	-0.25	2.07	0.62	-0.38	-0.76	-0.28	-1.25	-0.18
180471	-10.98	-0.81	-0.60	0.40	NA	-1.07	0.09	-0.57	-0.38	1.45
180476	UNS	0.28	1.70	0.69	43.90	3.95	0.56	0.73	0.31	3.48
180477	-0.86	-0.96	-0.53	-0.33	NA	-0.31	0.70	-0.58	-2.95	-0.46
180479	0.49	0.44	2.46	0.61	NA	~~NC~~	1.06	0.18	-0.77	0.07
180481	-2.19	-2.35	-2.05	-2.86	3.12	-2.09	-2.23	-2.36	-2.66	-1.61
180486	-0.17	-0.36	-0.30	-0.15	-1.81	-0.04	0.11	-0.38	-0.96	-0.10
180496	-20.74	-18.52	-9.90	-20.80	-3.27	-22.28	-6.72	-21.83	-33.04	NA

APPENDIX 7 : DETAILED RESULTS ON 18/172774_S2 (SOLUTION 2)

Lab ID	Benzo a anthracene				Benzo a pyrene				Benzo b fluoranthene				Benzo g,h,i perylene				Benzo j fluoranthene				Benzo k fluoranthene			
	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z
180402	306.650	1.808	0.59%	0.32	419.325	8.745	2.09%	0.26	655.550	5.059	0.77%	0.89	675.325	25.010	3.70%	4.51	371.475	3.363	0.91%	0.70	402.900	1.669	0.41%	1.82
180405	251.450	1.537	0.61%	-0.80	316.725	1.723	0.54%	-1.07	408.250	11.553	2.83%	-1.23	342.675	6.450	1.88%	-0.92	NA	NA	NA		368.125	11.667	3.17%	1.30
180415	285.500	2.082	0.73%	-0.11	484.000	3.559	0.74%	1.09	673.000	5.354	0.80%	1.04	411.000	1.414	0.34%	0.19	~~0.000~~	~~0.000~~	~~Pb. Moy.=0~~	NC	252.000	2.708	1.07%	-0.44
180429	NA	NA	NA		257.875	6.607	2.56%	-1.83	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	~~<40.2~~	~~0.000~~	~~0.00%~~	NC	~~<48.4~~	~~0.000~~	~~0.00%~~	NC	NA	NA	NA		~~<36.1~~	~~0.000~~	~~0.00%~~	NC	NA	NA	NA		~~<46.3~~	~~0.000~~	~~0.00%~~	NC
180437	304.500	1.000	0.33%	0.28	397.500	5.000	1.26%	-0.02	537.500	5.000	0.93%	-0.12	392.500	5.000	1.27%	-0.11	305.000	4.082	1.34%	0.26	295.000	0.816	0.28%	0.20
180441	312.765	3.301	1.06%	0.45	410.268	7.406	1.81%	0.14	561.343	3.775	0.67%	0.08	400.755	0.997	0.25%	0.02	281.400	10.759	3.82%	0.10	273.203	14.595	5.34%	-0.12
180453	281.573	0.844	0.30%	-0.19	383.455	1.372	0.36%	-0.21	545.695	2.641	0.48%	-0.05	434.915	0.499	0.11%	0.58	274.190	1.317	0.48%	0.05	281.848	0.986	0.35%	0.01
180458	1 863.265	245.378	13.17%	32.11	2 175.410	551.789	25.36%	22.95	3 582.640	559.655	15.62%	25.97	2 890.900	3 634.105	125.71%	40.74	~~0.000~~	~~0.000~~	~~Pb. Moy.=0~~	NC	1 434.245	164.504	11.47%	17.31
180470	284.575	4.430	1.56%	-0.13	407.333	0.415	0.10%	0.10	548.845	5.589	1.02%	-0.03	439.613	4.646	1.06%	0.66	275.418	6.046	2.20%	0.06	275.663	1.075	0.39%	-0.09
180471	171.700	1.534	0.89%	-2.43	364.720	2.637	0.72%	-0.45	514.730	3.672	0.71%	-0.32	395.625	1.479	0.37%	-0.06	NA	NA	NA		250.203	2.246	0.90%	-0.47
180476	~~<5~~	~~0.000~~	~~0.00%~~	NC	400.205	1.289	0.32%	0.01	560.738	2.083	0.37%	0.08	402.105	7.256	1.80%	0.05	559.473	1.462	0.26%	1.96	295.495	1.136	0.38%	0.21
180477	265.830	1.307	0.49%	-0.51	366.260	2.332	0.64%	-0.43	527.108	1.964	0.37%	-0.21	390.735	3.539	0.91%	-0.14	NA	NA	NA		276.338	1.761	0.64%	-0.08
180479	322.403	11.191	3.47%	0.65	417.233	4.439	1.06%	0.23	864.088	19.913	2.30%	2.67	415.190	8.439	2.03%	0.26	NA	NA	NA		~~290.450~~	~~6.199~~	~~2.13%~~	~~NC~~
180481	230.500	6.856	2.97%	-1.23	289.750	2.217	0.77%	-1.42	449.500	10.408	2.32%	-0.88	293.500	7.141	2.43%	-1.73	499.500	13.279	2.66%	1.56	217.000	0.816	0.38%	-0.97
180486	275.475	1.159	0.42%	-0.31	365.875	4.404	1.20%	-0.43	510.175	3.892	0.76%	-0.36	378.350	4.310	1.14%	-0.34	198.050	0.603	0.30%	-0.46	270.625	3.290	1.22%	-0.16
180496	147.695	2.190	1.48%	-2.92	188.433	1.510	0.80%	-2.73	400.263	5.495	1.37%	-1.30	205.963	0.368	0.18%	-3.16	138.643	0.808	0.58%	-0.85	154.308	2.406	1.56%	-1.91

Lab ID	Dibenzo a,h anthracene				Fluoranthene				Indeno 1,2,3 c,d pyrene				Phenanthrene				Sum BF			
	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z
180402	105.375	4.819	4.57%	0.77	733.275	2.906	0.40%	-0.63	1 225.175	32.526	2.65%	4.22	1 714.025	9.462	0.55%	1.46	1 429.925	8.539	0.60%	1.16
180405	69.325	0.846	1.22%	-0.96	614.475	5.878	0.96%	-2.70	588.500	1.817	0.31%	-1.13	1 177.600	10.379	0.88%	-2.51	776.375	21.744	2.80%	-1.14
180415	119.500	11.091	9.28%	1.45	751.000	3.742	0.50%	-0.32	777.500	60.236	7.75%	0.46	1 504.500	10.214	0.68%	-0.09	925.000	7.958	0.86%	-0.62
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	~~0.000~~	~~0.000~~	~~Pb. Moy.=0~~	NC
180430	~~<35.4~~	~~0.000~~	~~0.00%~~	NC	~~<75.6~~	~~0.000~~	~~0.00%~~	NC	~~<42~~	~~0.000~~	~~0.00%~~	~~NC~~	~~76.113~~	~~5.295~~	~~6.96%~~	~~-10.66~~	~~111.140~~	~~0.000~~	~~0.00%~~	~~-3.48~~
180437	99.750	3.304	3.31%	0.50	730.000	8.165	1.12%	-0.69	695.000	10.000	1.44%	-0.23	1 517.500	17.078	1.13%	0.00	1 137.500	5.972	0.53%	0.13
180441	92.403	1.065	1.15%	0.15	776.208	18.442	2.38%	0.12	721.835	2.979	0.41%	-0.01	1 546.580	3.734	0.24%	0.22	1 115.945	25.421	2.28%	0.06
180453	90.358	0.456	0.50%	0.05	730.403	2.978	0.41%	-0.68	720.795	1.767	0.25%	-0.01	1 535.013	3.282	0.21%	0.13	1 101.733	4.321	0.39%	0.01
180458	1 068.595	446.611	41.79%	47.05	4 209.070	425.393	10.11%	60.03	5 511.200	2 698.061	48.96%	40.24	7 810.790	2 738.998	35.07%	46.55	5 016.885	720.359	14.36%	13.80
180470	83.243	3.409	4.10%	-0.29	750.055	17.354	2.31%	-0.34	702.970	7.467	1.06%	-0.16	1 505.303	5.711	0.38%	-0.09	1 099.925	9.065	0.82%	0.00
180471	88.630	1.063	1.20%	-0.03	739.383	3.800	0.51%	-0.52	668.998	4.506	0.67%	-0.45	1 619.708	13.444	0.83%	0.76	764.933	5.742	0.75%	-1.18
180476	91.728	0.655	0.71%	0.12	770.910	2.396	0.31%	0.03	717.233	3.428	0.48%	-0.04	1 562.608	10.667	0.68%	0.34	1 415.705	4.486	0.32%	1.11
180477	97.598	1.282	1.31%	0.40	726.378	10.664	1.47%	-0.75	564.228	6.482	1.15%	-1.33	1 457.678	1.557	0.11%	-0.44	803.445	3.422	0.43%	-1.04
180479	110.818	7.382	6.66%	1.03	751.043	71.987	9.58%	-0.32	595.133	12.709	2.14%	-1.07	1 451.028	163.040	11.24%	-0.49	1 154.538	17.686	1.53%	0.19
180481	64.200	0.804	1.25%	-1.20	600.250	14.705	2.45%	-2.95	562.500	4.203	0.75%	-1.34	1 228.750	8.539	0.69%	-2.13	1 166.000	21.772	1.87%	0.23
180486	88.650	0.661	0.75%	-0.03	715.850	6.620	0.92%	-0.93	643.125	7.438	1.16%	-0.67	1 485.825	21.202	1.43%	-0.23	978.850	7.020	0.72%	-0.43
180496	44.763	0.249	0.56%	-2.14	381.823	1.925	0.50%	-6.76	353.720	4.167	1.18%	-3.10	NA	NA	NA	NA	693.213	4.043	0.58%	-1.43

Lab ID.	Z scores										
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h _ anthracene	Fluoranthene	Indeno_1,2,3 _c,d_pyrene	Phenanthrene	Sum_BF
180402	0.32	0.26	0.89	4.51	0.70	1.82	0.77	-0.63	4.22	1.46	1.16
180405	-0.80	-1.07	-1.23	-0.92	NA	1.30	-0.96	-2.70	-1.13	-2.51	-1.14
180415	-0.11	1.09	1.04	0.19	~~NC~~	-0.44	1.45	-0.32	0.46	-0.09	-0.62
180429	NA	-1.83	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	~~NC~~	~~NC~~	NA	~~NC~~	NA	~~NC~~	~~NC~~	~~NC~~	~~NC~~	~~-10.66~~	~~NC~~
180437	0.28	-0.02	-0.12	-0.11	0.26	0.20	0.50	-0.69	-0.23	0.00	0.13
180441	0.45	0.14	0.08	0.02	0.10	-0.12	0.15	0.12	-0.01	0.22	0.06
180453	-0.19	-0.21	-0.05	0.58	0.05	0.01	0.05	-0.68	-0.01	0.13	0.01
180458	32.11	22.95	25.97	40.74	~~NC~~	17.31	47.05	60.03	40.24	46.55	13.80
180470	-0.13	0.10	-0.03	0.66	0.06	-0.09	-0.29	-0.34	-0.16	-0.09	0.00
180471	-2.43	-0.45	-0.32	-0.06	NA	-0.47	-0.03	-0.52	-0.45	0.76	-1.18
180476	~~NC~~	0.01	0.08	0.05	1.96	0.21	0.12	0.03	-0.04	0.34	1.11
180477	-0.51	-0.43	-0.21	-0.14	NA	-0.08	0.40	-0.75	-1.33	-0.44	-1.04
180479	0.65	0.23	2.67	0.26	NA	~~NC~~	1.03	-0.32	-1.07	-0.49	0.19
180481	-1.23	-1.42	-0.88	-1.73	1.56	-0.97	-1.20	-2.95	-1.34	-2.13	0.23
180486	-0.31	-0.43	-0.36	-0.34	-0.46	-0.16	-0.03	-0.93	-0.67	-0.23	-0.43
180496	-2.92	-2.73	-1.30	-3.16	-0.85	-1.91	-2.14	-6.76	-3.10	NA	-1.43

Lab ID	Zeta Score (ζ)									
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3_ c,d_pyrene	Phenanthrene
180402	0.97	0.86	3.06	7.96	5.32	5.90	1.97	-0.94	8.15	2.26
180405	-1.52	-2.02	-2.33	-1.61	NA	1.57	-2.14	-2.48	-1.81	-2.29
180415	-0.07	1.08	0.97	0.27	UNS	-0.58	3.18	-0.14	0.74	-0.06
180429	NA	UNS	NA	NA	NA	NA	NA	NA	NA	NA
180430	UNS	UNS	NA	UNS	NA	UNS	UNS	UNS	UNS	-94.94
180437	0.44	-0.06	-0.29	-0.19	1.18	0.50	0.75	-0.53	-0.36	0.00
180441	1.21	0.52	0.67	0.13	0.88	-0.70	0.43	0.35	-0.04	0.86
180453	-1.01	-1.15	-0.39	2.64	0.80	0.05	0.16	-1.80	-0.09	0.43
180458	2.41	2.33	3.38	2.15	UNS	2.01	2.29	3.27	2.17	2.01
180470	-0.34	0.35	-0.12	2.09	0.69	-0.49	-0.85	-0.34	-0.76	-0.08
180471	-11.50	-1.27	-0.65	-0.09	NA	-1.09	-0.05	-0.52	-0.57	1.07
180476	~~UNS~~	0.08	1.03	0.26	42.94	3.22	0.39	0.13	-0.65	2.44
180477	-0.92	-0.87	-0.47	-0.21	NA	-0.18	0.72	-0.58	-2.78	-0.41
180479	0.43	0.26	2.33	0.21	NA	~~NC~~	0.84	-0.14	-1.19	-0.36
180481	-1.90	-2.72	-1.67	-2.62	3.44	-2.18	-2.41	-2.32	-2.10	-1.73
180486	-0.31	-0.52	-0.47	-0.31	-1.94	-0.23	-0.04	-0.43	-0.70	-0.12
180496	-21.93	-19.77	-11.68	-22.58	-3.62	-24.32	-7.12	-23.83	-36.47	NA

APPENDIX 8: DETAILED RESULTS ON 18/172774_S3 (SOLUTION 3)

CRM

Lab ID.	Benzo a anthracene				Benzo a pyrene				Benzo b fluoranthene				Benzo g,h,i perylene				Benzo j fluoranthene				Benzo k fluoranthene			
	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z
180402	6.938	0.127	1.83%	-0.60	~~<10~~	~~0.000~~	~~0.00%~~	~~NC~~	11.925	0.157	1.31%	-1.37	10.408	0.371	3.57%	-0.40	~~<10~~	~~0.000~~	~~0.00%~~	NC	~~<10~~	~~0.000~~	~~0.00%~~	NC
180405	7.625	0.050	0.66%	-0.26	9.575	0.472	4.93%	-0.75	10.600	0.572	5.39%	-1.87	9.875	0.126	1.27%	-0.64	NA	NA	NA		10.700	0.294	2.75%	1.18
180415	6.513	0.084	1.29%	-0.81	9.158	0.210	2.29%	-0.93	16.750	0.088	0.53%	0.46	10.103	0.186	1.84%	-0.54	~~0.000~~	~~0.000~~	~~Pb. Mov.=0~~	NC	6.855	0.303	4.41%	-0.44
180429	NA	NA	NA		11.278	1.513	13.42%	0.01	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	
180430	277.640	17.033	6.14%	134.52	298.755	8.992	3.01%	128.09	NA	NA	NA		192.055	6.467	3.37%	79.89	NA	NA	NA		568.493	12.291	2.16%	237.09
180437	9.000	0.000	0.00%	0.43	12.000	0.000	0.00%	0.33	16.250	0.500	3.08%	0.27	12.250	0.500	4.08%	0.41	5.250	0.500	9.52%	-0.36	9.000	0.000	0.00%	0.47
180441	9.110	0.022	0.24%	0.48	11.930	0.000	0.00%	0.30	15.860	0.108	0.68%	0.13	11.508	0.010	0.08%	0.08	8.630	0.124	1.44%	0.12	8.350	0.241	2.89%	0.19
180453	8.118	0.028	0.34%	-0.01	11.083	0.061	0.55%	-0.07	15.713	0.079	0.50%	0.07	12.078	0.108	0.90%	0.33	7.675	0.161	2.10%	-0.01	8.223	0.103	1.26%	0.14
180458	10.753	1.134	10.54%	1.30	17.828	9.948	55.80%	2.93	18.220	1.426	7.83%	1.02	31.135	10.076	32.36%	8.76	~~0.000~~	~~0.000~~	~~Pb. Mov.=0~~	NC	11.403	5.306	46.53%	1.48
180470	8.278	0.414	5.00%	0.07	11.738	0.833	7.10%	0.22	15.888	0.672	4.23%	0.14	13.020	0.833	6.40%	0.75	~~<40~~	~~0.000~~	~~0.00%~~	NC	7.835	0.514	6.57%	-0.03
180471	5.135	0.541	10.53%	-1.50	10.490	1.107	10.55%	-0.34	14.665	1.820	12.41%	-0.33	11.893	1.233	10.37%	0.25	NA	NA	NA		6.688	0.860	12.86%	-0.51
180476	~~<5~~	~~0.000~~	~~0.00%~~	NC	11.540	0.045	0.39%	0.13	16.300	0.212	1.30%	0.29	11.283	0.118	1.04%	-0.02	16.395	0.173	1.06%	1.22	8.560	0.104	1.21%	0.28
180477	~~<20~~	~~0.000~~	~~0.00%~~	NC	~~<20~~	~~0.000~~	~~0.00%~~	~~NC~~	~~<20~~	~~0.000~~	~~0.00%~~	NC	~~<20~~	~~0.000~~	~~0.00%~~	NC	~~<20~~	~~0.000~~	~~0.00%~~	NC	~~<20~~	~~0.000~~	~~0.00%~~	NC
180479	8.608	1.415	16.44%	0.23	11.980	2.406	20.08%	0.33	24.973	5.528	22.14%	3.58	12.125	2.187	18.04%	0.36	NA	NA	NA		~~8.760~~	~~2.222~~	~~25.36%~~	~~NC~~
180481	6.428	0.087	1.35%	-0.85	6.925	0.021	0.30%	-1.93	15.625	0.250	1.60%	0.04	7.290	0.088	1.20%	-1.78	21.150	0.238	1.13%	1.90	5.590	0.075	1.35%	-0.98
180486	8.075	0.171	2.11%	-0.03	10.650	0.058	0.54%	-0.27	15.200	0.115	0.76%	-0.13	11.100	0.258	2.33%	-0.10	5.175	0.096	1.85%	-0.37	7.850	0.058	0.74%	-0.02
180496	5.210	0.230	4.42%	-1.46	6.023	0.086	1.43%	-2.33	11.580	0.228	1.97%	-1.50	6.103	0.069	1.14%	-2.31	4.133	0.062	1.51%	-0.52	4.950	0.143	2.89%	-1.25

Lab ID.	Dibenzo a,h anthracene				Fluoranthene				Indeno 1,2,3 c,d pyrene				Phenanthrene				Sum BF			
	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z	x (µg/liter)	sr (µg/liter)	s_r en %	score z
180402	~~<4~~	~~0.000~~	~~0.00%~~	NC	18.953	0.135	0.71%	-1.08	18.053	0.408	2.26%	-1.19	43.645	0.638	1.46%	0.14	11.925	0.157	1.31%	-2.19
180405	~~<5~~	~~0.000~~	~~0.00%~~	NC	18.575	0.050	0.27%	-1.23	17.600	0.440	2.50%	-1.35	34.625	0.842	2.43%	-1.24	21.300	0.535	2.51%	-1.13
180415	2.575	0.083	3.24%	0.12	19.873	0.059	0.29%	-0.72	15.390	0.232	1.51%	-2.10	43.575	0.150	0.34%	0.13	23.605	0.370	1.57%	-0.87
180429	NA	NA	NA		NA	NA	NA		NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA
180430	42.593	2.911	6.83%	44.46	834.520	26.723	3.20%	321.85	371.855	18.500	4.97%	119.35	1 104.723	48.110	4.35%	163.29	~~1 546.723~~	~~28.802~~	~~1.86%~~	172.30
180437	3.000	0.000	0.00%	0.59	21.250	0.500	2.35%	-0.17	21.500	0.577	2.69%	-0.02	44.750	0.500	1.12%	0.31	30.500	0.577	1.89%	-0.08
180441	2.645	0.021	0.79%	0.19	22.370	0.252	1.13%	0.27	20.570	0.052	0.25%	-0.33	43.898	0.655	1.49%	0.18	32.840	0.377	1.15%	0.18
180453	2.583	0.013	0.49%	0.12	21.123	0.136	0.64%	-0.22	20.653	0.131	0.64%	-0.31	44.138	0.076	0.17%	0.22	31.610	0.128	0.40%	0.04
180458	39.685	20.250	51.03%	41.24	24.378	3.027	12.42%	1.06	18.408	2.571	13.97%	-1.07	52.193	7.806	14.96%	1.46	29.623	6.285	21.22%	-0.18
180470	~~<10~~	~~0.000~~	~~0.00%~~	NC	~~<30~~	~~0.000~~	~~0.00%~~	NC	20.710	0.810	3.91%	-0.29	~~<50~~	~~0.000~~	~~0.00%~~	NC	23.723	1.081	4.56%	-0.85
180471	2.655	0.289	10.90%	0.20	21.448	2.737	12.76%	-0.10	19.038	2.381	12.51%	-0.86	44.260	6.512	14.71%	0.24	21.353	2.679	12.55%	-1.12
180476	2.715	0.056	2.05%	0.27	22.480	0.255	1.13%	0.31	20.288	0.326	1.61%	-0.43	46.173	0.391	0.85%	0.53	41.255	0.220	0.53%	1.14
180477	~~<20~~	~~0.000~~	~~0.00%~~	NC	20.115	0.392	1.95%	-0.62	~~<20~~	~~0.000~~	~~0.00%~~	NC	40.998	0.664	1.62%	-0.26	~~<60~~	~~0.000~~	~~0.00%~~	3.27
180479	3.325	0.454	13.66%	0.95	18.648	0.787	4.22%	-1.20	17.270	2.863	16.58%	-1.46	34.460	8.684	25.20%	-1.27	33.733	7.744	22.96%	0.29
180481	1.828	0.022	1.21%	-0.71	17.975	0.250	1.39%	-1.47	14.475	0.096	0.66%	-2.41	34.050	0.500	1.47%	-1.33	42.365	0.237	0.56%	1.27
180486	2.600	0.000	0.00%	0.14	20.950	0.129	0.62%	-0.29	17.825	1.237	6.94%	-1.27	40.425	0.624	1.54%	-0.35	28.225	0.222	0.79%	-0.34
180496	1.265	0.079	6.27%	-1.34	11.078	0.036	0.32%	-4.20	10.180	0.180	1.77%	-3.87	NA	NA	NA	NA	20.663	0.318	1.54%	-1.20

Lab ID.	Z scores										
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h _anthracene	Fluoranthene	Indeno_1,2,3 _c,d_pyrene	Phenanthrene	Sum_BF
180402	-0.60	~~NC~~	-1.37	-0.40	~~NC~~	~~NC~~	~~NC~~	-1.08	-1.19	0.14	-2.19
180405	-0.26	-0.75	-1.87	-0.64	NA	1.18	~~NC~~	-1.23	-1.35	-1.24	-1.13
180415	-0.81	-0.93	0.46	-0.54	~~NC~~	-0.44	0.12	-0.72	-2.10	0.13	-0.87
180429	NA	0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA
180430	134.52	128.09	NA	79.89	NA	237.09	44.46	321.85	119.35	163.29	~~172.30~~
180437	0.43	0.33	0.27	0.41	-0.36	0.47	0.59	-0.17	-0.02	0.31	-0.08
180441	0.48	0.30	0.13	0.08	0.12	0.19	0.19	0.27	-0.33	0.18	0.18
180453	-0.01	-0.07	0.07	0.33	-0.01	0.14	0.12	-0.22	-0.31	0.22	0.04
180458	1.30	2.93	1.02	8.76	~~NC~~	1.48	41.24	1.06	-1.07	1.46	-0.18
180470	0.07	0.22	0.14	0.75	~~NC~~	-0.03	~~NC~~	~~NC~~	-0.29	~~NC~~	-0.85
180471	-1.50	-0.34	-0.33	0.25	NA	-0.51	0.20	-0.10	-0.86	0.24	-1.12
180476	~~NC~~	0.13	0.29	-0.02	1.22	0.28	0.27	0.31	-0.43	0.53	1.14
180477	~~NC~~	~~NC~~	~~NC~~	~~NC~~	~~NC~~	~~NC~~	~~NC~~	-0.62	~~NC~~	-0.26	~~NC~~
180479	0.23	0.33	3.58	0.36	NA	~~NC~~	0.95	-1.20	-1.46	-1.27	0.29
180481	-0.85	-1.93	0.04	-1.78	1.90	-0.98	-0.71	-1.47	-2.41	-1.33	1.27
180486	-0.03	-0.27	-0.13	-0.10	-0.37	-0.02	0.14	-0.29	-1.27	-0.35	-0.34
180496	-1.46	-2.33	-1.50	-2.31	-0.52	-1.25	-1.34	-4.20	-3.87	NA	-1.20

Lab ID.	Zeta Score (ζ)									
	Benzo_a_ anthracene	Benzo_a_ pyrene	Benzo_b_ fluoranthene	Benzo_g,h,i_ perylene	Benzo_j_ fluoranthene	Benzo_k_ fluoranthene	Dibenzo_a,h_ anthracene	Fluoranthene	Indeno_1,2,3_ c,d_pyrene	Phenanthrene
180402	-3.13	UNS	-5.62	-1.61	UNS	UNS	UNS	-2.73	-3.77	0.42
180405	-0.66	-1.38	-3.07	-1.43	NA	1.74	UNS	-1.65	-1.79	-1.86
180415	-0.90	-1.41	0.39	-1.12	UNS	-0.76	0.45	-0.52	-4.17	0.14
180429	NA	UNS	NA	NA	NA	NA	NA	NA	NA	NA
180430	45.55	85.35	NA	114.98	NA	64.24	171.40	29.16	40.77	15.98
180437	0.94	0.76	0.49	0.83	-4.33	1.34	1.28	-0.20	-0.02	0.50
180441	1.84	1.17	0.84	0.58	1.66	1.27	0.86	1.23	-2.11	1.22
180453	-0.09	-0.47	0.40	2.01	-0.38	1.35	0.60	-0.92	-1.60	1.21
180458	0.97	1.05	0.42	1.59	UNS	0.77	2.68	0.31	-0.49	0.52
180470	0.26	0.41	0.23	1.81	UNS	-0.12	UNS	UNS	-0.47	UNS
180471	-9.86	-0.99	-0.53	0.49	NA	-1.58	0.49	-0.15	-0.95	0.59
180476	UNS	1.27	2.43	-0.15	32.71	4.22	1.33	1.92	-3.23	6.02
180477	UNS	UNS	UNS	UNS	UNS	UNS	UNS	-0.77	UNS	-0.42
180479	0.24	0.37	2.43	0.37	NA	~~NC~~	1.11	-0.90	-1.37	-1.83
180481	-1.94	-4.50	0.04	-3.99	4.67	-3.02	-2.18	-1.70	-3.60	-1.88
180486	-0.05	-0.32	-0.12	-0.11	-2.81	-0.04	0.27	-0.20	-1.19	-0.32
180496	-15.01	-20.48	-10.59	-21.48	-3.47	-18.96	-6.88	-22.83	-38.40	NA

APPENDIX 9: CERTIFICATE OF ANALYSIS OF CRM

Institute for Reference Materials and Measurements

ERM European Reference Materials

CERTIFICATE OF ANALYSIS

ERM®-CZ100

861-867

FINE DUST (PM_{10}-LIKE)

PAH	Mass Fraction	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
Benzo[*a*]anthracene	0.91	0.07
Benzo[*a*]pyrene	0.72	0.05
Benzo[*b*]fluoranthene	1.42	0.14
Benzo[*j*]fluoranthene	0.75	0.14
Benzo[*k*]fluoranthene	0.67	0.06
Dibenzo[*a,h*]anthracene	0.18	0.04
Indeno[1,2,3-*c,d*]pyrene	1.07	0.10
Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene[3]	2.84	0.21

[1] Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values and their uncertainties are mass fractions based on the mass of the sample after conditioning as described in EN12341. They are traceable to the SI.

[2] The certified uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

[3] The mass fraction of the sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene was calculated as the sum of the individual certified values of each compound. The uncertainty was calculated as the combined expanded uncertainty of the uncertainties of the individual compounds.

This certificate is valid for one year after purchase.

Sales date: 31. JAN. 2018

The minimum amount of sample to be used is 50 mg.

NOTE

European Reference Material ERM®-CZ100 was produced and certified under the responsibility of the Institute for Reference Materials and Measurements of the European Commission's Joint Research Centre according to the principles laid down in the technical guidelines of the European Reference Materials® co-operation agreement between BAM-IRMM-LGC. Information on these guidelines is available on the internet (http://www.erm-crm.org).

Accepted as an ERM®, Geel, November 2010

Signed:

Prof. Dr. Hendrik Emons
European Commission
Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel, Belgium

JRC EUROPEAN COMMISSION

All following pages are an integral part of the certificate.

Page 1 of 3

Additional Material Information

	Mass Fraction
	Value [1] [mg/kg]
Anthracene	0.28
Benzo[*g*,*h*,*i*]pyrene	1.76
Chrysene	1.61
Coronene	0.84
Fluoranthene	4.67
Phenanthrene	2.23
Pyrene	4.59

[1] The mean values for additional compounds came from the accepted data sets of the characterisation study. The values are reported on the mass of the sample after conditioning the sample using conditions as described in EN12341.

DESCRIPTION OF THE SAMPLE

The material consists of about 0.5 g of fine dust that was processed in a way to resemble PM_{10} as close as possible. It was packed into amber glass vials, closed with a rubber stopper (coated with PTFE) and an aluminium cap under argon atmosphere.

ANALYTICAL METHODS USED FOR CERTIFICATION

- Gas chromatography mass spectrometry
- Gas chromatography isotope dilution mass spectrometry
- High performance liquid chromatography

PARTICIPANTS

- Agencija Republike Slovenije za Okolje, Lublijana (SI) (accredited to ISO/IEC 17025, Slovenian accreditation, LP-030)
- Executive Environment Agency, Sofia (BG) (accredited to ISO/IEC 17025, BAS, N°32-testing laboratory) *
- Eesti Keskkonnauuringute Keskus Oü, Tallinn (EE) (accredited to ISO/IEC 17025, EAK L008) *
- Environmental Protection Agency, Vilnius (LT) (accredited to ISO/IEC 17025, LA.01.064)
- Finnish Meteorological Institute (FMI), Helsinki (FI) (accredited to ISO/IEC 17025, FINAS, T097) *
- Helmholtz Zentrum München - Deutsches Forschungszentrum für Gesundheit und Umwelt (GmbH), Neuherberg (DE) (accredited to ISO/IEC 17025, DAC-PL-0141-01-10) *
- Institute for Reference Materials and Measurements (IRMM), Geel (BE) (accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)
- Institut National de l'environnement industriel et de risques (INERIS), Verneuil-en-Halatte (FR) (accredited to ISO/IEC 17025, COFRAC-Accreditation 1-0157) *
- Institut pro testování a certifikace (ITC), Zlin (CZ) (certified according to EN ISO 9001)
- Laboratoire National de métrologie d'Essais (LNE), Paris (FR), (accredited to ISO/IEC 17025, COFRAC-Accreditation 2-54) *
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- Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu delegatura w Jeleniej Górze, Jelenia Góra (PL) (accredited to ISO/IEC 17025, PCA, AB 075) *

* Measurements within the scope of accreditation to ISO 17025

SAFETY INFORMATION

The usual laboratory safety measures apply. As the material consists of fine particles, appropriate protection against inhalation is recommended.

INSTRUCTIONS FOR USE

The main purpose of the material is to assess performance of analytical methods for analysis of selected PAHs in PM_{10}. It can not be used to verify the performance of impactors, filters or particle size analysis.

The vials shall be shaken at least 2 min before opening to ensure the material rehomogenisation. The sample weighing shall be performed respecting conditions (i.e. temperature humidity and time) that are specified in the standard EN 12341. It means that before analysis, the sample has to be opened and kept for at least 48 h in an air-conditioned weighing room with a temperature of 20 °C ± 1 °C and a relative humidity of 50 % ± 5 % to reach equilibrium under weighing room conditions.

STORAGE

The materials shall be stored at 4 °C ± 3 °C in the dark.

However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

LEGAL NOTICE

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NOTE

A detailed technical report is available on www.erm-crm.org. A paper copy can be obtained from the Joint Research Centre, Institute for Reference Materials and Measurements on request.

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