JRC Scientific and Technical Reports

Report of the inter-laboratory comparison on the 15+1 EU priority PAHs

Report of the inter-laboratory comparison organised by the
Food Safety and Quality Unit
on the 15+1 EU priority Polycyclic Hydrocarbons in Liquid Smoke Condensate

Rupert Simon and Thomas Wenzl

EUR 22945 EN - 2007

JRC
EUROPEAN COMMISSION
Institute for Reference Materials and Measurements
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European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Address: CRL PAH
E-mail: Thomas.wenzl@ec.europa.eu
Tel.: +32 14 571 320
Fax: +32 14 571 783

http://www.irmm.jrc.be/html/homepage.htm
http://www.jrc.ec.europa.eu

JRC 40602

EUR 22945 EN
ISSN 1018-5593

Luxembourg: Office for Official Publications of the European Communities

Report of the inter-laboratory comparison 15+1 EU priority Polycyclic Aromatic Hydrocarbons in liquid smoke condensate

EC-JRC-IRMM
September 2007

Rupert Simon
Thomas Wenzl

Summary

The two test materials of the inter-laboratory comparison test were dispatched begin of July 2006. Each participant received two liquid smoke condensate test materials to be analysed for the 15+1 EU priority polycyclic aromatic hydrocarbons (PAHs). In total 28 sets of samples were sent to participating laboratories in 13 countries. Of these 28 participants 26 (93%) reported back results for at least one analyte.

Both test materials contained the 15+1 EU priority PAHs. The assigned value (X) for each analyte was calculated from the participant's results applying robust statistics.

The target standard deviation (σ_p) was calculated using the modified Horwitz equation as proposed by Thomson [1]. The resulting σ_p was then used in conjunction with the assigned value to derive z-scores from the participant's results.

An overview on the assigned values and the performance of the participants for individual analytes is given in Table 1:

Table 1: 15+1 EU and JECFA priority PAHs

Analyte	Assigned value X [ug/kg]		Total number of scores		Number of satisfactory scores		Relative number of satisfactory scores [%]	
	Mat. 1	Mat. 2	Mat. 1	Mat. 2	Mat. 1	Mat. 2	Mat. 1	Mat. 2
5-Methylchrysene	21.3	10.0	24	24	20	20	83	83
Benz[*a*]anthracene	18.7	13.2	26	26	23	22	88	85
Benzo[*a*]pyrene	5.0	13.4	26	26	21	21	81	81
Benzo[*b*]fluoranthene	13.3	23.0	21	23	15	18	71	78
Benzo[*c*]fluorene	11.8	20.9	17	19	13	12	76	63
Benzo[*ghi*]perylene	6.9	14.2	25	25	17	17	68	68
Benzo[*j*]fluoranthene	16.4	27.3	13	13	10	11	77	85
Benzo[*k*]fluoranthene	21.3	12.3	21	21	18	15	86	71
Chrysene	12.5	22.2	25	25	21	22	84	88
Cyclopenta[*cd*]pyrene	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.
Dibenz[*a,h*]anthracene	20.5	13.2	24	24	16	15	67	63
Dibenzo[*a,e*]pyrene	21.1	14.2	24	24	14	16	58	67
Dibenzo[*a,h*]pyrene	16.6	19.4	21	23	15	15	71	65
Dibenzo[*a,i*]pyrene	13.7	17.3	23	23	16	12	70	52
Dibenzo[*a,l*]pyrene	12.8	23.3	23	23	16	16	70	70
Indeno[*1,2,3-cd*]pyrene	23.7	14.1	24	25	14	17	58	68

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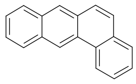
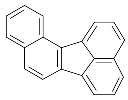
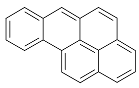
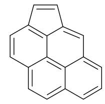
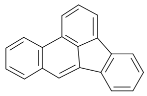
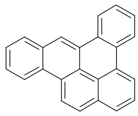
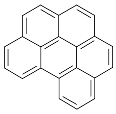
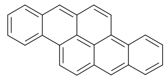
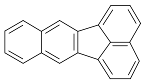
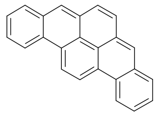
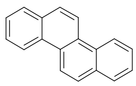
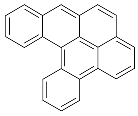
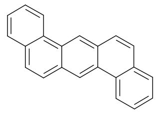
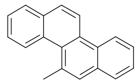
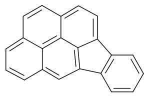
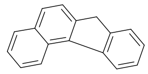
Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances containing two or more fused aromatic rings made up of carbon and hydrogen atoms. Hundreds of individual PAHs may be formed and released during the incomplete combustion or pyrolysis of wood used for smoke generation. The European Commission's Scientific Committee on Food (SCF) assessed 33 PAHs and identified 15 of them as of major concern for human health (referred to later as the 15 SCF PAHs). These 15 SCF PAHs should be monitored to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene as a marker for a "total-PAH content" [2]. In 2005 the European Union (EU) recommended research on the occurrence of these 15 PAHs in food [3]. In February of the same year the Joint Expert Committee on Food Additives of the Food and Agriculture Organisation of the United Nations and the World Health Organisation recommended to analyse for 13 of the 15 SCF PAHs in food and to include benzo[*c*]fluorene to help inform future evaluations [4]. When in 2006 the European Food Safety Authority (EFSA) invited the EU Member States to collect data on the occurrence of PAHs in food benzo[*c*]fluorene was added to the 15 SCF PAHs. This merged set is now referred to as the 15+1 EU priority PAHs [5] (Table 2).

Smoke flavourings based on the aqueous phase of condensed smoke, called primary smoke condensate (PSC), are on the market for more than hundred years. The use of smoke flavouring rather than traditional smoking was triggered by the ease of application and a more efficient use of the resources [6]. As further benefit the amount of (known) harmful substances such as PAHs, can be controlled easier in the flavouring than in smoke [7,8]. This control is the purpose of Regulation 2065/2003 laying down maximum permitted concentrations for benzo[*a*]pyrene (10 µg/kg) and benz[*a*]anthracene (20 µg/kg) in PSC produced for human consumption [9], whereas Commission Regulation (EC) No 627/2006 lays down the minimum performance criteria for the respective analytical methods applied in implementation of this control [10].

To support the implementation of these two pieces of EU-legislation the Institute for Reference Materials and Measurements (IRMM) organised this inter-laboratory comparison (ILC) on the analysis of the 15+1 EU priority PAHs in PSC.

Table 2: 15+1 EU and JECFA priority PAHs

1	Benz[*a*] anthracene (BaA)		9	Benzo[*j*] fluoranthene (BjF)	
2	Benzo[*a*] pyrene (BaP)		10	Cyclopenta-[*cd*]pyrene (CPP)	
3	Benzo[*b*] fluoranthene (BbF)		11	Dibenzo [*a,e*]pyrene (DeP)	
4	Benzo[*ghi*] perylene (BgP)		12	Dibenzo [*a,h*]pyrene (DhP)	
5	Benzo[*k*] fluoranthene (BkF)		13	Dibenzo [*a,i*]pyrene (DiP)	
6	Chrysene (CHR)		14	Dibenzo [*a,l*]pyrene (DlP)	
7	Dibenz[*a,h*] anthracene (DhA)		15	5-Methyl chrysene (5MC)	
8	Indeno[1,2,3-*cd*]pyrene (IcP)		+ 1	Benzo[*c*]fluorene (BcL)	

Test material

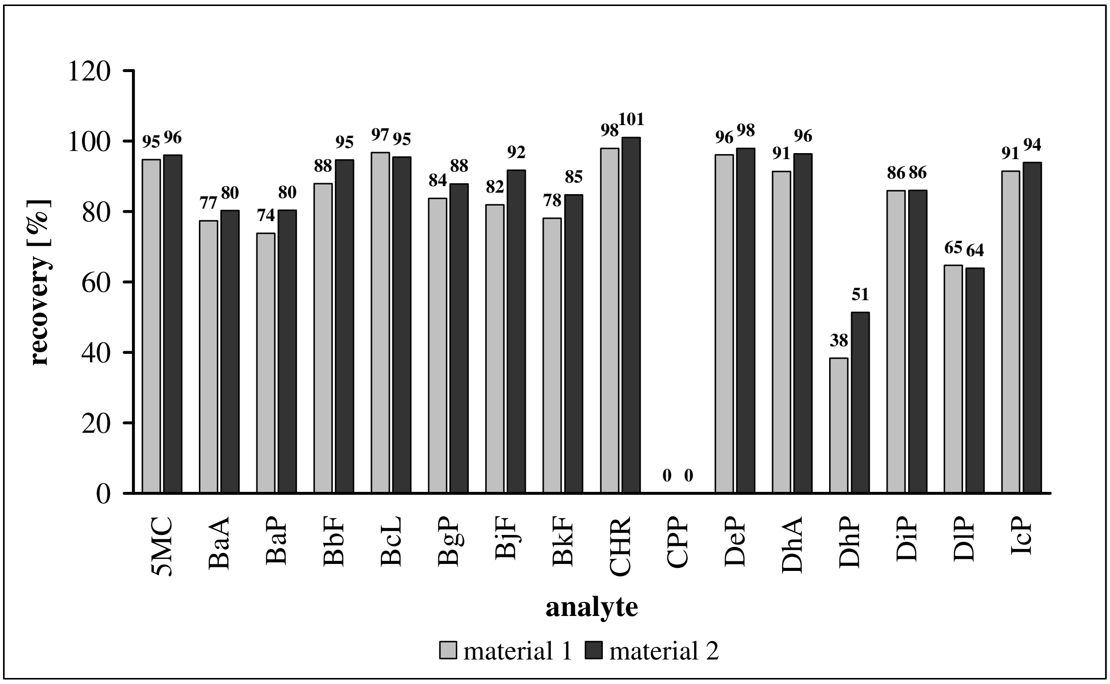
Smoke condensates from six different manufacturers were mixed in about equal amounts. Two times one litre were spiked with the 15+1 EU priority PAHs in 2-propanol in varying amounts to give the final concentrations as given in Table 3, vigorously mixed overnight, and aliquots were sealed in brown glass ampoules. Since the materials were liquid, they could be considered homogeneous.

Table 3: **Spiked amounts of the 15+1 analytes in the two materials used in this study (given in µg/kg)**

analyte	material1	material2
5-methylchrysene	26.7	12.5
benz[*a*]anthracene	25.2	16.7
benzo[*a*]pyrene	6.1	17.8
benzo[*b*]fluoranthene	15.7	27.7
benzo[*c*]fluorene	12.1	24.0
benzo[*ghi*]perylene	9.8	23.9
benzo[*j*]fluoranthene	19.4	31.2
benzo[*k*]fluoranthene	26.5	14.4
chrysene	14.5	28.8
cyclopenta[*cd*]pyrene	18.2	30.0
dibenz[*a,h*]anthracene	26.6	19.2
dibenzo[*a,e*]pyrene	27.9	19.2
dibenzo[*a,h*]pyrene	31.3	35.4
dibenzo[*a,i*]pyrene	20.6	30.1
dibenzo[*a,l*]prene	17.0	31.3
indeno[*1,2,3-cd*]pyrene	30.3	17.9

The test materials for the IRMM inter-laboratory comparison were dispatched begin of July 2006. Each participant received two liquid smoke condensate test materials to be analysed for the 15+1 EU priority PAHs. In total 28 sets of samples were sent to participating laboratories in 13 countries. Of these 28 participants 26 (93%) reported back results for at least one analyte (benzo[*a*]pyrene).

Figure 1: **Analyte recovery after six months of storage at 4°C in the dark expressed as per-cent of recovered content from the spiked amount for all 15+1 EU priority PAHs**



An analysis of the materials after ending the ILC showed that the contents of some analytes were particularly unstable even under optimum conditions of storage in a refrigerator at +4°C with the exclusion of light. The results of this analysis showed that for 5-methylchrysene, benzo[*b*]fluoranthene, benzo[*c*]fluorene, chrysene, dibenzo[*a,e*]pyrene, dibenz[*a,h*]anthracene, and indeno[*1,2,3-cd*]pyrene the contents found back were still above 90% of the spiked values. For the other analytes - including the regulated benzo[*a*]pyrene and benz[*a*]anthracene – the recovered values lay between 74 and 88%. For cyclopenta[*cd*]pyrene the data suggest that the analyte is extremely unstable in liquid smoke condensates and thus might not be present in real samples at all (Figure 1).

Results

Statistical evaluation of results

The procedure for the evaluation of the results followed ISO 13528 [11]. Additionally kernel density plots were used to identify multi modality in the reported values' distributions.

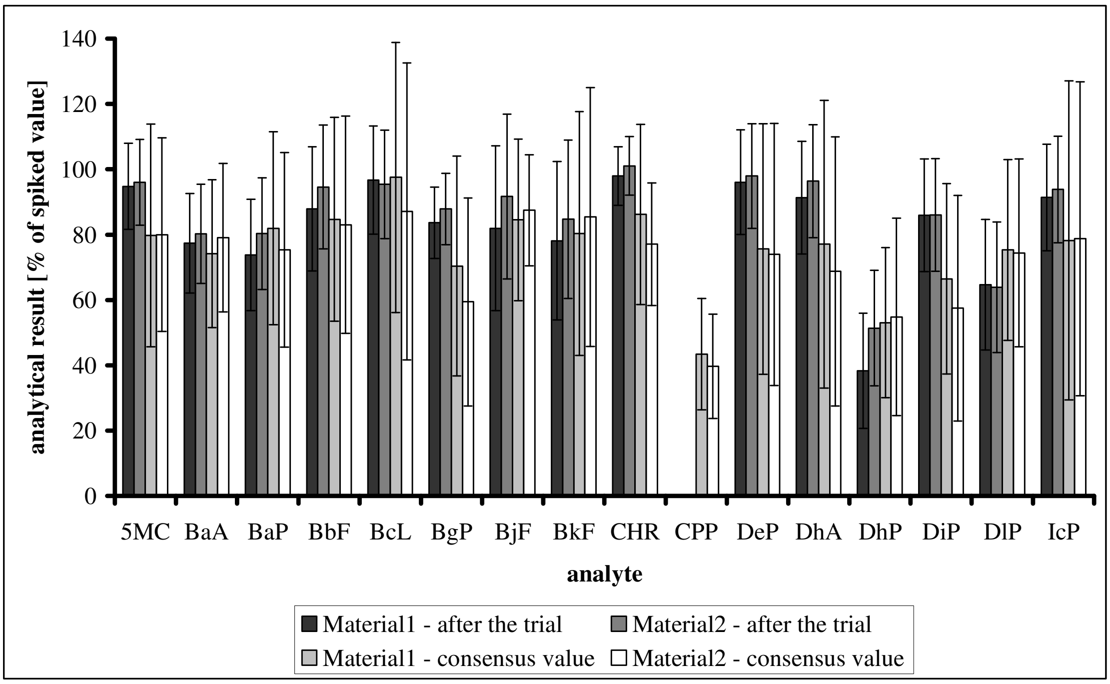
Identification of modes using kernel density plotting

Frequently analytical results from a collaborative study are not normally distributed or contain values from different populations giving rise to multiple distribution modes. These modes can be visualised by using Kernel density plots [12,13]. Kernel density plots are computed from the analytical results by representing the individual numeric values each as a normalised Gaussian distribution centred on the respective analytical value. The sum of these normal distributions form then the density distribution as presented in the respective graphs in the Annexes 1A and 1B. This method is implemented in an Excel Macro supplied by the Royal Society of Chemistry's Analytical Methods Committee (AMC), which was used for the calculation of the actual functions [12].

Determination of the Consensus value

The median values from the participants and the recovered amounts from the materials after six month (Figure 1) were compared (Figure 2). The comparison showed that for 50 % of the analytes (BaA, BaP, BbF, BcL, BjF, BkF, DhP, DlP, and IcP) the median values agreed with the recovered analyte contents after six month, while for other compounds a statistically significant disagreement was found (95 % interval). As mentioned above, for CPP the data suggested that the analyte was unstable in the matrix used and no evaluation of the results was made for this analyte. The z-scores for CPP were therefore not given in the tables (Annexes 1A and 1B).

Figure 2: Comparison of recovered analyte content after the inter-laboratory comparison at IRMM and the median values calculated from the participants analytical results (consensus value)



Calculation of the assigned value

The reported data of all analyte-material combinations were subjected to a kernel density analysis (so called bump hunting). In parallel the robust mean (median) of these data were calculated using again an Excel Macro from AMC [12]. The median and the location of the maximum of the kernel density are given in the annex together with the numerical values of the reported results. For consistency the median was taken as the assigned value *X* in all cases (consensus value).

Target standard deviation

The standard deviation for proficiency testing σ_p determines the criterion against which the differences of the reported results to the assigned values are compared. Thus, the final scoring of the individual laboratories depends not only on the reported result, but on σ_p as well. Generally the relative standard deviation of the reproducibility estimated by collaborative trials is considered to reflect best practice. As little or no precedent information can be found for the analysis of the substances involved, it is current practice to use a predictive model, namely the modified Horwitz function [1]. Using the respective function the standard deviation for proficiency testing σ_p was determined as 22%.

Z-Scores

The z-scores were calculated according to equation 1 as:

$$z = (x - X) / \sigma_p \quad \text{(equation 1)}$$

where z refers to the score, X to the reported value, X to the assigned value, and σ_p to the target relative standard deviation.

To get a quick overview on the individual performances and to identify potential biases an overview on all z-scores is given in Annex 2.

Measurement uncertainty and bias

The found value of the relative reproducibility standard deviation (RSD_R) of the results from the participants varied between 19.4 % for BjF and 62.4 % for IcP with average values of 42.3 % and 44.4 % for material 1 and 2, respectively. In general analytical data originating from several different methods showed higher RSD values than data from single method comparisons. Nevertheless, the values found in this PT for reproducibility were compliant to the minimum performance criteria for analytical methods used to analyse liquid smoke condensates for PAH-content given in Commission Regulation 627/2006 [10] for 11 of the analytes (5MC, BaA, BaP, BbF, BjF, BkF, CHR, DeP, DhP, DiP, and DlP). DhA and IcP showed higher values for both materials, BgP showed a higher value for material 2 (Table 4).

The consensus values were found to be biased in the two test materials for the compounds 5MC, BgP, CHR, DeP, and DiP. For DhA a bias was detected only in material 2. The analyte CPP was not recovered above the detection limit after the end of the ILC and could not be assessed for bias. For the eight remaining compounds (BaA, BaP, BbF, BcL, BjF, BkF, DhP, and DlP) the consensus values agreed with the measured values after end of the ILC (Fig. 2, Tab. 4).

Table 4: Relative reproducibility standard deviation (RSD_R) and bias of the reported values

	RSD_R [%]			Bias of the median [%]	
	found		required[1]	with respect to the found value at IRMM after PT	
Analyte	*Mat1*	*Mat2*	*627/2006*	*Mat1*	*Mat2*
5-Methylchrysene	43	37	50	-16*	-17*
Benz[*a*]anthracene	31	29	40	-4.1	-1.5
Benzo[*a*]pyrene	36	40	40	11	-6.3
Benzo[*b*]fluoranthene	37	40	50	-3.6	-12
Benzo[*c*]fluorene	42	52	n. a.	0.9	-8.7
Benzo[*ghi*]perylene	48	54**	50	-16*	-32*
Benzo[*j*]fluoranthene	29	19	50	3.1	-4.5
Benzo[*k*]fluoranthene	47	46	50	2.9	0.8
Chrysene	32	24	50	-12*	-24*
Cyclopenta[*cd*]pyrene	39	40	70	n. a.	n. a.
Dibenzo[*a,e*]pyrene	51	54	70	-21*	-25*
Dibenz[*a,h*]anthracene	57**	60**	50	-16	-29*
Dibenzo[*a,h*]pyrene	43	55	70	38	6.6
Dibenzo[*a,i*]pyrene	44	60	70	-23*	-33*
Dibenzo[*a,l*]pyrene	37	39	50	16	17
Indeno[*1,2,3-cd*]pyrene	62**	61**	50	-14	-16

n.a. = not applicable, * = statistically significant difference, ** = not compliant, [1] =

Conclusion

The analyte CPP showed extreme low stability in the matrix investigated suggesting that the respective compound may not be present in primary smoke condensates and thus not of concern with respect to smoke flavourings.

For three analytes the values for the precision were outside the limits given in Commission Regulation 627/2006 [10] and for six analytes a bias was found. These results suggested revising the used methods and procedures for possibilities of improvement regarding the respective analytes.

For seven of the 15+1 EU priority PAHs (BaA, BaP, BbF, BjF, BkF, DhP, and DlP) the performance characteristics found in this study complied with EU Regulation 627/2006 laying down quality criteria for analytical methods used to determine PAHs in primary smoke products, although the participating laboratories were free to use a method of choice [10]. In particular it could be shown that the laboratories were able to verify compliance with Commission Regulation 2065/2003 [9] of primary smoke condensates regarding the contents of benzo[*a*]pyrene and benz[*a*]anthracene.

Acknowledgements

We thank Forest Flavours Glasgow KY USA, Brøste Lyngby DK, Red Arrow Manitowoc WI USA, Symrise Holzminden DE, Unilever Sharnbrook UK, and Mastertaste Gloucestershire UK for providing the primary smoke condensates needed to prepare the materials used.
We thank José Angel Gomez Ruiz, Laszlo Hollosi, Lubomir Karasek, and Szilard Szilagyi for assistance during preparation of the materials.

Disclaimer

Neither the authors nor the institute accept any liability as to the application or use of the information contained within this report.

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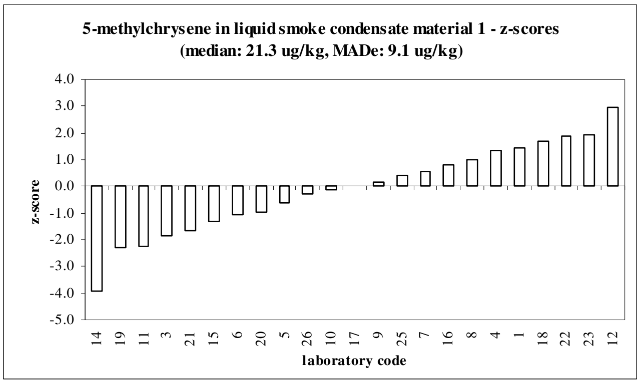
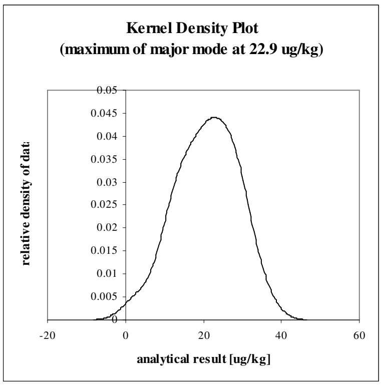
Annex 1A: Material 1

5-Methylchrysene

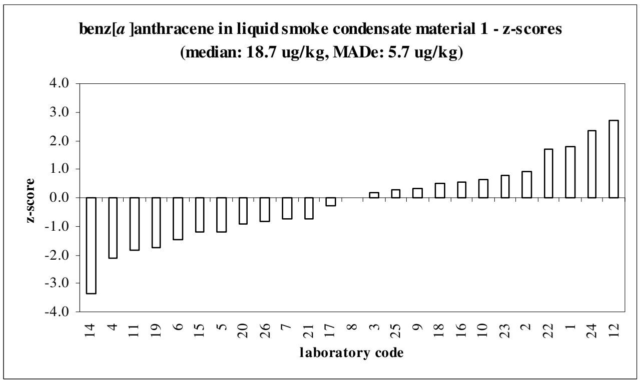
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	28.1	6.7	1.5	GC-HRMS
3	12.7	1.3	-1.8	HPLC-FLD
4	27.5	0.0	1.3	GC-MS
5	18.4	1.2	-0.6	HPLC-FLD/UV
6	16.3	5.0	-1.1	HPLC-FLD/UV
7	23.9	3.6	0.6	HPLC-FLD
8	26.0	0.9	1.0	HPLC-FLD/UV
9	22.0	0.0	0.1	HPLC-FLD
10	20.7	0.0	-0.1	GC-MS
11	10.8	3.8	-2.2	GC-MS
12	35.3	10.4	3.0	GC-MS
14	3.0	0.0	-3.9	HPLC-FLD/UV
15	15.2	3.0	-1.3	GC-MS/MS
16	25.0	4.9	0.8	HPLC-FLD
17	21.4	1.1	0.0	GC-HRMS
18	29.3	1.6	1.7	GC-MS
19	10.5	0.0	-2.3	HPLC-FLD
20	16.7	0.9	-1.0	HPLC-FLD/UV
21	13.5	0.0	-1.7	GC-HRMS
22	30.1	0.0	1.9	HPLC-FLD/UV
23	30.3	5.9	1.9	GC-HRMS
25	23.2	0.0	0.4	GC-MS
26	19.9	0.0	-0.3	HPLC-FLD/UV

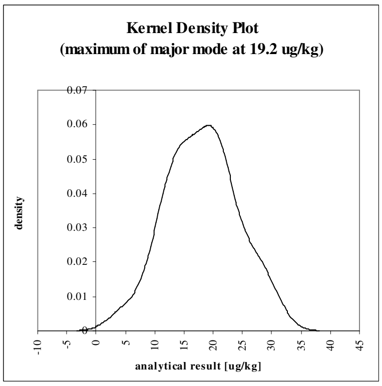




Benz[*a*]anthracene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	26.0	5.5	1.8	GC-HRMS
2	22.4	3.2	0.9	HPLC-FLD
3	19.4	3.0	0.2	HPLC-FLD
4	10.0	0.0	-2.1	GC-MS
5	13.8	1.8	-1.2	HPLC-FLD/UV
6	12.6	3.0	-1.5	HPLC-FLD/UV
7	15.6	1.2	-0.7	HPLC-FLD
8	18.7	0.6	0.0	HPLC-FLD/UV
9	20.0	0.0	0.3	HPLC-FLD
10	21.3	0.0	0.6	GC-MS
11	11.1	3.9	-1.8	GC-MS
12	29.9	8.7	2.7	GC-MS
14	4.9	0.0	-3.4	HPLC-FLD/UV
15	13.7	2.6	-1.2	GC-MS/MS
16	20.9	4.1	0.5	HPLC-FLD
17	17.6	0.7	-0.3	GC-HRMS
18	20.8	1.4	0.5	GC-MS
19	11.4	0.0	-1.8	HPLC-FLD
20	14.8	0.3	-0.9	HPLC-FLD/UV
21	15.7	0.0	-0.7	GC-HRMS
22	25.7	0.0	1.7	HPLC-FLD/UV
23	21.9	4.2	0.8	GC-HRMS
24	28.2	0.0	2.3	GC-MS
25	19.8	2.0	0.3	GC-MS
26	15.2	0.0	-0.8	HPLC-FLD

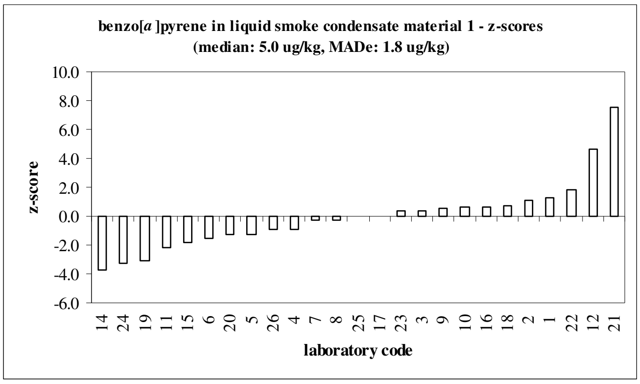


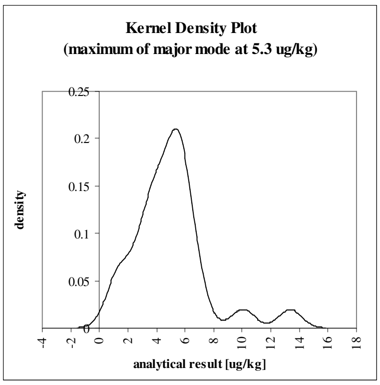


Annex 1A: Material 1

Benzo[a]pyrene

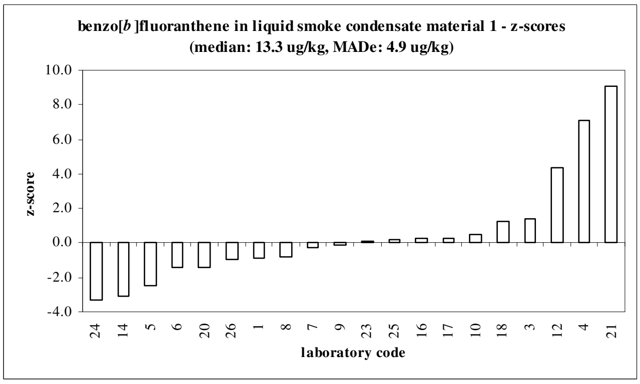
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	6.4	1.5	1.3	GC-HRMS
2	6.2	0.7	1.1	HPLC-FLD
3	5.5	0.6	0.4	HPLC-FLD
4	4.0	0.0	-0.9	GC-MS
5	3.7	0.9	-1.2	HPLC-FLD/UV
6	3.4	2.7	-1.5	HPLC-FLD/UV
7	4.7	0.5	-0.3	HPLC-FLD
8	4.7	0.3	-0.3	HPLC-FLD/UV
9	5.6	0.0	0.5	HPLC-FLD
10	5.7	0.0	0.6	GC-MS
11	2.6	0.9	-2.2	GC-MS
12	10.1	2.8	4.6	GC-MS
14	0.9	0.0	-3.7	HPLC-FLD/UV
15	3.0	0.6	-1.8	GC-MS/MS
16	5.8	1.1	0.7	HPLC-FLD
17	5.1	0.3	0.0	GC-HRMS
18	5.9	0.5	0.8	GC-MS
19	1.6	0.0	-3.1	HPLC-FLD
20	3.6	0.0	-1.3	HPLC-FLD/UV
21	13.4	0.0	7.6	GC-HRMS
22	7.0	0.0	1.8	HPLC-FLD/UV
23	5.4	0.9	0.3	GC-HRMS
24	1.4	0.0	-3.3	GC-MS
25	5.0	0.3	0.0	GC-MS
26	4.0	0.0	-1.0	HPLC-FLD/UV

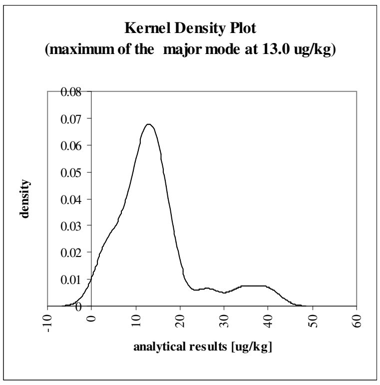




Benzo[*b*]fluoranthene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	10.8	3.1	-0.9	GC-HRMS
3	17.3	3.2	1.4	HPLC-FLD
4	34.0	0.0	7.1	GC-MS
5	6.0	0.8	-2.5	HPLC-FLD/UV
6	9.2	3.0	-1.4	HPLC-FLD/UV
7	12.6	0.8	-0.2	HPLC-FLD
8	11.0	0.6	-0.8	HPLC-FLD/UV
9	13.0	0.0	-0.1	HPLC-FLD
10	14.7	0.0	0.5	GC-MS
12	26.2	7.1	4.4	GC-MS
14	4.3	0.0	-3.1	HPLC-FLD/UV
16	14.1	2.8	0.3	HPLC-FLD
17	14.1	0.7	0.3	GC-HRMS
18	17.1	4.2	1.3	GC-MS
20	9.2	0.0	-1.4	HPLC-FLD/UV
21	39.9	0.0	9.1	GC-HRMS
23	13.6	2.6	0.1	GC-HRMS
24	3.7	0.0	-3.3	GC-MS
25	13.9	0.0	0.2	GC-MS
26	10.4	0.0	-1.0	HPLC-FLD

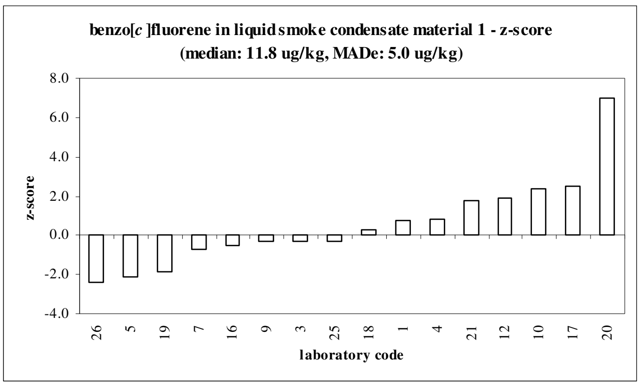


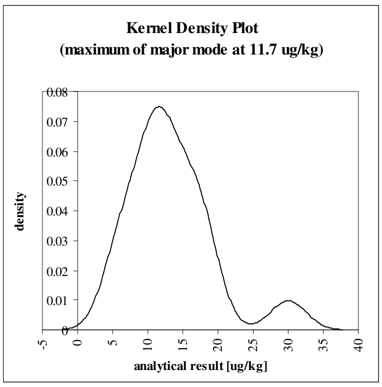


Annex 1A: Material 1

Benzo[*c*]fluorene

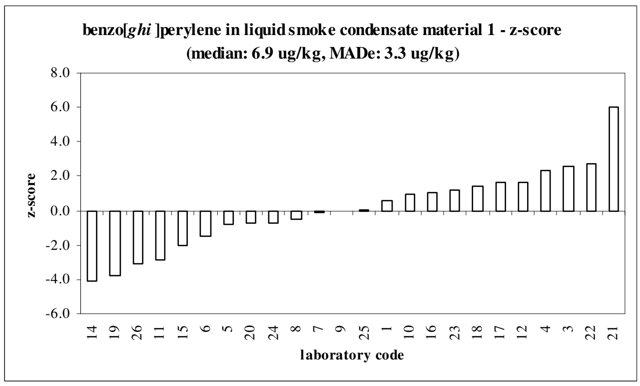
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	13.7	3.7	0.7	GC-HRMS
3	11.1	0.3	-0.3	HPLC-FLD
4	14.0	0.0	0.8	GC-MS
5	6.3	0.7	-2.1	HPLC-FLD/UV
7	9.9	0.4	-0.7	HPLC-FLD
9	11.0	0.0	-0.3	HPLC-FLD
10	18.0	0.0	2.4	GC-MS
12	16.8	5.0	1.9	GC-MS
16	10.5	2.1	-0.5	HPLC-FLD
17	18.4	1.0	2.5	GC-HRMS
18	12.5	1.5	0.3	GC-MS
19	6.9	0.0	-1.9	HPLC-FLD
20	30.0	0.0	7.0	HPLC-FLD/UV
21	16.4	0.0	1.8	GC-HRMS
25	11.1	0.0	-0.3	GC-MS
26	5.7	0.0	-2.4	HPLC-FLD

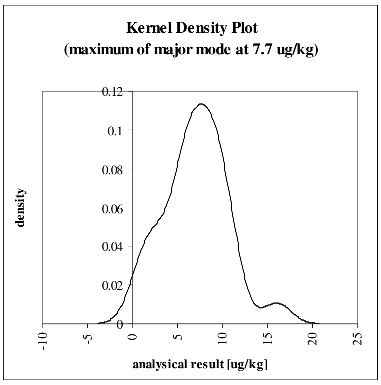




Benzo[*ghi*]perylene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	7.8	1.7	0.6	GC-HRMS
3	10.8	0.0	2.6	HPLC-FLD
4	10.5	0.0	2.4	GC-MS
5	5.7	0.5	-0.8	HPLC-FLD/UV
6	4.7	1.0	-1.5	HPLC-FLD/UV
7	6.7	2.1	-0.1	HPLC-FLD
8	6.2	0.6	-0.5	HPLC-FLD/UV
9	6.9	0.0	0.0	HPLC-FLD
10	8.4	0.0	1.0	GC-MS
11	2.5	0.9	-2.9	GC-MS
12	9.4	2.6	1.6	GC-MS
14	0.7	0.0	-4.1	HPLC-FLD/UV
15	3.8	0.0	-2.0	GC-MS/MS
16	8.5	1.7	1.0	HPLC-FLD
17	9.4	0.5	1.6	GC-HRMS
18	9.1	1.6	1.4	GC-MS
19	1.2	0.0	-3.8	HPLC-FLD
20	5.8	0.3	-0.7	HPLC-FLD/UV
21	16.1	0.0	6.0	GC-HRMS
22	11.0	0.0	2.7	HPLC-FLD/UV
23	8.8	1.6	1.2	GC-HRMS
24	5.8	0.0	-0.7	GC-MS
25	7.0	0.0	0.0	GC-MS
26	2.3	0.0	-3.1	HPLC-FLD

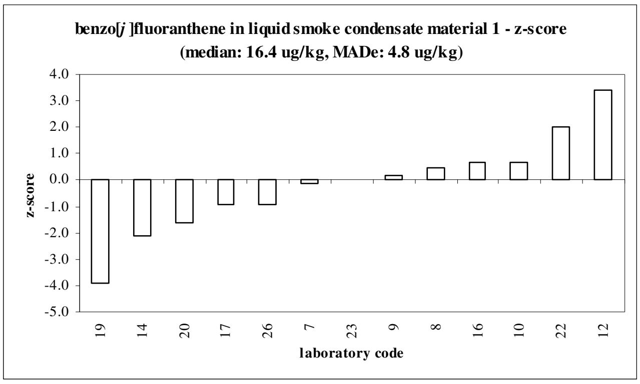


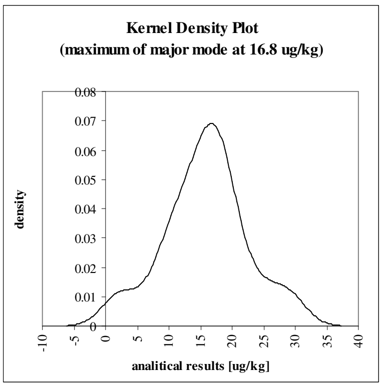


Annex 1A: Material 1

Benzo[*j*]fluoranthene

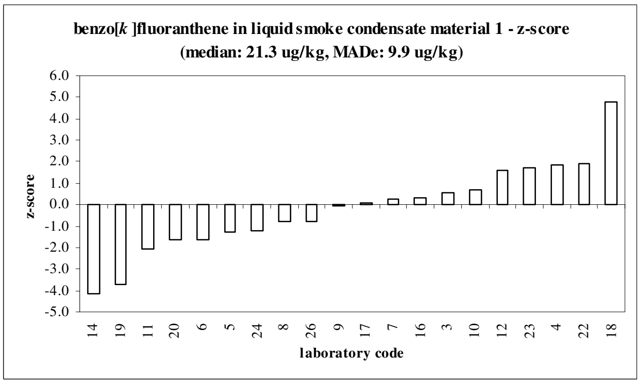
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
7	15.9	1.3	-0.1	HPLC-FLD
8	18.1	4.0	0.5	HPLC-FLD/UV
9	17.0	0.0	0.2	HPLC-FLD
10	18.9	0.0	0.7	GC-MS
14	8.8	0.0	-2.1	HPLC-FLD/UV
16	18.9	3.6	0.7	HPLC-FLD
17	13.1	0.6	-0.9	GC-HRMS
19	2.3	0.0	-3.9	HPLC-FLD
20	10.6	0.4	-1.6	HPLC-FLD/UV
23	16.4	2.9	0.0	GC-HRMS
26	13.2	0.0	-0.9	HPLC-FLD

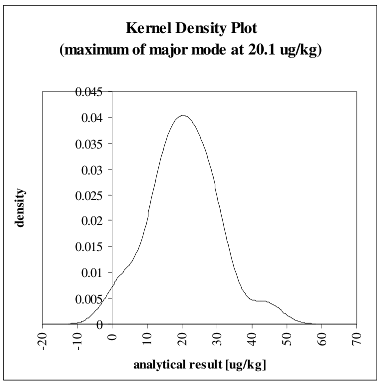




Benzo[*k*]fluoranthene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
3	24.0	1.1	0.6	HPLC-FLD
4	30.0	0.0	1.9	GC-MS
5	15.5	1.1	-1.2	HPLC-FLD/UV
6	13.8	4.0	-1.6	HPLC-FLD/UV
7	22.4	0.9	0.2	HPLC-FLD
8	17.5	1.5	-0.8	HPLC-FLD/UV
9	21.0	0.0	-0.1	HPLC-FLD
10	24.5	0.0	0.7	GC-MS
11	11.7	4.1	-2.0	GC-MS
12	28.8	8.4	1.6	GC-MS
14	1.7	0.0	-4.2	HPLC-FLD/UV
16	22.7	4.5	0.3	HPLC-FLD
17	21.5	1.1	0.0	GC-HRMS
18	43.8	1.9	4.8	GC-MS
19	3.8	0.0	-3.7	HPLC-FLD
20	13.7	0.4	-1.6	HPLC-FLD/UV
22	30.3	0.0	1.9	HPLC-FLD/UV
23	29.3	5.3	1.7	GC-HRMS
24	15.5	0.0	-1.2	GC-MS
26	17.7	0.0	-0.8	HPLC-FLD

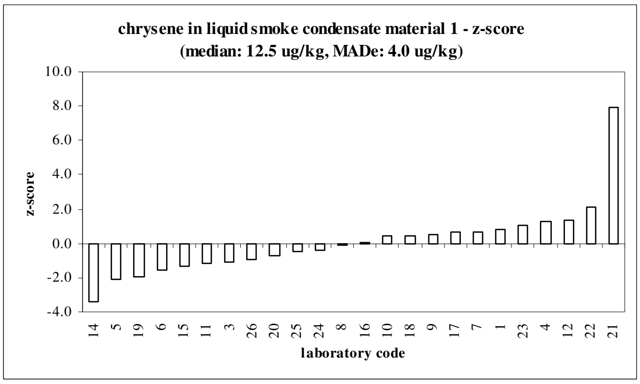


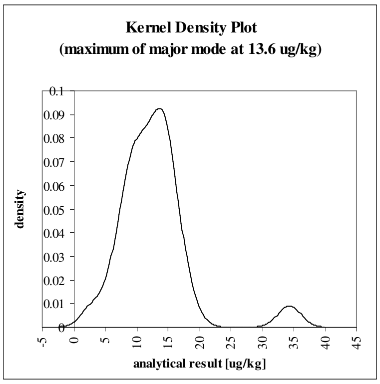


Annex 1A: Material 1

Chrysene

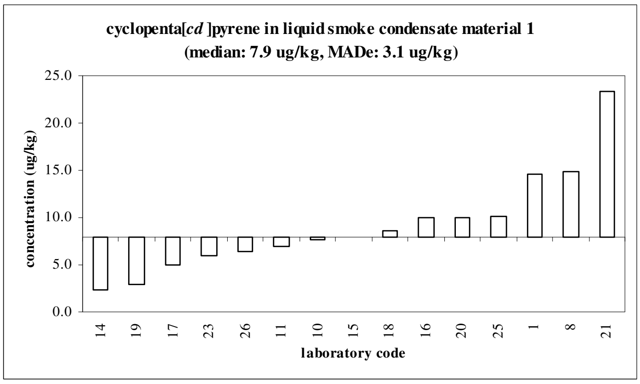
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	14.7	3.2	0.8	GC-HRMS
3	9.6	0.5	-1.1	HPLC-FLD
4	16.0	0.0	1.3	GC-MS
5	6.8	1.4	-2.1	HPLC-FLD/UV
6	8.3	2.0	-1.5	HPLC-FLD/UV
7	14.3	0.3	0.7	HPLC-FLD
8	12.2	0.5	-0.1	HPLC-FLD/UV
9	14.0	0.0	0.5	HPLC-FLD
10	13.7	0.0	0.4	GC-MS
11	9.3	3.3	-1.2	GC-MS
12	16.3	4.8	1.4	GC-MS
14	3.1	0.0	-3.4	HPLC-FLD/UV
15	8.9	0.0	-1.3	GC-MS/MS
16	12.8	2.5	0.1	HPLC-FLD
17	14.3	0.7	0.6	GC-HRMS
18	13.8	0.8	0.5	GC-MS
19	7.1	0.0	-2.0	HPLC-FLD
20	10.5	0.7	-0.7	HPLC-FLD/UV
21	34.3	0.0	7.9	GC-HRMS
22	18.3	0.0	2.1	HPLC-FLD/UV
23	15.4	2.9	1.0	GC-HRMS
24	11.3	0.0	-0.4	GC-MS
25	11.2	0.0	-0.5	GC-MS
26	9.9	0.0	-0.9	HPLC-FLD

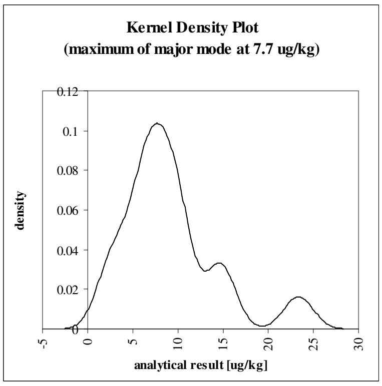




Cyclopenta[*cd*]pyrene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	14.7	3.2	n.a.	GC-HRMS
8	14.8	3.0	n.a.	HPLC-FLD/UV
10	7.7	0.0	n.a.	GC-MS
11	6.9	2.4	n.a.	GC-MS
14	2.3	0.0	n.a.	GC-MS
15	7.9	0.0	n.a.	GC-MS/MS
16	10.0	0.0	n.a.	HPLC-FLD/UV
17	5.0	0.3	n.a.	GC-HRMS
18	8.6	0.7	n.a.	GC-MS
19	2.9	0.0	n.a.	GC-HRMS
20	10.0	0.0	n.a.	HPLC-FLD/UV
21	23.4	0.0	n.a.	GC-HRMS
23	6.0	1.2	n.a.	GC-HRMS
25	10.2	0.0	n.a.	GC-MS
26	6.5	0.0	n.a.	HPLC-FLD/UV

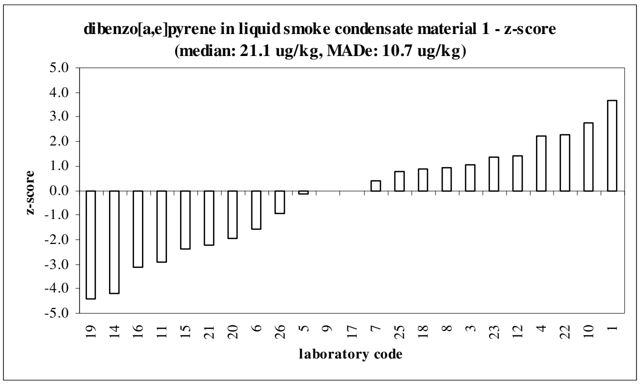


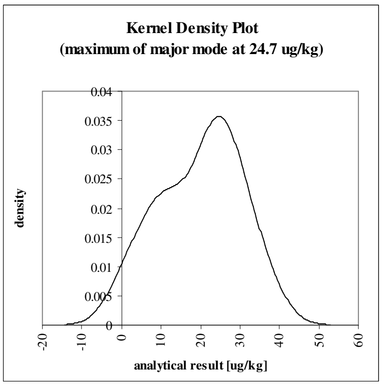


Annex 1A: Material 1

Dibenzo[*a,e*]pyrene

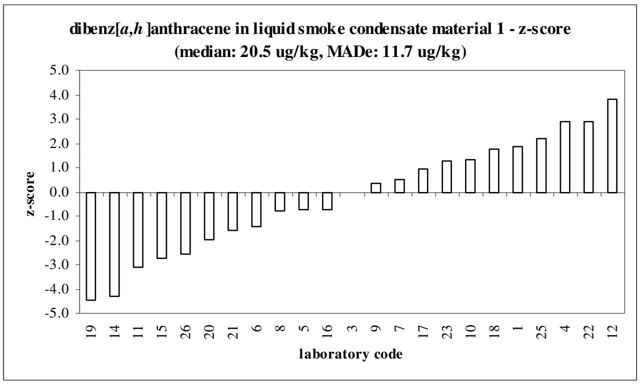
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	38.0	13.8	3.6	GC-HRMS
3	26.0	0.9	1.1	HPLC-FLD
4	31.5	0.0	2.2	GC-MS
5	20.5	1.5	-0.1	HPLC-FLD/UV
6	13.9	4.0	-1.6	HPLC-FLD/UV
7	22.9	2.1	0.4	HPLC-FLD
8	25.4	1.7	0.9	HPLC-FLD/UV
9	21.0	0.0	0.0	HPLC-FLD
10	33.8	0.0	2.7	GC-MS
11	7.5	2.6	-2.9	GC-MS
12	27.6	7.6	1.4	GC-MS
14	1.6	0.0	-4.2	GC-MS
15	10.0	0.0	-2.4	GC-MS/MS
16	6.7	1.1	-3.1	HPLC-FLD
17	21.1	1.3	0.0	GC-HRMS
18	25.1	0.8	0.9	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	12.2	1.7	-1.9	HPLC-FLD/UV
21	10.7	0.0	-2.2	GC-HRMS
22	31.6	0.0	2.3	HPLC-FLD/UV
23	27.4	4.5	1.3	GC-HRMS
25	24.7	0.0	0.8	GC-MS
26	16.7	0.0	-1.0	HPLC-FLD

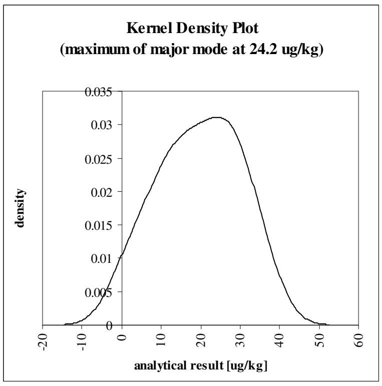




Dibenz[*a,h*]anthracene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	28.9	6.0	1.9	GC-HRMS
3	20.5	0.2	0.0	HPLC-FLD
4	33.5	0.0	2.9	GC-MS
5	17.1	0.7	-0.8	HPLC-FLD/UV
6	14.0	4.0	-1.4	HPLC-FLD/UV
7	22.9	0.7	0.5	HPLC-FLD
8	17.0	2.2	-0.8	HPLC-FLD/UV
9	22.0	0.0	0.3	HPLC-FLD
10	26.5	0.0	1.3	GC-MS
11	6.4	2.2	-3.1	GC-MS
12	37.7	10.2	3.8	GC-MS
14	1.2	0.0	-4.3	HPLC-FLD/UV
15	8.1	0.0	-2.7	GC-MS/MS
16	17.2	3.3	-0.7	HPLC-FLD
17	24.7	1.3	0.9	GC-HRMS
18	28.4	0.7	1.8	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	11.5	0.3	-2.0	HPLC-FLD/UV
21	13.3	0.0	-1.6	GC-HRMS
22	33.5	0.0	2.9	HPLC-FLD/UV
23	26.3	4.7	1.3	GC-HRMS
25	30.5	0.0	2.2	GC-MS
26	9.0	0.0	-2.6	HPLC-FLD

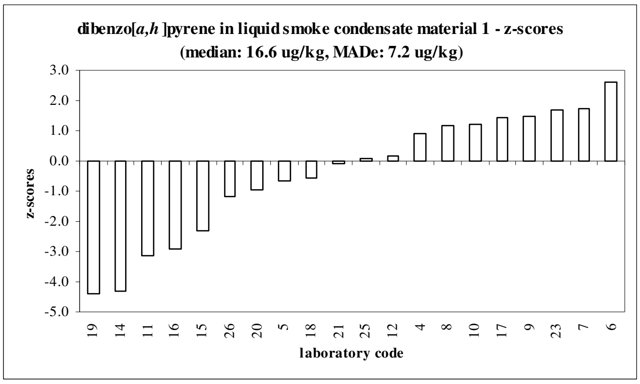


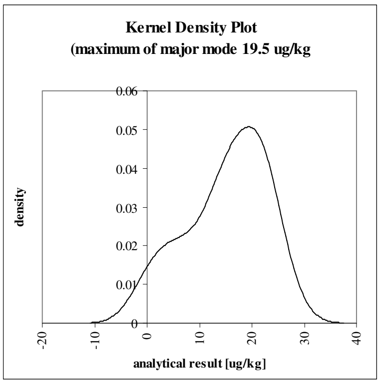


Annex 1A: Material 1

Dibenzo[*a,h*]pyrene

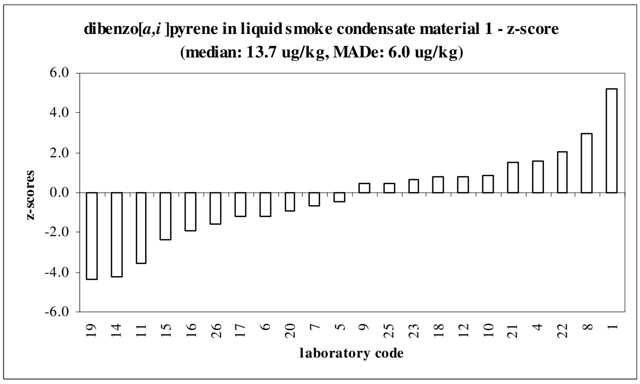
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
4	20.0	0.0	20.5	GC-MS
5	14.2	1.1	-14.8	HPLC-FLD/UV
6	26.2	8.0	57.8	HPLC-FLD/UV
7	22.9	1.6	38.0	HPLC-FLD
8	20.9	1.8	25.6	HPLC-FLD/UV
9	22.0	0.0	32.5	HPLC-FLD
10	21.1	0.0	26.8	GC-MS
11	5.1	1.8	-69.3	GC-MS
12	17.2	4.1	3.6	GC-MS
14	0.9	0.0	-94.8	HPLC-FLD/UV
15	8.2	0.0	-50.7	GC-MS/MS
16	6.0	1.2	-63.9	HPLC-FLD
17	21.9	1.3	31.9	GC-HRMS
18	14.6	2.7	-12.0	GC-MS
19	0.5	0.0	-97.0	HPLC-FLD
20	13.2	0.4	-20.8	HPLC-FLD/UV
21	16.4	0.0	-1.5	GC-HRMS
23	22.8	3.7	37.0	GC-HRMS
25	16.9	0.0	1.8	GC-MS
26	12.3	0.0	-25.9	HPLC-FLD/UV

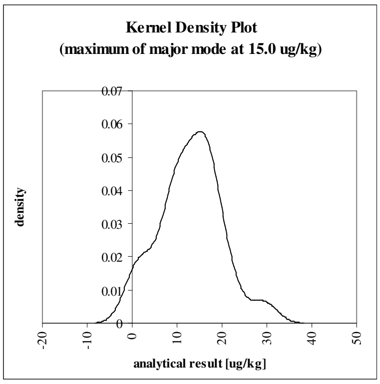




Dibenzo[*a,i*]pyrene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	29.4	8.2	5.2	GC-HRMS
4	18.5	0.0	1.6	GC-MS
5	12.4	1.1	-0.4	HPLC-FLD/UV
6	10.2	3.0	-1.2	HPLC-FLD/UV
7	11.7	4.0	-0.7	HPLC-FLD
8	22.6	5.9	2.9	HPLC-FLD/UV
9	15.0	0.0	0.4	HPLC-FLD
10	16.3	0.0	0.9	GC-MS
11	3.0	1.0	-3.6	GC-MS
12	16.2	4.7	0.8	GC-MS
14	1.0	0.0	-4.2	HPLC-FLD
15	6.5	0.0	-2.4	GC-MS/MS
16	8.0	0.0	-1.9	HPLC-FLD
17	10.1	0.5	-1.2	GC-HRMS
18	16.0	0.9	0.8	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	10.9	0.6	-0.9	HPLC-FLD/UV
21	18.3	0.0	1.5	GC-HRMS
22	19.9	0.0	2.1	HPLC-FLD/UV
23	15.8	2.7	0.7	GC-HRMS
25	15.1	0.0	0.4	GC-MS
26	9.0	0.0	-1.6	HPLC-FLD

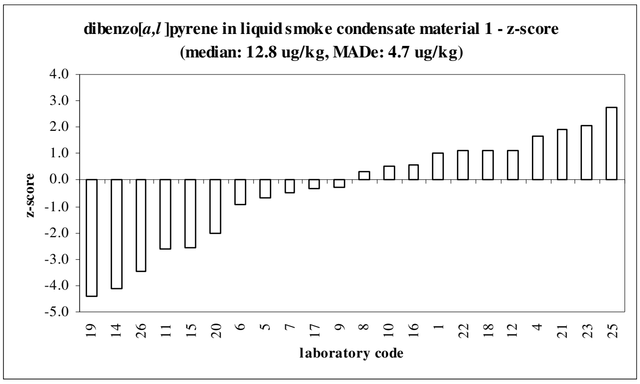


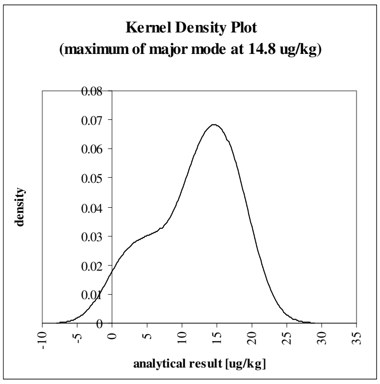


Annex 1A: Material 1

Dibenzo[*a,l*]pyrene

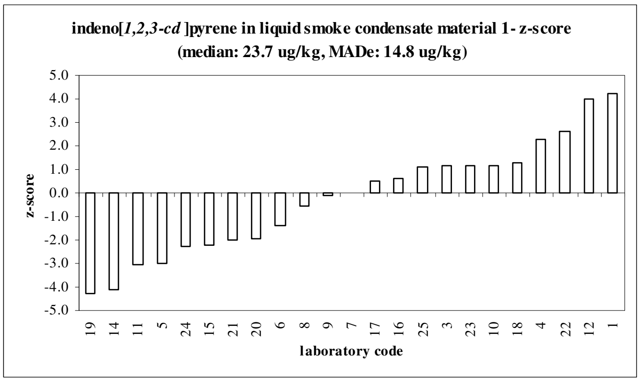
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	15.6	3.6	1.0	GC-HRMS
4	17.5	0.0	1.7	GC-MS
5	11.0	1.3	-0.7	HPLC-FLD/UV
6	10.2	4.0	-0.9	HPLC-FLD/UV
7	11.4	1.8	-0.5	HPLC-FLD
8	13.7	1.0	0.3	HPLC-FLD/UV
9	12.0	0.0	-0.3	HPLC-FLD
10	14.3	0.0	0.5	GC-MS
11	5.4	1.9	-2.6	GC-MS
12	16.0	4.6	1.1	GC-MS
14	1.2	0.0	-4.1	GC-MS
15	5.5	0.0	-2.6	GC-MS/MS
16	14.5	2.8	0.6	HPLC-FLD
17	11.9	0.5	-0.3	GC-HRMS
18	16.0	0.9	1.1	GC-MS
19	0.4	0.0	-4.4	HPLC-FLD
20	7.2	0.1	-2.0	HPLC-FLD/UV
21	18.3	0.0	1.9	GC-HRMS
22	15.9	0.0	1.1	HPLC-FLD/UV
23	18.7	3.0	2.1	GC-HRMS
25	20.6	0.0	2.8	GC-MS
26	3.1	0.0	-3.4	HPLC-FLD

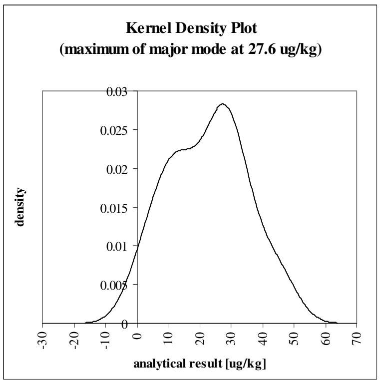

dibenzo[*a,l*]pyrene in liquid smoke condensate material 1 - z-score (median: 12.8 ug/kg, MADe: 4.7 ug/kg)


Kernel Density Plot (maximum of major mode at 14.8 ug/kg)

Indeno[*1,2,3-cd*]pryene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	45.8	9.6	2.2	GC-HRMS
3	29.7	2.6	-0.1	HPLC-FLD
4	35.5	0.0	0.7	GC-MS
5	8.0	1.4	-3.2	HPLC-FLD/UV
6	16.6	5.0	-2.0	HPLC-FLD/UV
7	23.7	1.3	-0.9	HPLC-FLD
8	20.7	0.8	-1.4	HPLC-FLD/UV
9	23.0	0.0	-1.0	HPLC-FLD
10	29.8	0.0	-0.1	GC-MS
11	7.7	2.7	-3.2	GC-MS
12	44.6	12.7	2.1	GC-MS
14	2.3	0.0	-4.0	HPLC-FLD/UV
15	12.0	0.0	-2.6	GC-MS/MS
16	27.0	5.3	-0.5	HPLC-FLD
17	26.3	1.4	-0.6	GC-HRMS
18	30.5	0.5	0.0	GC-MS
19	1.5	0.0	-4.1	HPLC-FLD
20	13.7	1.6	-2.4	HPLC-FLD/UV
21	13.2	0.0	-2.5	GC-HRMS
22	37.4	0.0	1.0	HPLC-FLD/UV
23	29.7	5.0	-0.1	GC-HRMS
24	11.8	0.0	-2.7	GC-MS
25	29.6	0.0	-0.1	GC-MS

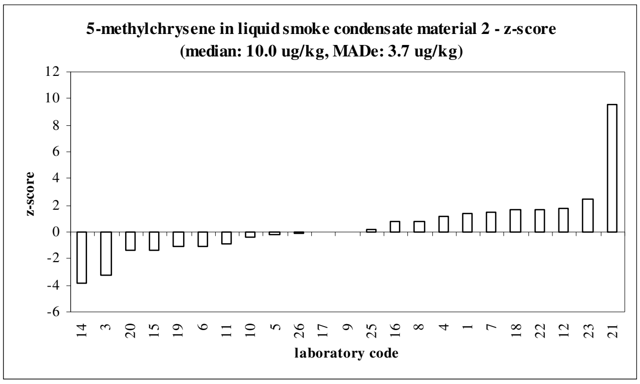

indeno[*1,2,3-cd*]pyrene in liquid smoke condensate material 1- z-score (median: 23.7 ug/kg, MADe: 14.8 ug/kg)

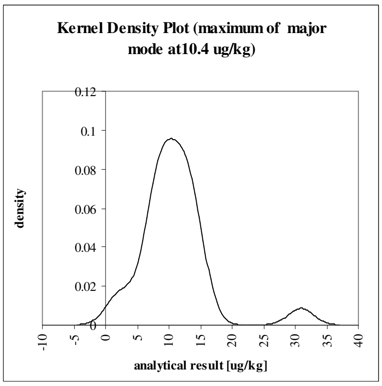

Kernel Density Plot (maximum of major mode at 27.6 ug/kg)

Annex 1B: Material 2

5-Methylchrysene

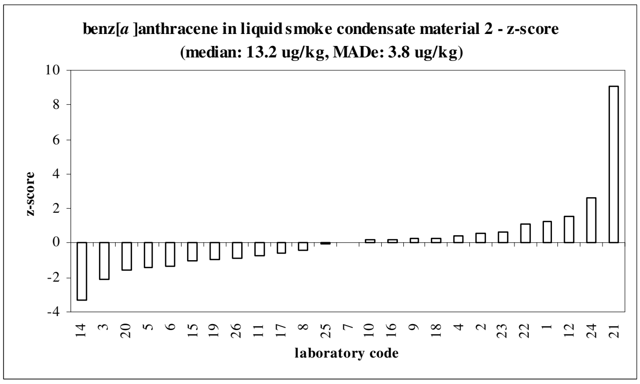
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	13.0	3.1	1.3	GC-HRMS
3	3.0	0.4	-3.2	HPLC-FLD
4	12.5	0.0	1.1	GC-MS
5	9.5	1.2	-0.2	HPLC-FLD/UV
6	7.7	2.0	-1.1	GC-HRMS
7	13.3	0.5	1.5	HPLC-FLD
8	11.8	0.6	0.8	HPLC-FLD/UV
9	10.0	0.0	0.0	HPLC-FLD
10	9.1	0.0	-0.4	GC-MS
11	8.1	2.9	-0.9	GC-MS
12	14.0	3.7	1.8	GC-MS
14	1.5	0.0	-3.9	HPLC-FLD/UV
15	7.0	0.0	-1.4	GC-MS/MS
16	11.7	2.3	0.8	HPLC-FLD
17	9.9	0.5	0.0	GC-HRMS
18	13.8	1.6	1.7	GC-MS
19	7.6	0.0	-1.1	HPLC-FLD
20	6.9	0.9	-1.4	HPLC-FLD/UV
21	30.9	0.0	9.5	GC-HRMS
22	13.8	0.0	1.7	HPLC-FLD/UV
23	15.4	3.0	2.5	GC-HRMS
25	10.5	0.0	0.2	GC-MS
26	9.8	0.0	-0.1	HPLC-FLD

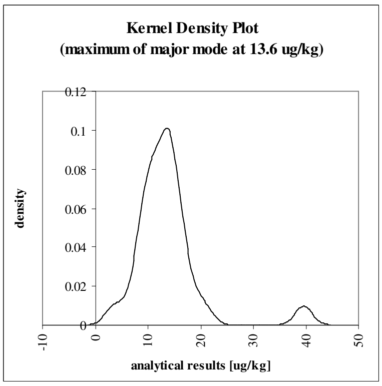




Benz[*a*]anthracene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
14	3.6	0.0	-3.3	HPLC-FLD/UV
3	7.1	0.1	-2.1	HPLC-FLD
20	8.6	1.3	-1.6	HPLC-FLD/UV
5	9.1	1.8	-1.4	HPLC-FLD/UV
6	9.4	3.0	-1.3	HPLC-FLD/UV
15	10.1	2.0	-1.1	GC-MS/MS
19	10.4	0.0	-1.0	HPLC-FLD
26	10.7	0.0	-0.9	HPLC-FLD
11	11.0	3.8	-0.8	GC-MS
17	11.6	0.7	-0.6	GC-HRMS
8	11.9	0.7	-0.4	HPLC-FLD/UV
25	13.1	1.3	0.0	GC-MS
7	13.2	1.0	0.0	HPLC-FLD
10	13.8	0.0	0.2	GC-MS
16	13.8	2.8	0.2	HPLC-FLD
9	14.0	0.0	0.3	HPLC-FLD
18	14.1	1.4	0.3	GC-MS
4	14.5	0.0	0.4	GC-MS
2	14.9	1.7	0.6	HPLC-FLD
23	15.0	2.9	0.6	GC-HRMS
22	16.4	0.0	1.1	HPLC-FLD/UV
1	16.9	3.4	1.3	GC-HRMS
12	17.8	4.9	1.6	GC-MS

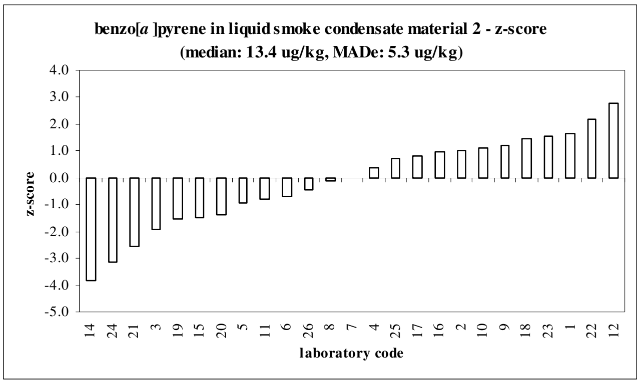


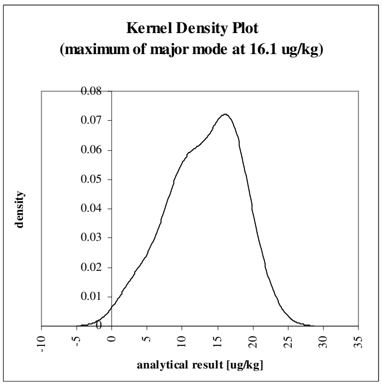


Annex 1B: Material 2

Benzo[*a*]pyrene

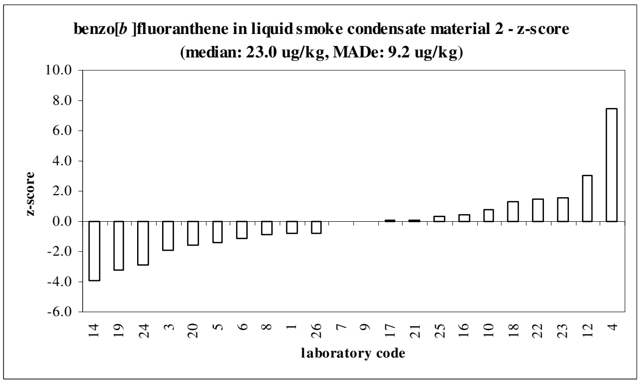
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	18.3	4.1	1.7	GC-HRMS
2	16.4	1.4	1.0	HPLC-FLD
3	7.8	0.1	-1.9	HPLC-FLD
4	14.5	0.0	0.4	GC-MS
5	10.7	0.9	-0.9	HPLC-FLD/UV
6	11.4	10.7	-0.7	HPLC-FLD/UV
7	13.4	1.0	0.0	HPLC-FLD
8	13.1	0.4	-0.1	HPLC-FLD/UV
9	17.0	0.0	1.2	HPLC-FLD
10	16.7	0.0	1.1	GC-MS
11	11.0	3.8	-0.8	GC-MS
14	2.1	0.0	-3.8	HPLC-FLD/UV
15	9.1	1.8	-1.5	GC-MS/MS
16	16.3	3.2	1.0	HPLC-FLD
17	15.9	0.7	0.8	GC-HRMS
18	17.7	0.5	1.4	GC-MS
19	8.8	0.0	-1.5	HPLC-FLD
20	9.4	0.2	-1.4	HPLC-FLD/UV
21	5.8	0.0	-2.6	GC-HRMS
22	19.9	0.0	2.2	HPLC-FLD/UV
23	18.1	3.3	1.6	GC-HRMS
24	4.2	0.0	-3.1	GC-MS
25	15.6	1.0	0.7	GC-MS
26	12.0	0.0	-0.5	HPLC-FLD

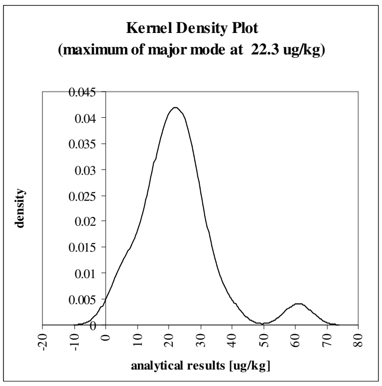




Benzo[*b*]fluoranthene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	18.9	5.0	-0.8	GC-HRMS
3	13.4	1.8	-1.9	HPLC-FLD
4	61.0	0.0	7.5	GC-MS
5	15.9	0.8	-1.4	HPLC-FLD/UV
6	17.1	5.0	-1.2	HPLC-FLD/UV
7	23.0	1.5	0.0	HPLC-FLD
8	18.6	0.8	-0.9	HPLC-FLD/UV
9	23.0	0.0	0.0	HPLC-FLD
10	27.2	0.0	0.8	GC-MS
12	38.3	10.6	3.0	GC-MS
14	3.1	0.0	-3.9	HPLC-FLD/UV
16	25.2	5.0	0.4	HPLC-FLD
17	23.3	1.3	0.1	GC-HRMS
18	29.6	4.0	1.3	GC-MS
19	6.9	0.0	-3.2	HPLC-FLD
20	15.0	1.0	-1.6	HPLC-FLD/UV
21	23.4	0.0	0.1	GC-HRMS
22	30.3	0.0	1.4	HPLC-FLD/UV
23	30.8	5.8	1.5	GC-HRMS
24	8.6	0.0	-2.8	GC-MS
25	24.8	0.0	0.3	GC-MS
26	19.1	0.0	-0.8	HPLC-FLD

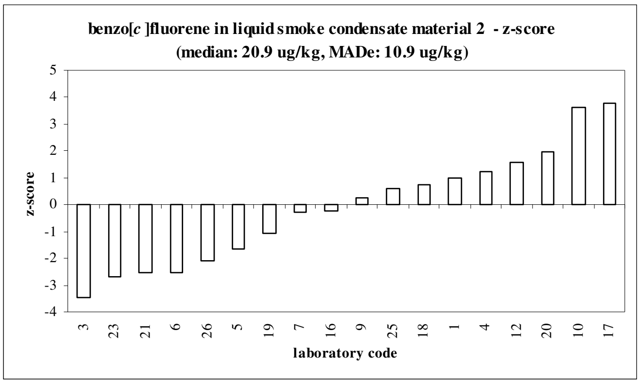


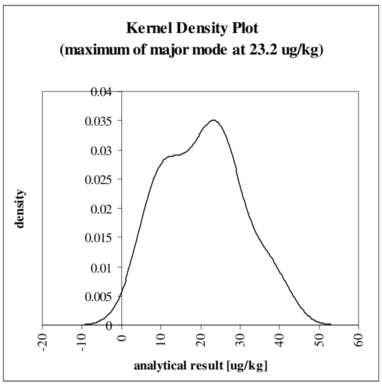


Annex 1B: Material 2

Benzo[*c*]fluorene

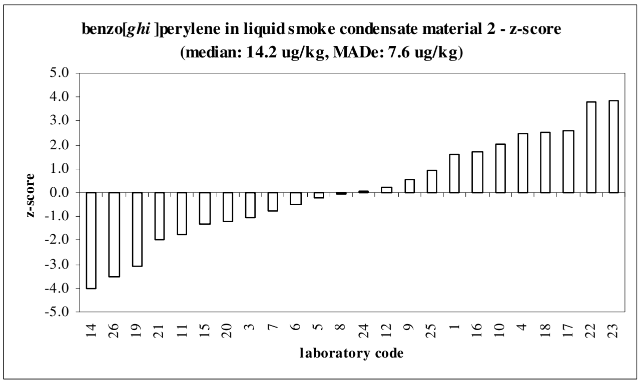
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	25.5	6.9	1.0	GC-HRMS
3	5.0	1.1	-3.5	HPLC-FLD
4	26.5	0.0	1.2	GC-MS
5	13.4	0.7	-1.6	HPLC-FLD/UV
6	9.4	2.0	-2.5	HPLC-FLD/UV
7	19.7	3.3	-0.3	HPLC-FLD
9	22.0	0.0	0.2	HPLC-FLD
10	37.7	0.0	3.7	GC-MS
12	28.1	7.8	1.6	GC-MS
16	19.8	3.9	-0.3	HPLC-FLD
17	38.3	2.1	3.8	GC-HRMS
18	24.3	2.6	0.7	GC-MS
19	15.9	0.0	-1.1	HPLC-FLD
20	30.0	0.0	2.0	HPLC-FLD/UV
21	9.2	0.0	-2.6	GC-HRMS
23	8.7	1.6	-2.7	GC-HRMS
25	23.6	0.0	0.6	GC-MS
26	11.2	0.0	-2.1	HPLC-FLD

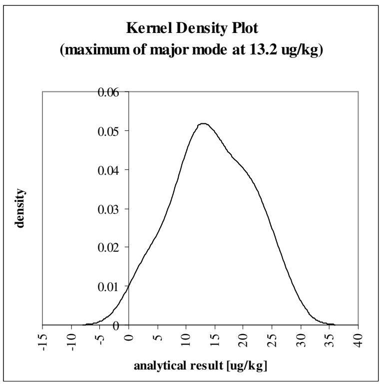




Benzo[*ghi*]perylene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	19.1	4.2	1.6	GC-HRMS
3	11.0	2.2	-1.0	HPLC-FLD
4	22.0	0.0	2.5	GC-MS
5	13.6	0.5	-0.2	HPLC-FLD/UV
6	12.6	4.0	-0.5	HPLC-FLD/UV
7	11.8	1.2	-0.8	HPLC-FLD
8	14.0	0.4	-0.1	HPLC-FLD/UV
9	16.0	0.0	0.6	HPLC-FLD
10	20.5	0.0	2.0	GC-MS
11	8.7	3.0	-1.8	GC-MS
12	14.9	4.5	0.2	GC-MS
14	1.6	0.0	-4.0	HPLC-FLD/UV
15	10.2	0.0	-1.3	GC-MS/MS
16	19.6	3.9	1.7	HPLC-FLD
17	22.3	1.2	2.6	GC-HRMS
18	22.1	2.0	2.5	GC-MS
19	4.5	0.0	-3.1	HPLC-FLD
20	10.4	0.1	-1.2	HPLC-FLD/UV
21	8.0	0.0	-2.0	GC-HRMS
22	26.0	0.0	3.8	HPLC-FLD/UV
23	26.3	4.9	3.9	GC-HRMS
24	14.4	0.0	0.1	GC-MS
25	17.2	0.0	1.0	GC-MS
26	3.3	0.0	-3.5	HPLC-FLD

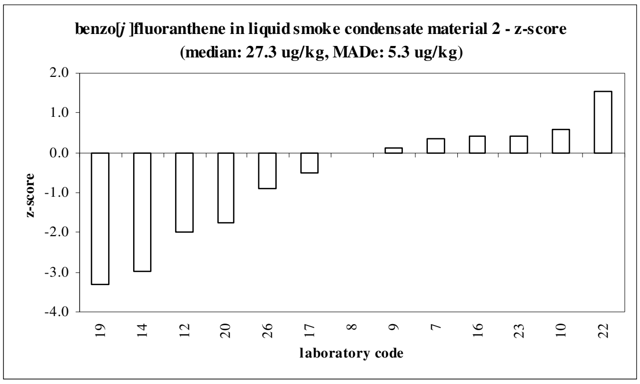


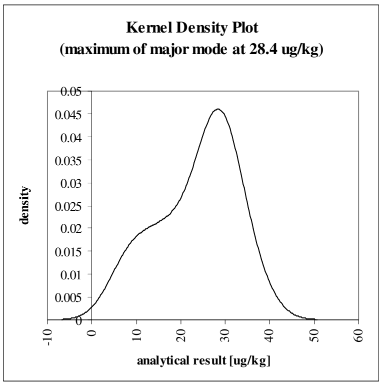


Annex 1B: Material 2

Benzo[*j*]fluoranthene

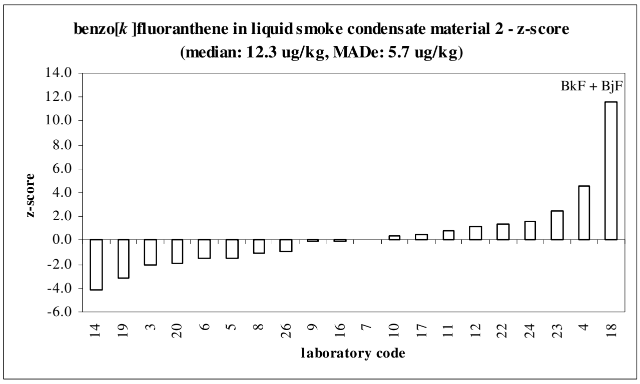
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
7	29.4	2.4	0.3	HPLC-FLD
8	27.3	2.5	0.0	HPLC-FLD/UV
9	28.0	0.0	0.1	HPLC-FLD
10	30.9	0.0	0.6	GC-MS
12	15.4	3.7	-2.0	GC-MS
14	9.5	0.0	-3.0	HPLC-FLD/UV
16	29.8	5.8	0.4	HPLC-FLD
17	24.4	1.5	-0.5	GC-HRMS
19	7.5	0.0	-3.3	HPLC-FLD
20	16.8	2.3	-1.8	HPLC-FLD/UV
22	36.5	0.0	1.5	HPLC-FLD/UV
23	29.9	5.6	0.4	GC-HRMS
26	22.0	0.0	-0.9	HPLC-FLD

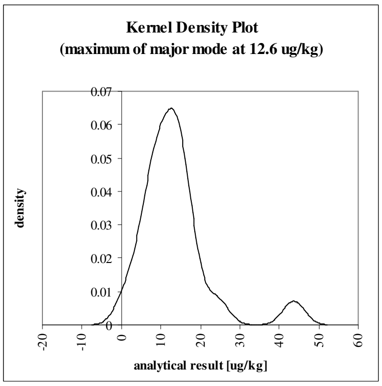




Benzo[*k*]fluoranthene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
3	6.7	1.4	-2.1	HPLC-FLD
4	24.5	0.0	4.5	GC-MS
5	8.3	1.1	-1.5	HPLC-FLD/UV
6	8.2	2.0	-1.5	HPLC-FLD/UV
7	12.5	1.8	0.1	HPLC-FLD
8	9.3	0.3	-1.1	HPLC-FLD/UV
9	12.0	0.0	-0.1	HPLC-FLD
10	13.4	0.0	0.4	GC-MS
11	14.5	5.1	0.8	GC-MS
12	15.4	3.7	1.1	GC-MS
14	1.0	0.0	-4.2	HPLC-FLD/UV
16	12.2	2.4	-0.1	HPLC-FLD
17	13.8	0.9	0.5	GC-HRMS
18	43.7	1.9	11.6	GC-MS
19	3.9	0.0	-3.1	HPLC-FLD
20	7.0	0.6	-2.0	HPLC-FLD/UV
22	16.0	0.0	1.3	HPLC-FLD/UV
23	19.0	3.5	2.5	GC-HRMS
24	16.7	0.0	1.6	GC-MS
26	9.9	0.0	-0.9	HPLC-FLD

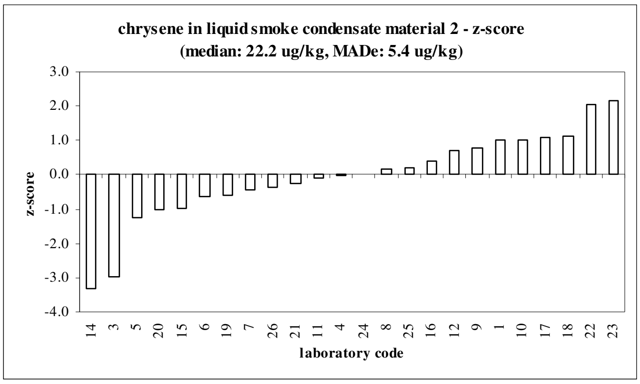


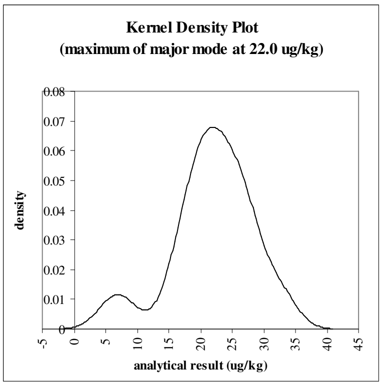


Annex 1B: Material 2

Chrysene

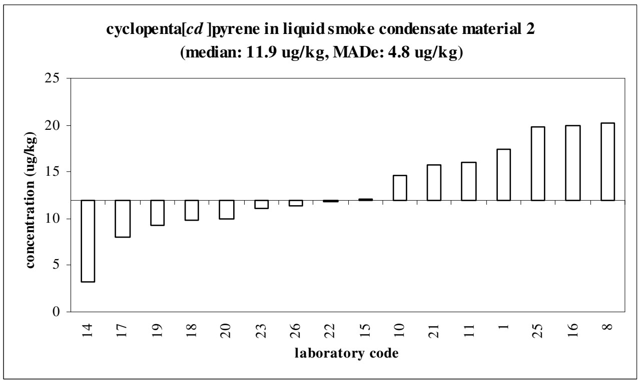
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	27.1	5.9	1.0	GC-HRMS
3	7.8	1.9	-2.9	HPLC-FLD
4	22.0	0.0	0.0	GC-MS
5	16.1	1.4	-1.2	HPLC-FLD/UV
6	19.1	6.0	-0.6	HPLC-FLD/UV
7	20.1	2.2	-0.4	HPLC-FLD
8	23.1	1.4	0.2	HPLC-FLD/UV
9	26.0	0.0	0.8	HPLC-FLD
10	27.2	0.0	1.0	GC-MS
11	21.7	7.6	-0.1	GC-MS
12	25.7	6.6	0.7	GC-MS
14	6.0	0.0	-3.3	HPLC-FLD/UV
15	17.4	0.0	-1.0	GC-MS/MS
16	24.2	4.8	0.4	HPLC-FLD
17	27.5	1.7	1.1	GC-HRMS
18	27.7	2.1	1.1	GC-MS
19	19.3	0.0	-0.6	HPLC-FLD
20	17.2	2.6	-1.0	HPLC-FLD/UV
21	21.0	0.0	-0.3	GC-HRMS
22	32.1	0.0	2.0	HPLC-FLD/UV
23	32.8	6.3	2.2	GC-HRMS
24	22.3	0.0	0.0	GC-MS
25	23.2	0.0	0.2	GC-MS
26	20.4	0.0	-0.4	HPLC-FLD

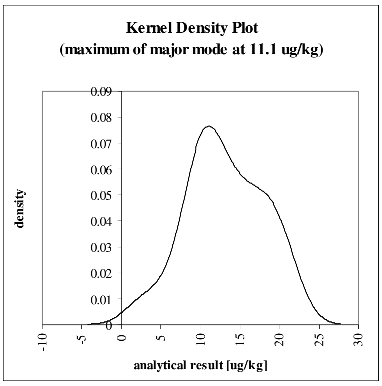




Cyclopenta[*cd*]pyrene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	17.4	3.7	n.a.	GC-HRMS
8	20.2	1.2	n.a.	HPLC-FLD/UV
10	14.6	0.0	n.a.	GC-MS
11	16.0	5.6	n.a.	GC-MS
14	3.2	0.0	n.a.	GC-MS
15	12.1	0.0	n.a.	GC-MS/MS
16	20.0	0.0	n.a.	HPLC-FLD
17	8.0	0.6	n.a.	GC-HRMS
18	9.9	0.7	n.a.	GC-MS
19	9.3	0.0	n.a.	HPLC-FLD/UV
20	10.0	0.0	n.a.	HPLC-FLD/UV
21	15.8	0.0	n.a.	GC-HRMS
22	11.8	0.0	n.a.	HPLC-FLD/UV
23	11.1	2.1	n.a.	GC-HRMS
25	19.8	0.0	n.a.	GC-MS
26	11.4	0.0	n.a.	HPLC-FLD/UV

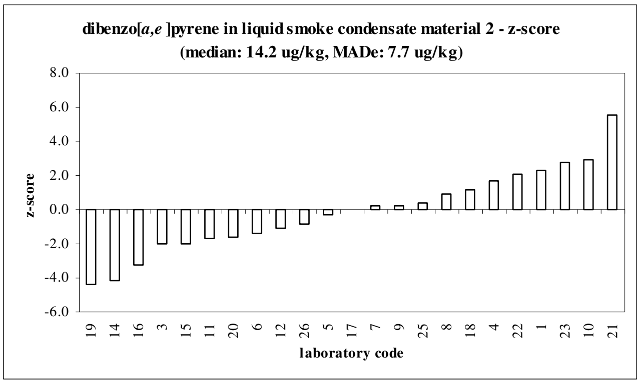


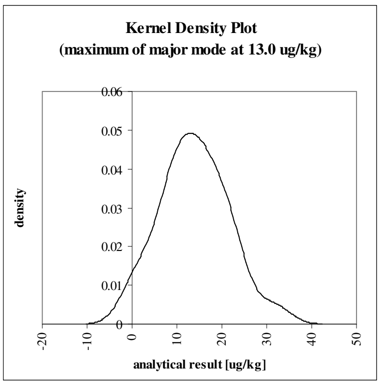


Annex 1B: Material 2

Dibenzo[*a,e*]pyrene

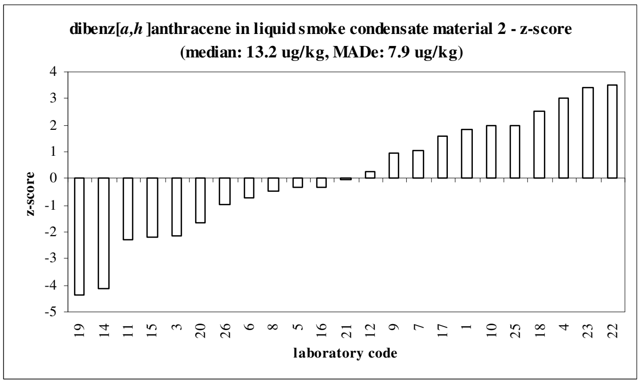
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	21.5	7.7	2.3	GC-HRMS
3	7.9	2.8	-2.0	HPLC-FLD
4	19.5	0.0	1.7	GC-MS
5	13.4	1.5	-0.3	HPLC-FLD/UV
6	9.9	3.0	-1.4	HPLC-FLD/UV
7	14.9	2.2	0.2	HPLC-FLD
8	17.0	0.6	0.9	HPLC-FLD/UV
9	15.0	0.0	0.3	HPLC-FLD
10	23.4	0.0	2.9	GC-MS
11	9.0	3.2	-1.7	GC-MS
12	10.9	3.3	-1.1	GC-MS
14	1.1	0.0	-4.2	GC-MS
15	8.0	0.0	-2.0	GC-MS/MS
16	4.2	0.6	-3.2	HPLC-FLD
17	14.2	0.8	0.0	GC-HRMS
18	17.8	0.8	1.2	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	9.3	0.4	-1.6	HPLC-FLD/UV
21	31.6	0.0	5.6	GC-HRMS
22	20.7	0.0	2.1	HPLC-FLD/UV
23	22.8	4.4	2.7	GC-HRMS
25	15.3	0.0	0.4	GC-MS
26	11.6	0.0	-0.8	HPLC-FLD

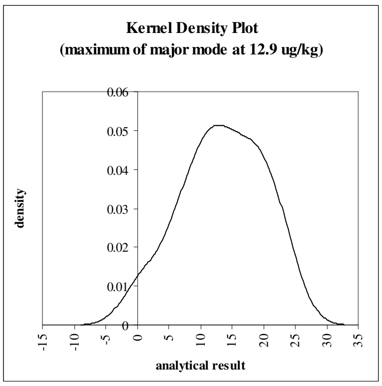




Dibenz[*a,h*]anthracene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	18.5	3.9	1.8	GC-HRMS
3	6.9	3.1	-2.2	HPLC-FLD
4	22.0	0.0	3.0	GC-MS
5	12.2	0.7	-0.3	HPLC-FLD/UV
6	11.1	3.0	-0.7	HPLC-FLD/UV
7	16.2	1.0	1.0	HPLC-FLD
8	11.9	0.8	-0.5	HPLC-FLD/UV
9	16.0	0.0	1.0	HPLC-FLD
10	18.9	0.0	2.0	GC-MS
11	6.5	2.3	-2.3	GC-MS
12	13.9	4.2	0.2	GC-MS
14	1.2	0.0	-4.1	GC-MS
15	6.8	0.0	-2.2	GC-MS/MS
16	12.3	2.1	-0.3	HPLC-FLD
17	17.8	1.0	1.6	GC-HRMS
18	20.6	0.7	2.5	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	8.5	0.2	-1.6	HPLC-FLD/UV
21	13.2	0.0	0.0	GC-HRMS
22	23.5	0.0	3.5	HPLC-FLD/UV
23	23.1	4.5	3.4	GC-HRMS
25	19.0	0.0	2.0	GC-MS
26	10.4	0.0	-1.0	HPLC-FLD

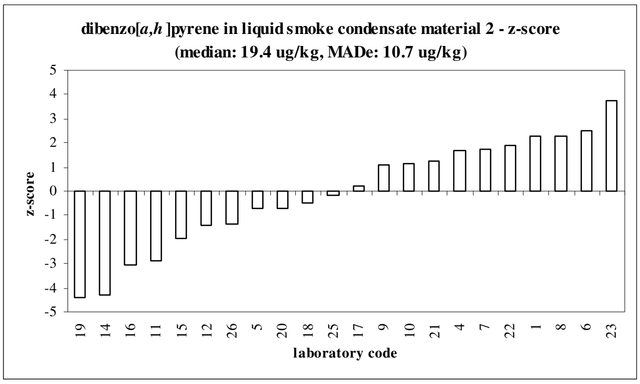


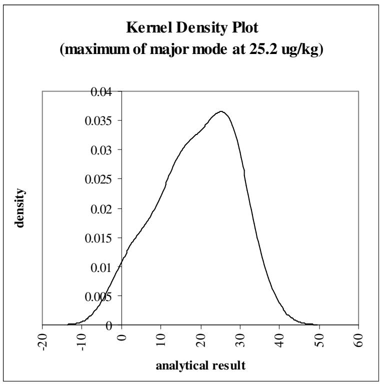


Annex 1B: Material 2

Dibenzo[*a,h*]pyrene

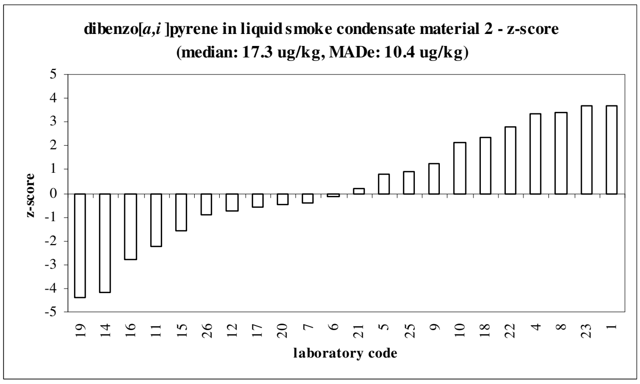
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	29.1	15.0	2.3	GC-HRMS
4	26.5	0.0	1.7	GC-MS
5	16.4	1.1	-0.7	HPLC-FLD/UV
6	30.1	9.0	2.5	HPLC-FLD/UV
7	26.8	1.6	1.7	HPLC-FLD
8	29.2	4.8	2.3	HPLC-FLD/UV
9	24.0	0.0	1.1	HPLC-FLD
10	24.3	0.0	1.1	GC-MS
11	7.0	2.4	-2.9	GC-MS
12	13.3	4.0	-1.4	GC-MS
14	1.0	0.0	-4.3	HPLC-FLD/UV
15	10.9	0.0	-2.0	GC-MS/MS
16	6.4	1.0	-3.1	HPLC-FLD
17	20.3	1.6	0.2	GC-HRMS
18	17.2	0.8	-0.5	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	16.5	0.3	-0.7	HPLC-FLD/UV
21	24.8	0.0	1.3	GC-HRMS
22	27.5	0.0	1.9	HPLC-FLD/UV
23	35.4	6.6	3.7	GC-HRMS
25	18.6	0.0	-0.2	GC-MS
26	13.6	0.0	-1.4	HPLC-FLD

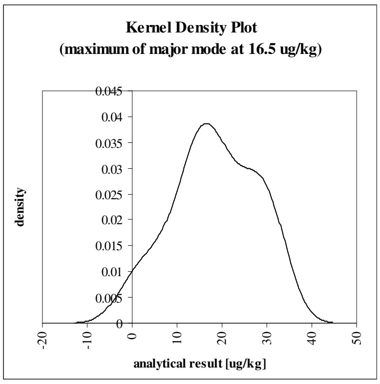




Dibenzo[*a,i*]pyrene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	31.4	8.5	3.7	GC-HRMS
4	30.0	0.0	3.3	GC-MS
5	20.3	1.1	0.8	HPLC-FLD/UV
6	16.7	5.0	-0.2	HPLC-FLD/UV
7	15.8	2.6	-0.4	HPLC-FLD
8	30.2	9.5	3.4	HPLC-FLD/UV
9	22.0	0.0	1.2	HPLC-FLD
10	25.4	0.0	2.1	GC-MS
11	8.7	3.0	-2.3	GC-MS
12	14.4	4.3	-0.8	GC-MS
14	1.5	0.0	-4.2	GC-MS
15	11.3	0.0	-1.6	GC-MS/MS
16	6.6	1.1	-2.8	HPLC-FLD
17	15.1	0.9	-0.6	GC-HRMS
18	26.2	0.7	2.3	GC-MS
19	0.5	0.0	-4.4	HPLC-FLD
20	15.6	0.3	-0.4	HPLC-FLD/UV
21	18.0	0.0	0.2	GC-HRMS
22	28.0	0.0	2.8	HPLC-FLD/UV
23	31.3	5.8	3.7	GC-HRMS
25	20.7	0.0	0.9	GC-MS
26	13.9	0.0	-0.9	HPLC-FLD

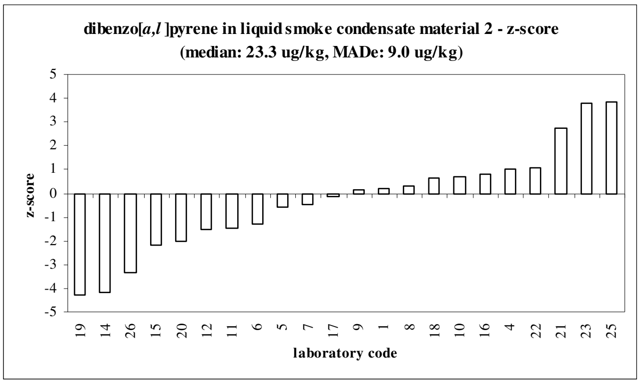


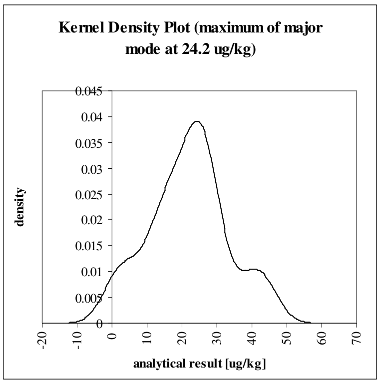


Annex 1B: Material 2

Dibenzo[*a,l*]pyrene

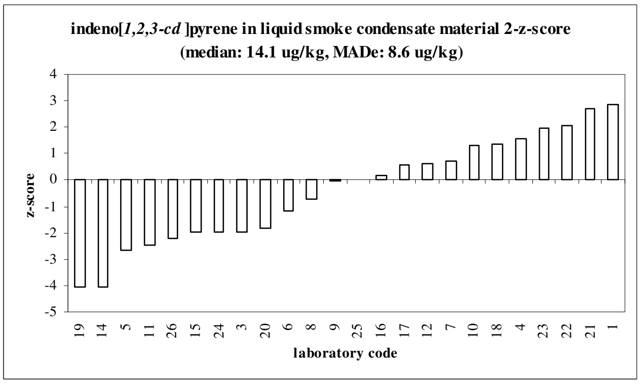
labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	24.3	5.5	0.2	GC-HRMS
4	28.5	0.0	1.0	GC-MS
5	20.4	1.3	-0.6	HPLC-FLD/UV
6	16.7	5.0	-1.3	HPLC-FLD/UV
7	21.0	4.5	-0.4	HPLC-FLD
8	25.0	1.1	0.3	HPLC-FLD/UV
9	24.0	0.0	0.1	HPLC-FLD
10	26.7	0.0	0.7	GC-MS
11	15.8	5.5	-1.5	GC-MS
12	15.6	4.7	-1.5	GC-MS
14	2.0	0.0	-4.2	HPLC-FLD/UV
15	12.2	0.0	-2.2	GC-MS/MS
16	27.5	5.4	0.8	HPLC-FLD
17	22.6	1.6	-0.1	GC-HRMS
18	26.5	0.9	0.6	GC-MS
19	1.4	0.0	-4.3	HPLC-FLD
20	13.0	0.9	-2.0	HPLC-FLD/UV
21	37.4	0.0	2.7	GC-HRMS
22	28.8	0.0	1.1	HPLC-FLD/UV
23	42.8	8.1	3.8	GC-HRMS
25	43.1	0.0	3.9	GC-MS
26	6.3	0.0	-3.3	HPLC-FLD

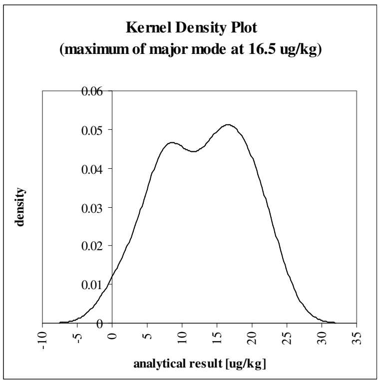




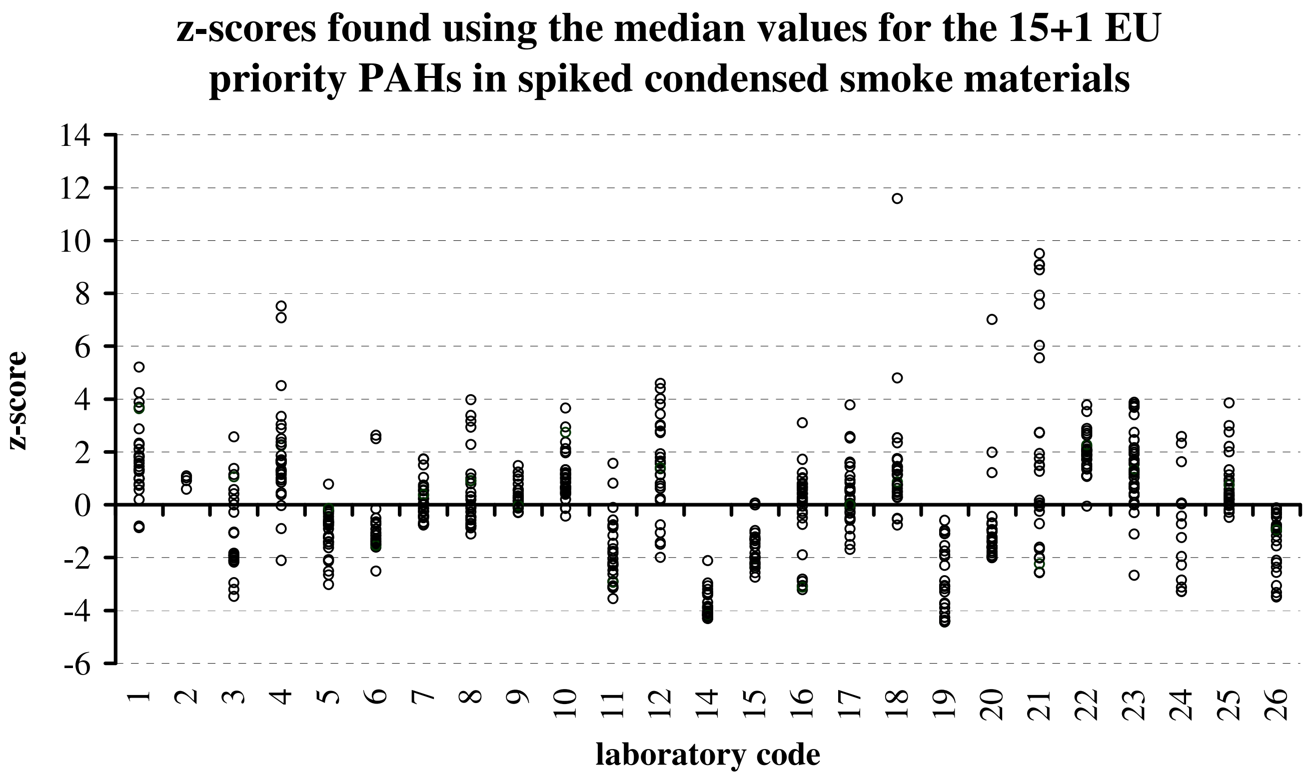
Indeno[*1,2,3-cd*]pyrene

labcode	average [µg/kg]	uncertainty [µg/kg]	z-score	technique
1	23.0	4.7	2.9	GC-HRMS
3	8.1	3.1	-2.0	HPLC-FLD
4	19.0	0.0	1.6	GC-MS
5	5.9	1.4	-2.7	HPLC-FLD/UV
6	10.5	3.0	-1.2	HPLC-FLD/UV
7	16.4	2.1	0.7	HPLC-FLD
8	11.9	0.4	-0.7	HPLC-FLD/UV
9	14.0	0.0	0.0	HPLC-FLD
10	18.2	0.0	1.3	GC-MS
11	6.4	2.2	-2.5	GC-MS
12	16.0	4.8	0.6	GC-MS
14	1.6	0.0	-4.0	HPLC-FLD/UV
15	8.0	0.0	-2.0	GC-MS/MS
16	14.6	2.9	0.2	HPLC-FLD
17	15.9	0.9	0.6	GC-HRMS
18	18.4	0.5	1.4	GC-MS
19	1.5	0.0	-4.1	HPLC-FLD
20	8.5	0.2	-1.8	HPLC-FLD/UV
21	22.6	0.0	2.7	GC-HRMS
22	20.5	0.0	2.1	HPLC-FLD/UV
23	20.3	3.9	2.0	GC-HRMS
24	8.0	0.0	-2.0	GC-MS
25	14.2	0.0	0.0	GC-MS
26	7.3	0.0	-2.2	HPLC-FLD





Annex 2: Overview on the z-scores for all samples and analytes



Annex 3: Avis of sample dispatch

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements
IRMM

Geel, 29.06.2006

Inter-laboratory comparison study on the determination of 16 EU priority PAHs in primary smoke condensates.

Dear Madame/Sir

The interlaboratory comparison study on the determination of 16 EU priority PAHs will start begin of next week with the dispatch of the samples. Please expect the arrival of the samples in your laboratory in the course of the week. If you do not get the samples by Friday (07.07.2006), please contact me or my collegue Rupert Simon.

The set of samples consists of two primary smoke condensate samples spiked with the PAHs of concern. Although the study is organised according to the "International harmonized protocol for the proficiency testing of analytical chemistry laboratories", we would like to draw your attention to the homogeneity of the test materials:
Segregation of the test materials could happen during transport or sample storage. We recognised over a period of several weeks the formation of a thin layer of sample components on the inner surface of the sample containers, where PAHs were adsorbed. In order to guarantee homogeneity and comparability of the test materials sent to the individual participants, we recommend to rinse the inner walls of the sample containers carefully with methanol (or an other suitable organic solvent that is compatible with the applied sample preparation procedure) and combine it with the smoke condensate samples. The amount of smoke condensate in the containers shall be determined by differential weighing. The stability of some of the PAHs under investigation is also not very good. Cyclopenta[cd]pyrene has shown to degrade significantly over a period of several weeks. Therefore we recommend for your own benefit to analyse the samples as soon as possible.

Proposed procedure:
1) Weigh the filled sample container to the nearest 0.01 g.
2) Fill the whole sample into a suitable vial.
3) Rinse the sample container with methanol or an other suitable organic solvent that is compatible with the applied sample preparation procedure.
4) Weigh the dry, empty sample container to the nearest 0.01 g and calculate the amount of smoke condensate sample from the difference.

Deadline for reporting results: 21.07.2006

If you have any questions, please contact me (Thomas.Wenzl@ec.europa.eu) or my collegue Rupert Simon (Rupert.Simon@ec.europa.eu).

With best regards

Thomas Wenzl

Annex 4: Letter accompanying shipment

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements, IRMM
Food Safety and Quality

Geel, 03.07.2006

Participant 1
Laboratory lane 12345
EU-67890 Test Town

Inter-laboratory comparison study on the determination of 16 EU priority PAHs in primary smoke condensates.

Dear Dr. Expert,

The set of samples consists of two primary smoke condensate samples spiked with the PAHs of concern. The samples are split in two vials each for easier handling. Although the study is organised according to the "International harmonized protocol for the proficiency testing of analytical chemistry laboratories", we would like to draw your attention to the homogeneity of the test materials: Segregation of the test materials could happen during transport or sample storage. We recognised over a period of several weeks the formation of a thin layer of sample components on the inner surface of the sample containers, where PAHs were adsorbed. In order to guarantee homogeneity and comparability of the test materials sent to the individual participants, we recommend to rinse the inner walls of the sample containers carefully with methanol (or an other suitable organic solvent that is compatible with the applied sample preparation procedure) and combine it with the smoke condensate samples. The amount of smoke condensate in the containers shall be determined by differential weighing. The stability of some of the PAHs under investigation is also not very good. Cyclopenta[cd]pyrene has shown to degrade significantly over a period of several weeks. Therefore we recommend for your own benefit to analyse the samples as soon as possible.

Proposed procedure:
1) Weigh the filled sample container to the nearest 0.01 g.
2) Fill the whole sample into a suitable vial.
3) Rinse the sample container with methanol or an other suitable organic solvent that is compatible with the applied sample preparation procedure.
4) Weigh the dry, empty sample container to the nearest 0.01 g and calculate the amount of smoke condensate sample from the difference.

Deadline for reporting results: 21.07.2006

The answer form will be asking for two results. If you have only one result, please fill in a numerical zero in the field for the second result.

If you have any questions, please contact us by email or telephone (Thomas.Wenzl@ec.europa.eu, +32 14 571 320) or Rupert Simon (Rupert.Simon@ec.europa.eu, +32 14 571 246).

With best regards

Thomas Wenzl and Rupert Simon

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European Commission

EUR 22945 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Report of the Inter-Laboratory Comparison on the 15+1 EU Priority PAHs
Author(s): Rupert Simon and Thomas Wenzl
Luxembourg: Office for Official Publications of the European Communities
2007 – 34 pp. – 21 x 29,7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593

Abstract
Two test materials were dispatched begin of July 2006. Each participant received two liquid smoke condensate test materials to be analysed for the 15+1 EU priority polycyclic aromatic hydrocarbons (PAHs). In total 28 sets of samples were sent to participating laboratories in 13 countries. Both test materials contained the 15+1 EU priority PAHs. The assigned value (X) for each analyte was calculated from the participant's results applying robust statistics. The target standard deviation (σp) was calculated using the modified Horwitz equation as proposed by Thomson. The resulting σp was then used in conjunction with the assigned value to derive z-scores from the participant's results.

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