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BAM-U013b: Polycyclic aromatic hydrocarbons in soil

Certification Report

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List of Abbreviations

BIPM	International Bureau of Weights and Measures
CCQM	Consultative Committee for Amount of Substance – Metrology in Chemistry
CIPM	International Committee for Weights and Measures
CIPM MRA	Mutual Recognition Arrangement of CIPM members
DAD	Diode array detector
EPA	U. S. Environmental Protection Agency
F	Fluorescence detector
GC	Gas chromatography
HPLC	High performance liquid chromatography
LOD	Limit of detection
MS	Mass spectrometry
PFE	Pressurised fluid extraction
PTFE	Polytetrafluoroethylene
UV	Ultraviolet detector

1 Introduction

1.1 PAH congeners of interest and available analytical procedures

Polycyclic aromatic hydrocarbons (PAHs) belong to the priority organic pollutants in environmental matrices and are widely monitored by field laboratories. The quantification of PAHs in soil using liquid chromatography (HPLC-UV/DAD/F) has been standardised more than ten years ago [1] and the application of GC-MS for this purpose has meanwhile been standardised as well [2].

BAM-U013b replaces the certified reference material ERM-CC013a which displayed similar PAH contents in the mg/kg level in a similar soil matrix and which has been sold out meanwhile. The measurements aimed at the extractable contents of 16 priority pollutant PAHs according to the EPA list.

1.2 Strategy of the certification project

A real world material, representative for a moderately polluted industrial soil with regard to PAH contents and congener pattern was selected as starting material. Fortification of environmental matrices with the respective analytes is generally avoided whenever possible. GC-MS and HPLC are the two analytical procedures available for the determination of PAH and are equally often used in practice. Therefore, both chromatographic procedures along with usually applied extraction procedures were employed for the characterisation of the PAH contents. This certification exercise was organised by BAM as interlaboratory comparison with 11 laboratories which had been invited on basis of their proficiency for this analyte/matrix combination during consecutive rounds of BAM's proficiency testing scheme "Contaminated Sites". The calibration and measurement capability (CMC) of BAM with regard to PAHs was internationally recognised by way of key comparisons [3] of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) of the International Bureau of Weights and Measures (BIPM). Each participating laboratory analysed two different units of the candidate material in triplicate. Traceability was established using calibration standard solutions certified for the contents of these congeners and in case of GC-MS additionally deuterated or ^{13}C-labelled PAHs were applied as internal standards (see Clause 5.1).

2 Candidate material

The loamy sandy soil was sampled from a former gasworks site in Berlin, Germany. The specific location was chosen because it displayed a PAH pattern typical for an aged contamination originating from industrial immission over decades. Particles larger than 6 mm were removed from the bulk material on the site and the material was air-dried to constant weight before further processing. After drying to constant mass, the material was classified by means of an automatic sieving station. A total amount of 38.8 kg of the fraction ≤ 125 µm was collected. Thereafter, this material was homogenised by means of a 120 L stainless steel barrel in a drum hoop mixer (J. Engelsmann AG, Ludwigshafen; Germany). The barrel was equipped with a mixing insert inside for improving the mixing intensity and moved for several days (approx. 110 h total). Further homogenisation and bottling was achieved using a spinning riffler with 10 tubes and the so-called cross-riffling procedure. The whole material was subdivided into 10 portions (1-10). Each portion was subdivided further into 10 portions. These were recombined such that each of the 10 recombined portions (1r – 10r) consisted of equal amounts of the original 10 portions (1 -10). These were subdivided to the final 400 units of the candidate material.

The units were bottled in 100 mL amber screw-capped glass bottles containing (77.5 ± 1.4) g each and units were numbered in the order of leaving the bottling process. The screw caps equipped with PTFE foil inserts were tightly closed and sealed with shrinking foil. All units were stored at -20 °C directly after bottling.

3 Homogeneity study

The accredited procedure employed for this study involved pressurised fluid extraction (PFE) with toluene followed by GC-MS. The minimum sample intake for one determination was chosen in a way that no significant heterogeneity within the bottle is to be expected. Measurements with sample intakes of 2 g, 5 g, and 7 g (six replicate determinations each) revealed no significantly different standard deviations. Therefore, a mass of 5 g was used for each replicate determination during the homogeneity study and is recommended as minimum sample intake in the certificate.

Twenty units were selected equidistantly from the whole batch of the 400 units numbered in the order of bottling. The selected units were analysed in triplicate each. All 20 units were extracted once under repeatability conditions on each of three consecutive days. All extracts were analysed under repeatability conditions in that all 60 extracts were quantified against one calibration after randomisation. Table 1 contains the synopsis of the 1-way analysis of variance (ANOVA).

Table 1: Results of the 1-way ANOVA on the candidate material

PAH congener	$MS_{between}$ [a] ($mg^2\ kg^{-2}$)	MS_{within} [b] ($mg^2\ kg^{-2}$)	F_{obs} [c]	F_{crit} [d]	u_{bb} [e] ($mg\ kg^{-1}$)
Naphthalene	0.003032	0.002991	1.0138	1.8529	0.01493
Acenaphthylene	0.013452	0.009900	1.3588	1.8529	0.03441
Acenaphthene	8.2482E-05	4.8229E-05	1.7102	1.8529	0.003479
Fluorene	0.002417	0.002079	1.1627	1.8529	0.012449
Phenanthrene	0.250511	0.11813	2.1207	1.8529	0.210068
Anthracene	0.014013	0.0086179	1.6260	1.8529	0.042406
Fluoranthene	0.455428	0.232820	1.9561	1.8529	0.272401
Pyrene	0.378022	0.197468	1.9144	1.8529	0.245330
Benz[*a*]anthracene	0.08641	0.047301	1.8267	1.8529	0.114171
Chrysene	0.241453	0.139799	1.7271	1.8529	0.184078
Benzo[*b*]fluoranthene	0.106818	0.045694	2.3377	1.8529	0.142741
Benzo[*k*]fluoranthene	0.185878	0.135420	1.3726	1.8529	0.129689
Benzo[*a*]pyrene	0.129999	0.066681	1.9496	1.8529	0.145279
Indeno[1,2,3-*cd*]pyrene	0.507670	0.170279	2.9814	1.8529	0.335356
Dibenz[*ah*]anthracene	0.000893	0.000844	1.0588	1.8529	0.007927
Benzo[*ghi*]perylene	0.086254	0.048670	1.7722	1.8529	0.111929
Sum of 16 PAH	22.49507	10.76910	2.0889	1.8529	1.977032

[a] *Mean of squared deviations between bottles (from 1-way ANOVA)*
[b] *Mean of squared deviations within bottles (from 1-way ANOVA)*
[c] *Observed F-value: $MS_{between}/MS_{within}$*
[d] *Critical F-value on the 95% level of confidence*
[e] *Standard uncertainty between the bottles: Estimate of inhomogeneity contribution to the total uncertainty according to [6].*

The results of this study indicate that the material is sufficiently homogeneous for the use as reference material. The estimates of inhomogeneity contributions u_{bb} potentially hidden by the measurement uncertainty and to be included to the total uncertainty were estimated according to ISO Guide 35 [6] as the maximum of the values obtained from Eq. (1) and (2).

$$u_{bb}=\sqrt{\frac{MS_{between}-MS_{within}}{n}} \quad (1) \qquad u_{bb(2)} = \frac{S_{method}}{\sqrt{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

Where:

S_{method} = Method variability ($=\sqrt{MS_{within}}$)
n = Number of replicate determinations
N = Number of bottles analysed

4 Stability study

4.1 Initial stability study

From earlier experience with PAHs in various matrices a temperature-driven deterioration of the PAH content was to be expected also for this material. Selected units of the candidate material were submitted to a so-called isochronous [4] accelerated ageing at temperatures between 4 and 60 °C over periods of 1 - 6 months as shown in Table 2. After the respective periods of time individual units were stored at -20 °C. All units were analysed for PAH under repeatability conditions together with reference samples which had been kept at -20 °C since bottling. For PAH quantification an accredited procedure involved PFE extraction with methanol followed by HPLC-DAD/F detection was employed. Since this procedure does not yield reliable values for acenaphthylene and acenaphthene in the concentration range observed in the candidate material no stability data are available for these congeners. Though stability problems with these analytes are highly unlikely from earlier experience with similar matrices the values derived from the certification exercise are classified as “indicative” rather than “certified”.

Table 2: Accelerated ageing of selected units of BAM-U013b, exposition temperatures and periods

Ageing time [Months]	+4 °C	+20 °C	+40 °C	+60 °C	Remark
1	x	x	x	x	*initial study*
3	x	x	x	x	*initial study*
6	x	x	x		*initial study*
12	x	x	x		*post certification monitoring*
24	x	x			*post certification monitoring*
36	x	x			*post certification monitoring*

Data evaluation and expiry date estimation strictly followed the procedures as comprehensively described in [5]: From semi-logarithmic plots of measured single values over time, effective deterioration rates k_eff were determined and tested against an Arrhenius model describing the temperature dependence of the deterioration rates. Most of the PAHs matched the model, some of them excellently. Activation energies as determined from the model were in the region between 32 and 92 kJ mol^{-1} depending on the PAH considered. Figures 1 and 2 show the dependence of the logarithm of the effective deterioration rate k_eff on the inverse temperature by way of example for anthracene and benzo[*a*]anthracene. The activation energies ΔE are 75.3 kJ mol^{-1} and 38.8 kJ mol^{-1}, respectively.

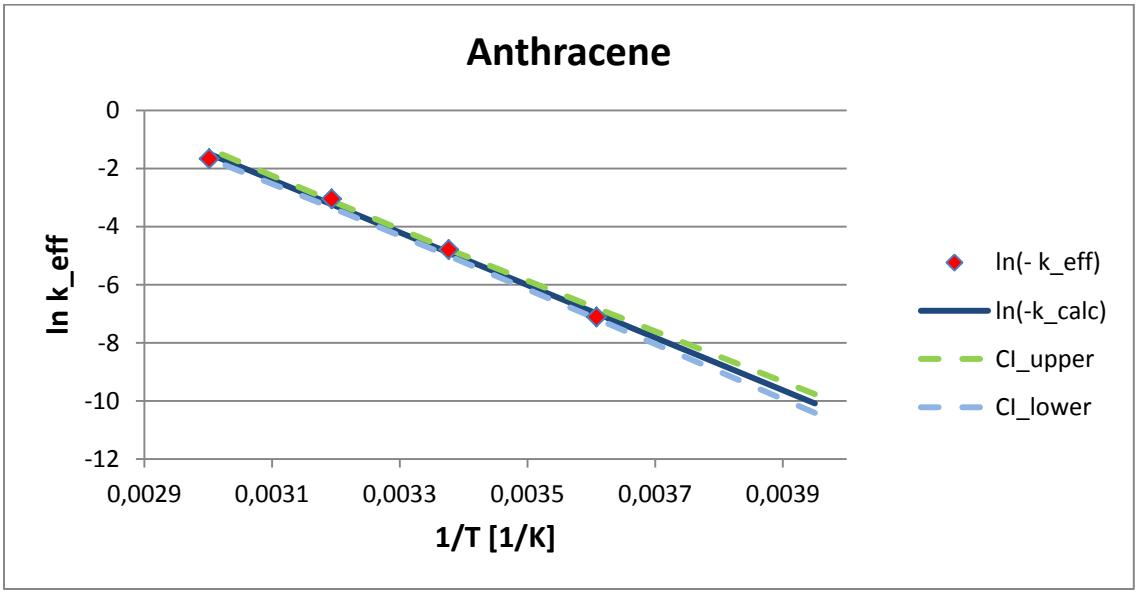


Fig. 1: Effective deterioration rate versus inverse temperature for anthracene.

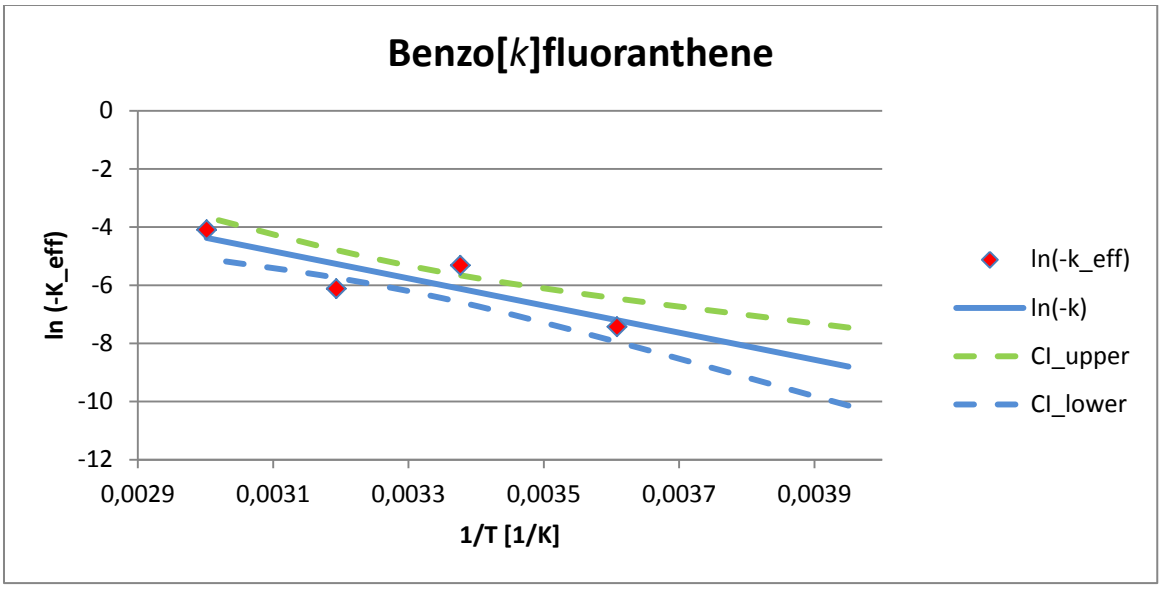


Fig. 2: Effective deterioration rate versus inverse temperature for benzo[*k*]fluoranthene.

For chrysene, a poor stability estimate was derived from this initial study. Though a sufficient long-term stability is considered likely from earlier experience also for this analyte in similar matrices an additional uncertainty contribution accounting u_{lts} for the estimated long term stability was included in the uncertainty of the certified value (see Clause 5.2.2).

Table 3: Estimated period in months after which the certified values fall out of their certified uncertainties *U* at the storage temperature of -20 °C.

PAH congener	Period (months)
Naphthalene	1573.7
Acenaphthylene	
Acenaphthene	
Fluorene	5776.1
Phenanthrene	525.8
Anthracene	1717.7
Fluoranthene	673.8
Pyrene	694.5
Benz[*a*]anthracene	2323.1
Chrysene	36.0
Benzo[*b*]fluoranthene	1262.9
Benzo[*k*]fluoranthene	134.8
Benzo[*a*]pyrene	782.7
Dibenz[*a,h*]anthracene	439.4
Benzo[*ghi*]perylene	63.1
Indeno[1,2,3-*cd*]pyrene	443.3
PAH Sum	1372.1

4.2 Post-certification stability monitoring

The first rough estimation of stability will be updated by further measurements of units stored at +4° C and +20 °C over the period of availability of the material. The post-certification measurements will be conducted in time and using the estimate given in Table 3. Several units investigated during the initial stability study were stored again at +4 °C or +20 °C, respectively. That way, information on the long term stability of units of BAM-U013b having been opened at least once for withdrawal of material is expected in the course of the post certification monitoring. Earlier experience with similar materials including BAM-CC013a does not indicate any enhanced deterioration of once opened bottles if they are closed and stored thereafter according to the instructions given in the certificate (see also Clause 6.2).

5 Certification study

5.1 Design of the certification study

The certification exercise was organised as intercomparison of selected laboratories with known proficiency for the matrix/analyte combination in question. The proficiency had been demonstrated in consecutive rounds of the proficiency testing scheme “Contaminated Sites” run by BAM.

Table 4: Participants in the certification exercise in alphabetical order

BAM Bundesanstalt für Materialforschung und –prüfung	Berlin (DE)
Chemisches Labor Dr. Barbara Graser	Schonungen (DE)
Chemisches Labor Dr. Wirts und Partner GmbH	Hannover (DE)
Chemlab GmbH	Bensheim (DE)
Eurofins Umwelt West GmbH	Wesseling (DE)
Infraserv GmbH & Co. Höchst KG	Frankfurt/Main (DE)
Institut Koldingen GmbH	Sarstedt (DE)
GEO-data GmbH	Garbsen (DE)
Lausitzer Analytik GmbH	Spremberg (DE)
SGS Institut Fresenius GmbH	Herten (DE)
Wessling GmbH	Hannover (DE)

The different options for extraction as well as instrumental quantification (GC-MS and HPLC-DAD/F) currently in use were covered by the participants (Table 5).

Two units of the candidate material had to be analysed by each laboratory in triple each. A rough information on the level of content of the PAH congeners to be expected was provided in order to allow a reasonable adjustment of individual calibrations. Certified calibration standards SRM 1647d or SRM 2260 were used as calibrants (see also Clause 5.2.3). Laboratories using GC-MS applied the respective deuterated PAH congeners as internal standards, while HPLC measurements were done with external calibration.

Table 5: Extraction and determination methods

Laboratory	Extraction	Determination method
1	PFE; acetone/petrol ether (1:1)	HPLC-DAD/F
2	Shaking; hexane/acetone (1:1)	GC-MS
3	Sonication; acetonitrile	HPLC-DAD/F
4	Sonication; acetonitrile	HPLC-DAD/F
5	Sonication; acetonitrile	HPLC-DAD/F
6	Soxhlet; hexane	GC-MS
7	Hot extraction; acetone/petrol ether (1:1)	GC-MS
8	Sonication/shaking; hexane/acetone (2:1)	GC-MS
9	Shaking; acetone/petrol ether (1:1)	GC-MS
10	Sonication; tetrahydrofuran	HPLC-DAD/F
11	PFE; toluene	GC-MS

5.2 Evaluation of results and certified values

The results of the certification study are listed comprehensively in Table 6 and were evaluated in accordance with ISO Guide 35 [6] and the specific requirements of the ERM agreement [7]. For all measurement data see the ANNEX. The computer software SoftCRM [8] was used for statistical tests and data treatment.

5.2.1 Statistical evaluation

Since the participants in the intercomparison used different extraction techniques and solvents, followed their own procedures, and applied both GC and HPLC for separation, a certain scatter of results was to be expected from experience. Thus there was no good reason for assuming that the

single values measured by the different laboratories would belong to a common mother distribution. This was confirmed by the statistical analysis within which the following statistical parameters were calculated:

- *the mean of laboratory means*
- *the standard deviation of the distribution of laboratory means, and the standard deviation of the mean of laboratory means*
- *the confidence interval of the mean of laboratory means at the 0.05 significance level*

and the following statistical tests were carried out (at significance levels of 0.05 and 0.01):

- *Cochran test for the identification of outliers with respect to laboratory variance*
- *Grubbs test for the identification of outliers with respect to the mean*
- *Dixon and Nalimov test for the verification of possible outlier indications*
- *Kolmogorov-Smirnov Test (Lilliefors version) for the normality test*
- *Tests for skewness and kurtosis as well variance homogeneity (Scheffé and Bartlett)*

As usually observed in such intercomparisons the data sets differ significantly (*Scheffé*-Test) and variances are inhomogeneous (*Bartlett*-Test at the significance level of 0.01).

The most important results of the calculations and tests for a data evaluation based upon the laboratory means are given in Table 6.

A number of outliers were identified in the *Cochran*, *Grubbs*, *Dixon* and *Nalimov*-Tests. Laboratory C04 was classified as significant outlier in the data sets of most PAH congener. Therefore, the results of laboratory C04 were removed altogether. The remaining data set was recalculated and additional outliers were removed from individual data sets. Table 7 contains the data sets after elimination of all outliers.

Table 6: Evaluation of the certification study (after complete elimination of outliers)

	Mean[a] (mg/kg)	SD[b] (mg/kg)	*u*(x)[c] (mg/kg)	Data[d] sets	Cochran[e] (0.01)	Grubbs[e] 0.01(0.05)	Dixon[e] 0.01(0.05)	Nalimov[e] 0.01(0.05)	Gauss[f] 0.05;0.01	**Certify**	Labs deleted
Naphthalene	0.7309	0.3332	0.105	10	0,01				no;yes	yes	C04
Acenaphthylene	0.6611	0.4139	0.146	8	C03,C11,C05	-(-)	-(-)	-(C03)	yes	yes	C04
Acenaphthene	0.1483	0.0335	0.012	8	C08	-(-)	-(-)	-(-)	yes	yes	C10,C04
Fluorene	0.4474	0.0955	0.030	10	C03	-(C07)	-(-)	-(C07)	yes	yes	C04
Phenanthrene	8.3596	0.8663	0.274	10	C02	-(-)	-(-)	-(-)	yes	yes	C04
Anthracene	1.4507	0.1895	0.060	10	-	-(-)	-(-)	-(-)	yes	yes	C04
Fluoranthene	13.9631	1.6423	0.519	10	-	-(-)	-(-)	-(-)	yes	yes	C04
Pyrene	11.3327	1.4584	0.461	10	-	-(-)	-(-)	-(C01)	yes	yes	C04
Benz[*a*]anthracene	6.0319	0.5803	0.184	10	-	-(-)	-(-)	-(C05)	yes	yes	C04
Chrysene	5.3676	0.5664	0.179	10	-	-(-)	-(-)	-(C01)	yes	yes	C04
Benzo[*b*]fluoranthene	6.5015	1.4661	0.464	10	C03	-(-)	-(-)	-(C09)	no;yes	yes	C04
Benzo[*k*]fluoranthene	3.1597	0.3133	0.099	10	C02	-(-)	-(-)	-(-)	yes	yes	C04
Benzo[*a*]pyrene	6.5542	0.4785	0.160	9	C01	-(-)	-(-)	-(C11)	yes	yes	C01,C04
Dibenz[*a*,*h*]anthracene	1.0255	0.2382	0.072	11	C03,C02, C06	-(-)	-(-)	-(-)	yes	yes	C04
Benzo[*ghi*]perylene	4.9678	0.7329	0.244	9	C02,C03	-(-)	-(-)	-(-)	yes	yes	C03,C04
Indeno[1,2,3*cd*]pyrene	4.4867	0.4756	0.159	9	C02,C05	-(C11)	-(-)	C11(C11)	yes	yes	C04,C11
PAH Sum	75.3695	6.9607	2.201	10	C03,C05	-(-)	-(-)	-(-)	yes	yes	C04

[a] *Mean of laboratory means after elimination of outliers*
[b] *Standard deviation of the mean of laboratory means*
[c] *Standard uncertainty of the mean of means*
[d] *Number of data sets used for the evaluation of Mean, SD, u(x) after elimination of outliers (see right column)*
[e] *Laboratory data identified as outlier by the respective test on the given level of significance*
[f] *Results of the test for normality*

5.2.2 Certified values and combined uncertainties

The means of laboratory means were taken as the best estimates w_{char} for the values to be certified. The standard deviations of the mean of laboratory means were taken as the uncertainty contributions u_{char} from the characterisation.
Besides this uncertainty of characterisation u_{char} the contribution from a possibly undetected inhomogeneity u_{bb} (see Clause 3) was included in the combined uncertainty u_{com} (Eq. 3) as recommended in [6,9]. In case of chrysene an additional factor u_{lts} was included in order to account for the relatively poor stability estimate from the initial stability study (see Clause 3).

$$u_{com,r}^2 = u_{char,r}^2 + u_{bb,r}^2 + u_{lts,r}^2 \qquad (3)$$

The index r indicates that the relative values for the three uncertainty contributions were related to w_{char} before calculation of u_{com}. Table 8 contains the final values including the expanded uncertainty U which were derived according to Eq. 4 with the coverage factor k = 2.

$$U = k \cdot u_{com} \qquad (4)$$

Table 8: Certified mass fractions of PAH congeners in BAM-U013b in mg/kg (before rounding)

	value	u_{bb}	u_{char}	u_{lts}	u_{com}	$U(k=2)$
Naphthalene	0.7309	0.009	0.105	0	0.106	0.211
Acenaphthylene	0.6611	0.018	0.146	0	0.147	0.295
Acenaphthene	0.1483	0.006	0.012	0	0.013	0.027
Fluorene	0.4474	0.008	0.030	0	0.031	0.063
Phenanthrene	8.3596	0.199	0.274	0	0.339	0.677
Anthracene	1.4507	0.033	0.060	0	0.068	0.136
Fluoranthene	13.9631	0.327	0.519	0	0.614	1.228
Pyrene	11.3327	0.272	0.461	0	0.536	1.071
Bbenz[*a*]anthracene	6.0319	0.146	0.184	0	0.234	0.469
Chrysene	5.3676	0.125	0.179	0.524	0.568	1.135
Benzo[*b*]fluoranthene	6.5015	0.216	0.464	0	0.512	1.023
Benzo[*k*]fluoranthene	3.1597	0.065	0.099	0	0.118	0.237
Benzo[*a*]pyrene	6.5542	0.098	0.160	0	0.187	0.375
Dibenz[*a,h*]anthracene	1.0255	0.015	0.072	0	0.073	0.147
Benzo[*ghi*]perylene	4.9678	0.124	0.244	0	0.274	0.548
Indeno[1,2,3-*cd*]pyrene	4.4867	0.251	0.159	0	0.297	0.593
PAH sum	75.3695	1.972	2.201	0	2.956	5.911

The values and the expanded uncertainties are rounded according to the recommendations of DIN 1333 [10] and are given with respect to sample intake mass in Table 9. The water content of BAM-U013b is (3.2 ± 0.2)% and has been proven to remain stable if the material is handled according to the instructions in the certificate (see Clause 6).

Table 9: Certified mass fractions of PAH congeners in BAM-U013b in mg/kg (after rounding)

	Value	*U*	*Remarks*
Naphthalene	0.73	0.21	
Acenaphthylene*	*0.66*	*0.30*	indicative
Acenaphthene*	*0.148*	*0.027*	indicative
Fluorene	0.45	0.07	
Phenanthrene	8.4	0.7	
Anthracene	1.45	0.14	
Fluoranthene	14.0	1.3	
Pyrene	11.3	1.1	
Benz[*a*]anthracene	6.0	0.5	
Chrysene	5.4	1.2	
Benzo[*b*]fluoranthene	6.5	1.0	
Benzo[*k*]fluoranthene	3.16	0.24	
Benzo[*a*]pyrene	6.6	0.4	
Dibenz[*a*,*h*]anthracene	1.03	0.15	
Benzo[*ghi*]perylene	5.0	0.6	
Indeno[1,2,3-*cd*]pyrene	4.5	0.6	
PAH sum	75.4	6.0	

* *As no stability data were obtained for these congeners the values are classified as indicative (see Clause 4)*

5.2.3 Traceability

All certified values refer to the extractable amount of PAHs and are conventional to this extent. However, different extraction methods and solvents have been used such that systematic biases will (at least partially) cancel out. It is known from experience that there is no significant bias among the applied methods and the completeness of extraction was demonstrated for many similar materials.

In order to ensure traceability of the extractable content as defined above, certified calibration standards SRM 1647d or SRM 2260, respectively, were employed by the participants. Outside of this study it had been established before that these standard solutions were equivalent to standards prepared using pure crystalline PAH congeners with certified purity and available as BCR CRM from the IRMM in Geel, Belgium.

6 Information on the proper use of BAM-U013b

6.1 Shelf life

From the initial stability study a preliminary shelf life of three years at -20 °C is estimated. Since the dispatch to the end user may occur at any time during this period the certified properties will be valid for 12 months beginning with the dispatch of the material from BAM. The validity of this information will be maintained by post-certification stability monitoring.

6.2 Transport, storage and use

The stability of the content of PAH allows the dispatch of the material at ambient temperature. On receiving, it is to be stored at -20 °C. Before withdrawing a sub-sample the bottle has to have reached ambient temperature. Thereafter, the bottle must be closed tightly and stored at -20 °C. The water content remains stable when the material is treated as described.

6.3 Safety instructions

The soil was not sterilised, however, it is supposed to not exhibit any biological activity due to having been air-dried to constant mass and displaying a water content of 3.2%. No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with polycyclic aromatic hydrocarbons.

It is strongly recommended to handle and dispose the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal.

6.4 Legal notice

Neither the Federal Institute for Materials Research and Testing (BAM) nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights, or assume any liability with respect to the use of, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

7 References

[1] ISO 13877:1998 – Soil quality -- Determination of polynuclear aromatic hydrocarbons -- Method using high-performance liquid chromatography

[2] ISO 18287:2006 – Soil quality -- Determination of polycyclic aromatic hydrocarbons (PAH) -- Gas chromatographic method with mass spectrometric detection (GC-MS)

[3] *http://www.bipm.fr/en/committees/cc/ccqm/*

[4] A. Lamberty, H. Schimmel, J. Pauwels. The study of the stability of reference materials by isochronous measurements. *Fres. J. Anal. Chem.* (1998) 360: 359–361

[5] W. Bremser, R. Becker, H. Kipphardt, P. Lehnik-Habrink, U. Panne and A. Töpfer. Stability testing in an integrated scheme. Accred Qual Assur (2006) 11: 489–495.

[6] ISO Guide 35:2006. Reference materials – General and statistical principles for certification. ISO, Geneva, Switzerland

[7] For detailed information on the ERM agreement see: www.erm-crm.org/ermcrm

[8] SoftCRM V.1.22 (developed and funded under Contract SMT4 - CT98 – 6533 of the STANDARDS, MEASUREMENTS & TESTING PROGRAMME)

[9] Guide To The Expression Of Uncertainty In Measurement. ISO, Geneva (1993). (ISBN 92-67-10188-9, Reprinted 1995)

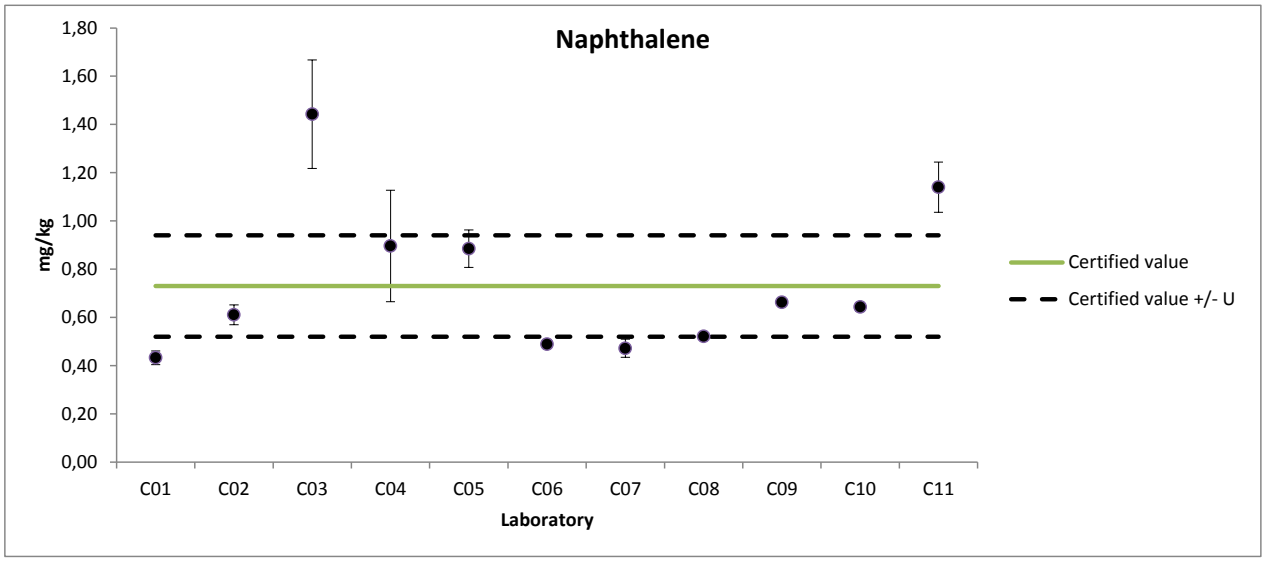
[10] DIN 1333:1992 - Presentation of numerical data

ANNEX

Results of the certification intercomparison

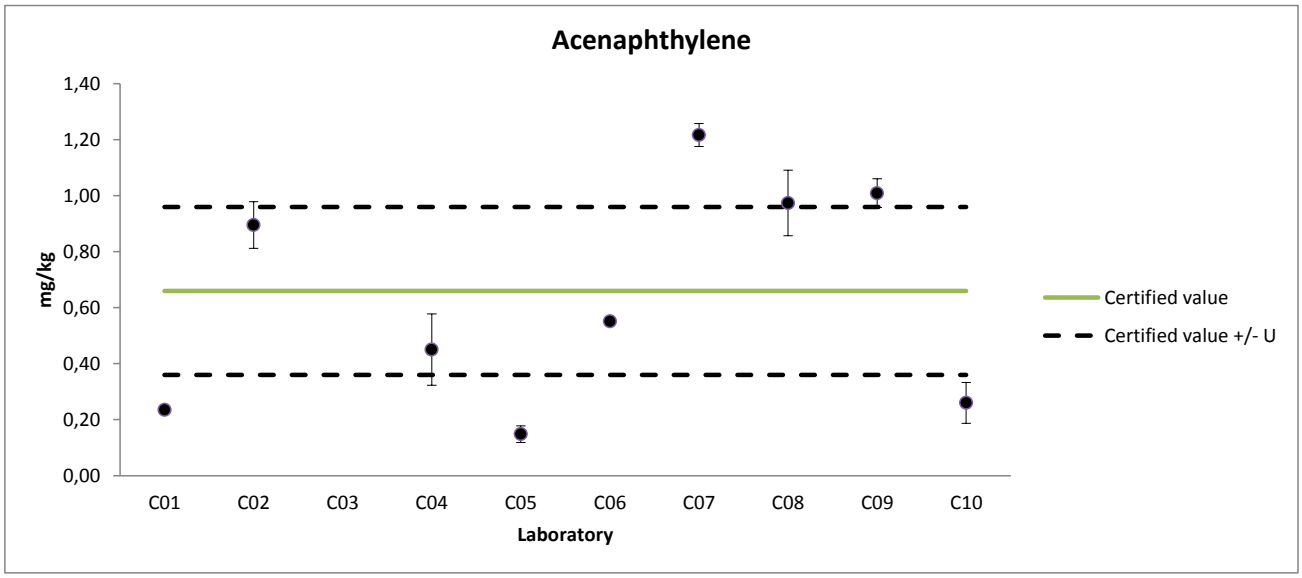
Naphthalene								
Laboratory	**Replicate determination (mg/kg)**						Mean (mg/kg)	Standard deviation (mg/kg)
	#1	#2	#3	#4	#5	#6		
C01	0.45	0.40	0.43	0.41	0.47	0.44	0.43	0.03
C02	0.65	0.59	0.65	0.54	0.62	0.60	0.61	0.04
C03	1.20	1.30	1.42	1.85	1.49	1.40	1.44	0.22
C04	*0.64*	*0.56*	*1.04*	*1.04*	*1.08*	*1.02*	*0.90*	*0.23*
C05	0.80	0.88	0.87	0.84	0.89	1.03	0.88	0.08
C06	0.46	0.49	0.49	0.48	0.49	0.52	0.49	0.02
C07	0.43	0.51	0.42	0.48	0.50	0.49	0.47	0.04
C08	0.53	0.53	0.53	0.51	0.51	0.51	0.52	0.01
C09	0.66	0.67	0.67	0.65	0.67	0.65	0.66	0.01
C10	0.66	0.66	0.61	0.65	0.64	0.64	0.64	0.02
C11	1.28	1.14	1.14	1.18	0.96	1.16	1.14	0.10

Values of laboratory C04 were excluded from evaluation of the certified value.



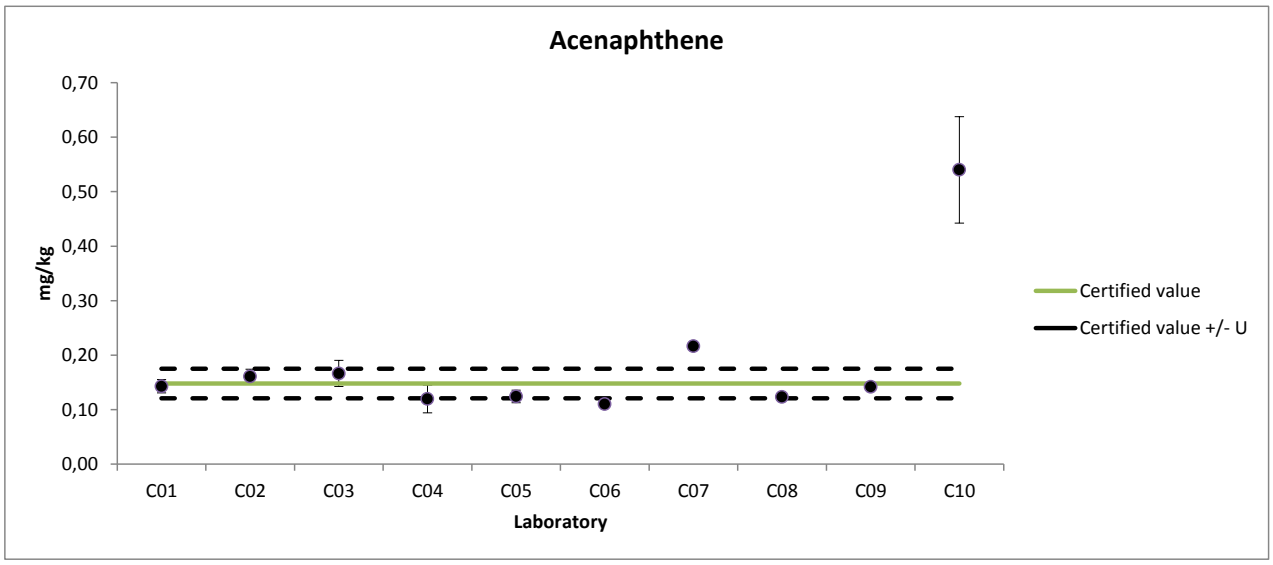
Acenaphthylene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5#	#6		
C01	0.22	0.23	0.25	0.23	0.26	0.23	0.24	0.02
C02	1.03	0.88	0.97	0.81	0.84	0.86	0.90	0.08
C03								
C04	*0.56*	*0.56*		*0.32*		*0.36*	*0.45*	*0.13*
C05	0.13	0.15	0.18	0.18	0.11	0.13	0.15	0.03
C06	0.56	0.56	0.54	0.53	0.55	0.57	0.55	0.02
C07	1.20	1.20	1.20	1.30	1.20	1.20	1.22	0.04
C08	1.08	1.07	1.09	0.86	0.87	0.87	0.97	0.12
C09	1.06	1.05	1.06	0.95	0.97	0.96	1.01	0.05
C10	0.29	0.28	0.34	0.29	0.23	0.13	0.26	0.07
C11								

Values of laboratory C04 were excluded from evaluation of the certified value.



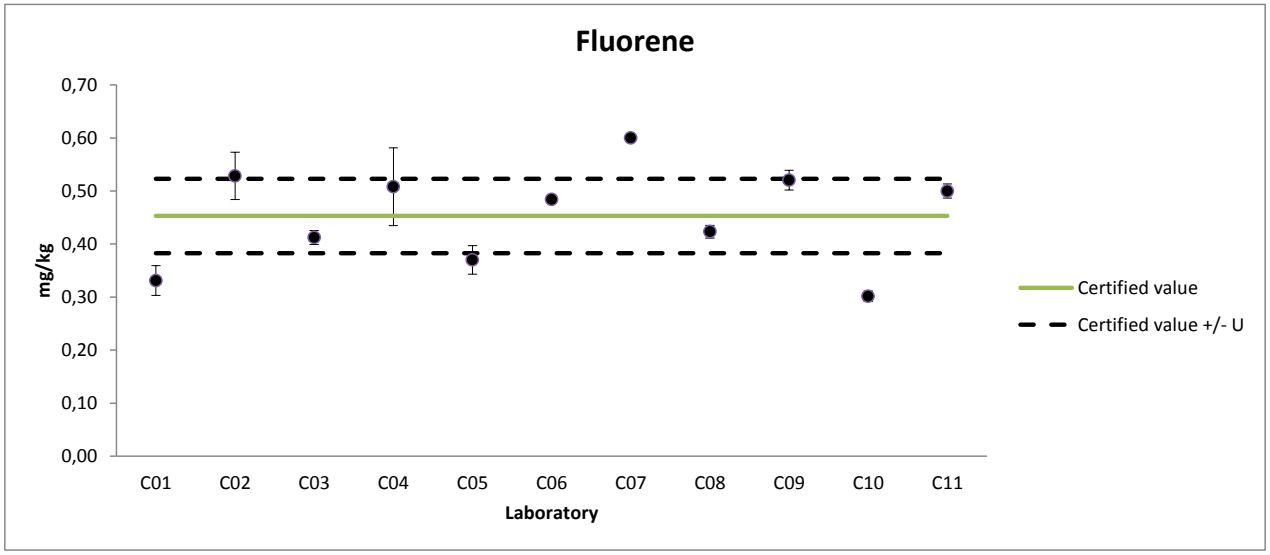
Acenaphthene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	0.13	0.14	0.16	0.13	0.14	0.15	0.14	0.01
C02	0.17	0.17	0.18	0.15	0.15	0.15	0.16	0.01
C03	0.14	0.14	0.20	0.18	0.17	0.17	0.17	0.02
C04	*0.13*	*0.08*	*0.11*	*0.15*	*0.11*	*0.14*	*0.12*	*0.03*
C05	0.12	0.11	0.11	0.14	0.13	0.13	0.12	0.01
C06	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.00
C07	0.22	0.21	0.21	0.23	0.22	0.21	0.22	0.01
C08	0.12	0.12	0.12	0.12	0.13	0.13	0.12	0.00
C09	0.14	0.14	0.15	0.14	0.14	0.14	0.14	0.00
C10	*0.67*	*0.66*	*0.48*	*0.50*	*0.46*	*0.47*	*0.54*	*0.10*
C11								

Values of laboratories C04, C10 were excluded from evaluation of the certified value.



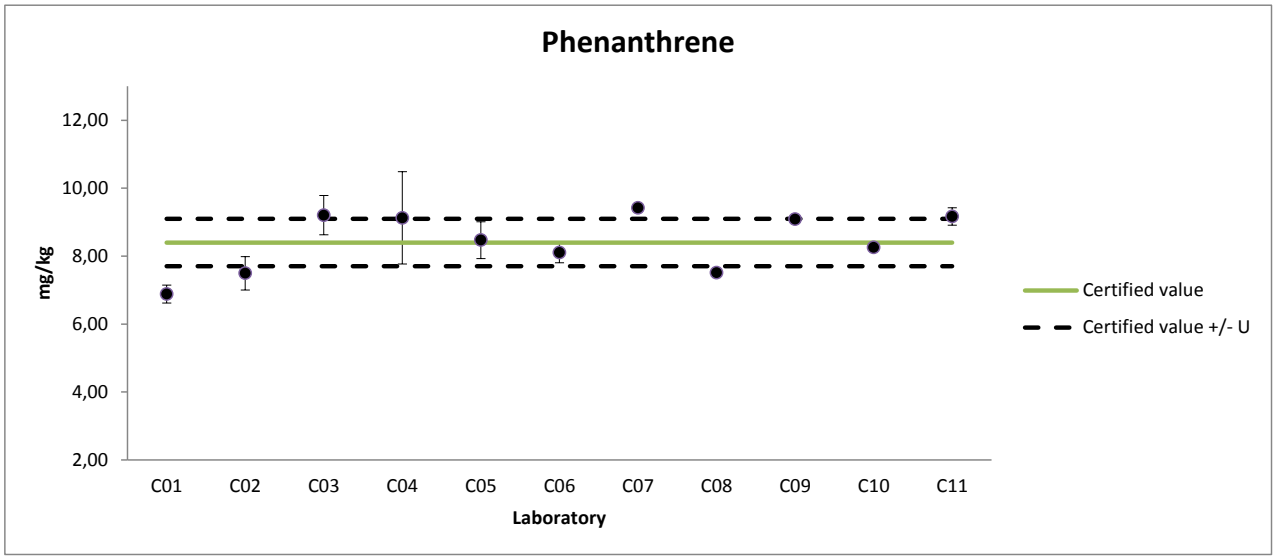
Fluorene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	0.33	0.30	0.36	0.30	0.37	0.34	0.33	0.03
C02	0.58	0.54	0.57	0.46	0.52	0.51	0.53	0.04
C03	0.42	0.39	0.43	0.40	0.42	0.42	0.41	0.01
C04	*0.47*	*0.38*	*0.51*	*0.58*	*0.54*	*0.56*	*0.51*	*0.07*
C05	0.37	0.40	0.40	0.37	0.34	0.34	0.37	0.03
C06	0.49	0.49	0.49	0.49	0.48	0.47	0.48	0.01
C07	0.60	0.60	0.60	0.61	0.59	0.60	0.60	0.01
C08	0.43	0.43	0.44	0.41	0.41	0.42	0.42	0.01
C09	0.50	0.50	0.52	0.53	0.53	0.54	0.52	0.02
C10	0.31	0.30	0.29	0.31	0.31	0.29	0.30	0.01
C11	0.51	0.50	0.50	0.50	0.52	0.48	0.50	0.01

Values of laboratory C04 were excluded from evaluation of the certified value.



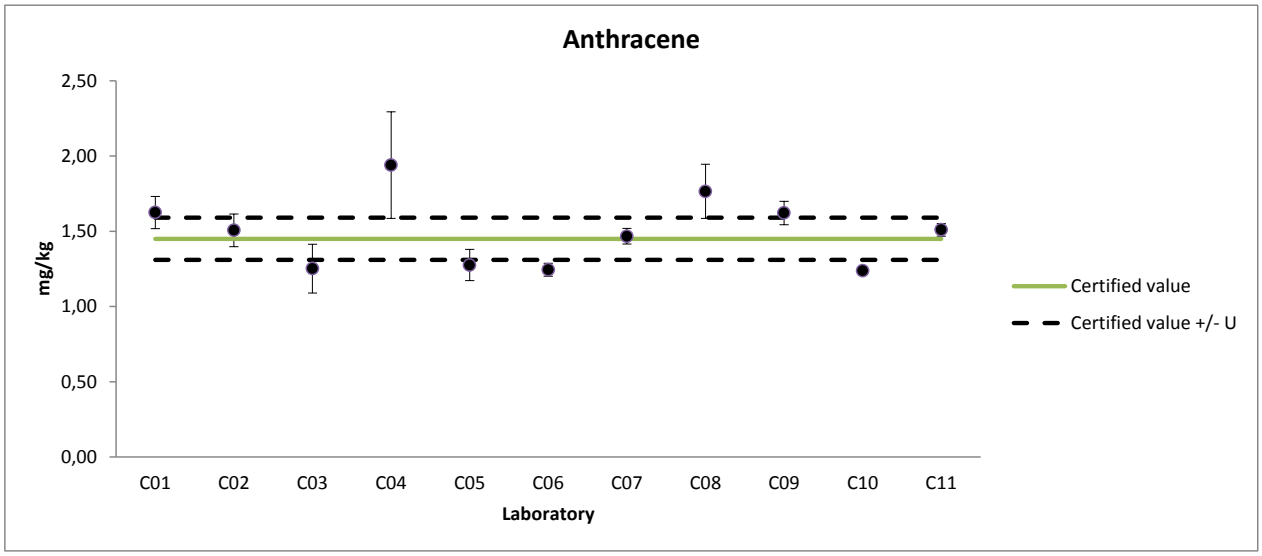
Phenanthrene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	6.84	6.53	7.27	6.67	6.93	7.06	6.88	0.26
C02	7.90	7.95	7.83	6.69	7.24	7.37	7.50	0.49
C03	9.81	9.86	8.82	8.44	9.44	8.88	9.21	0.58
C04	*8.09*	*6.83*	*9.97*	*9.82*	*9.83*	*10.22*	*9.13*	*1.36*
C05	7.73	8.23	8.21	8.47	9.15	9.04	8.47	0.54
C06	8.14	8.14	7.81	8.45	8.39	7.70	8.10	0.30
C07	9.50	9.30	9.40	9.60	9.40	9.30	9.42	0.12
C08	7.54	7.53	7.66	7.41	7.47	7.47	7.51	0.09
C09	9.20	9.09	9.13	9.04	8.98	9.09	9.09	0.07
C10	8.36	8.31	8.30	8.22	8.14	8.21	8.26	0.08
C11	9.24	9.08	9.01	9.24	8.84	9.59	9.17	0.26

Values of laboratory C04 were excluded from evaluation of the certified value.



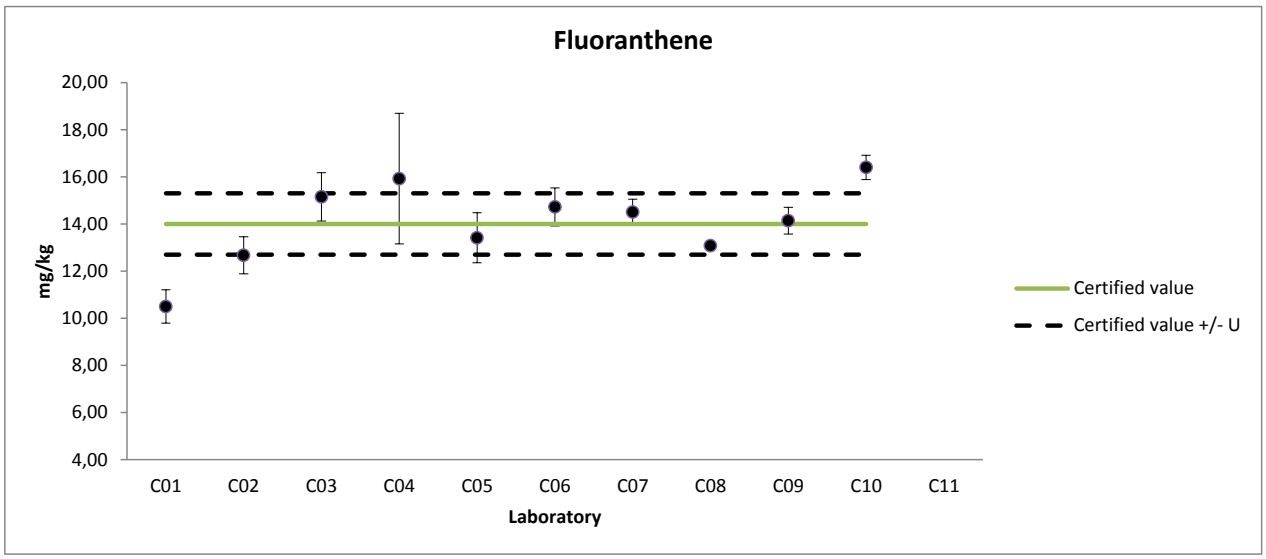
Anthracene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	1.82	1.56	1.57	1.53	1.62	1.65	1.62	0.11
C02	1.64	1.53	1.59	1.44	1.34	1.50	1.51	0.11
C03	1.45	1.47	1.17	1.14	1.16	1.13	1.25	0.16
C04	*2.29*	*1.91*	*1.48*	*2.20*	*1.55*	*2.21*	*1.94*	*0.35*
C05	1.36	1.40	1.34	1.22	1.15	1.19	1.28	0.10
C06	1.30	1.18	1.25	1.26	1.27	1.21	1.25	0.04
C07	1.50	1.50	1.40	1.50	1.50	1.40	1.47	0.05
C08	1.91	1.92	1.96	1.60	1.62	1.59	1.77	0.18
C09	1.70	1.68	1.69	1.52	1.56	1.57	1.62	0.08
C10	1.26	1.23	1.23	1.23	1.28	1.20	1.24	0.03
C11	1.51	1.53	1.43	1.55	1.53	1.52	1.51	0.04

Values of laboratory C04 were excluded from evaluation of the certified value.



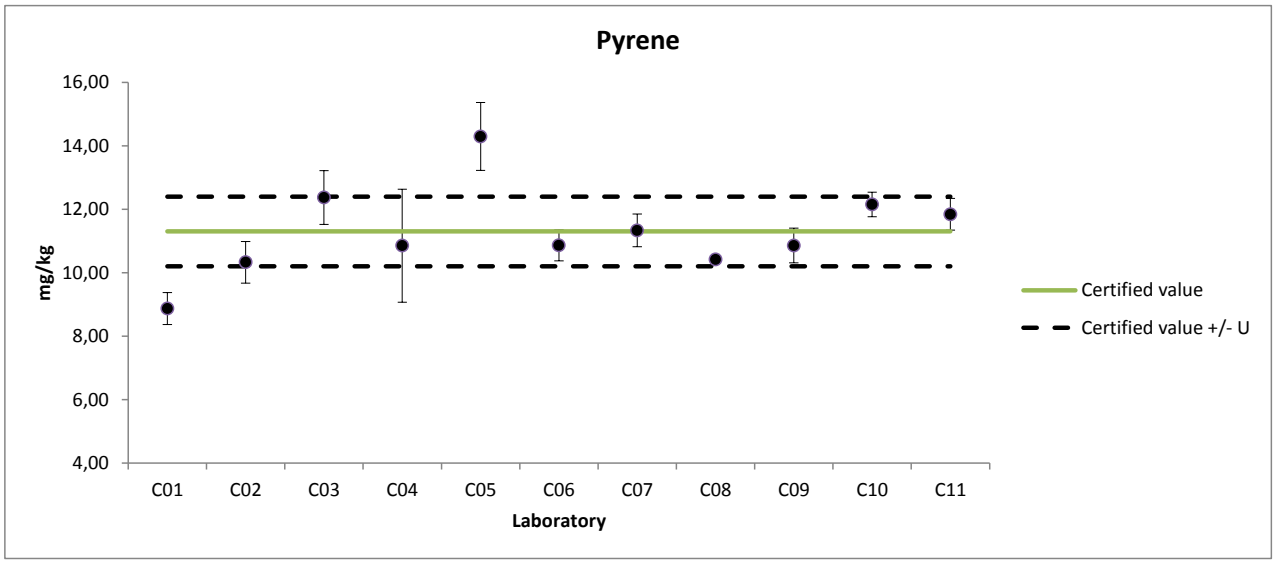
Fluoranthene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	9.67	11.27	10.90	9.66	11.09	10.37	10.49	0.71
C02	13.35	13.50	13.19	11.71	11.85	12.41	12.67	0.79
C03	13.91	14.20	15.68	16.58	14.81	15.75	15.15	1.03
C04	*12.77*	*11.99*	*17.38*	*17.73*	*18.14*	*17.54*	*15.92*	*2.77*
C05	12.41	12.37	12.83	14.15	13.72	15.01	13.41	1.06
C06	14.67	14.19	13.69	15.76	15.59	14.44	14.72	0.81
C07	15.00	14.00	15.00	15.00	14.00	14.00	14.50	0.55
C08	13.07	13.16	13.36	12.86	12.93	13.07	13.07	0.18
C09	14.89	14.55	14.49	13.59	13.70	13.63	14.14	0.57
C10	15.54	16.53	16.55	16.06	16.85	16.88	16.40	0.52
C11	15.11	14.96	14.87	15.08	14.89	15.48	15.07	0.23

Values of laboratory C04 were excluded from evaluation of the certified value.



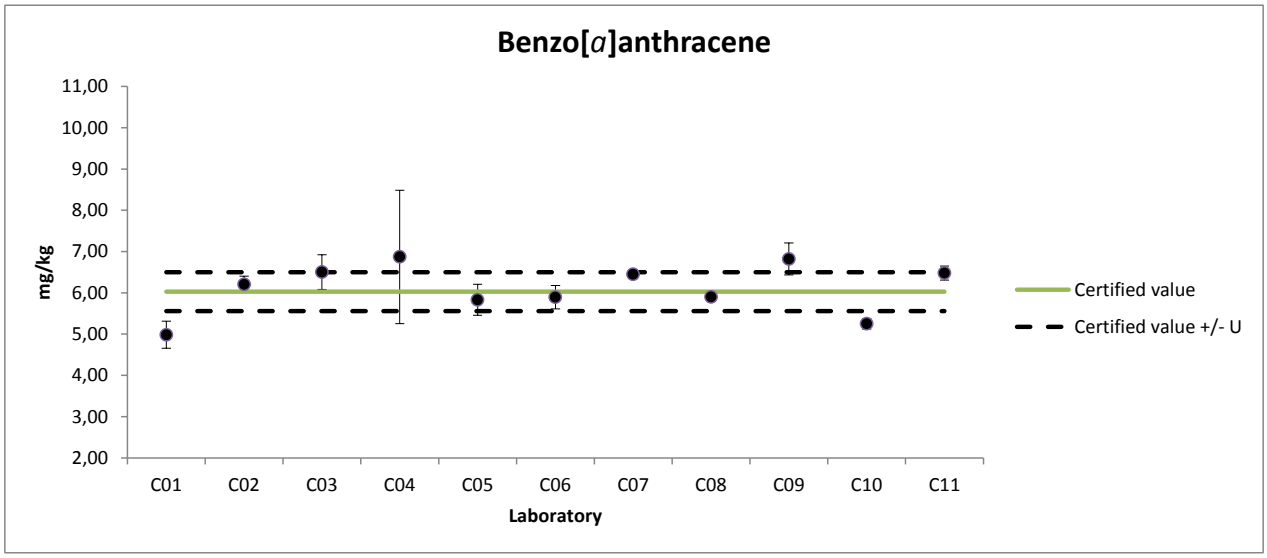
Pyrene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	8.22	8.71	9.42	8.41	9.38	9.07	8.87	0.50
C02	10.97	10.92	10.78	9.44	9.72	10.14	10.33	0.66
C03	13.42	13.15	11.58	11.94	12.73	11.40	12.37	0.85
C04	*9.84*	*7.75*	*12.25*	*11.07*	*12.40*	*11.79*	*10.85*	*1.78*
C05	13.16	13.26	13.56	15.12	15.26	15.41	14.30	1.07
C06	11.21	10.66	10.25	11.36	11.31	10.40	10.87	0.49
C07	12.00	11.00	11.00	12.00	11.00	11.00	11.33	0.52
C08	10.48	10.34	10.55	10.32	10.38	10.44	10.42	0.09
C09	11.53	11.27	11.24	10.39	10.41	10.30	10.86	0.55
C10	12.76	12.31	12.04	12.02	11.59	12.18	12.15	0.39
C11	11.91	11.47	11.49	11.97	11.47	12.75	11.84	0.50

Values of laboratory C04 were excluded from evaluation of the certified value.



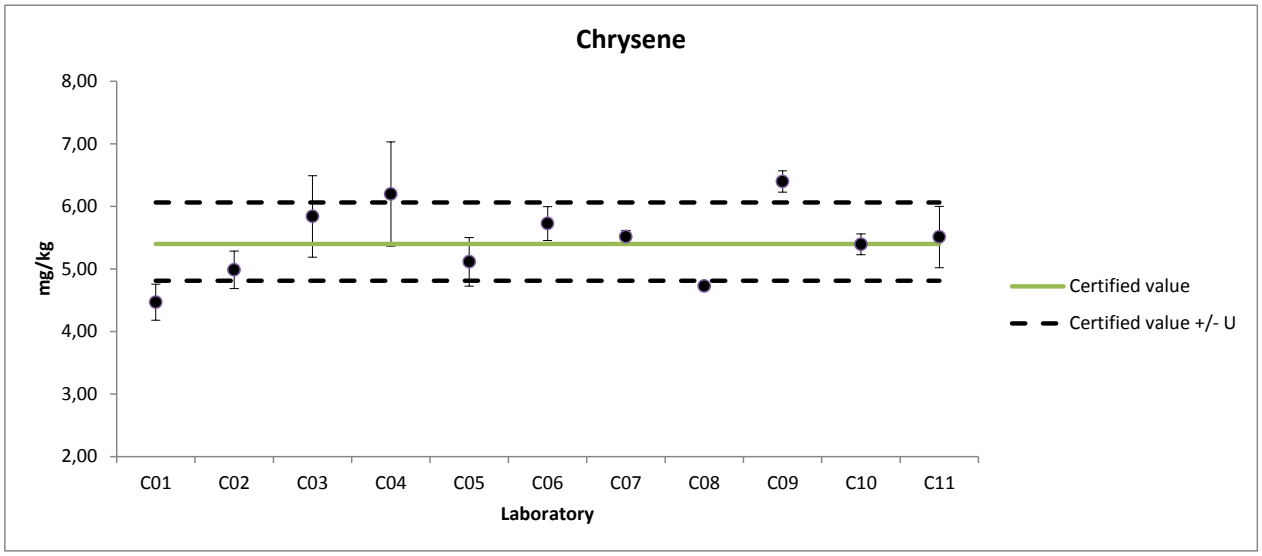
Benzo[*a*]anthracene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	4.65	5.21	5.50	4.66	5.02	4.86	4.98	0.33
C02	6.48	6.26	6.38	6.02	6.02	6.08	6.21	0.20
C03	6.91	7.08	6.39	5.93	6.33	6.38	6.50	0.42
C04	*5.50*	*4.45*	*8.07*	*6.72*	*8.03*	*8.45*	*6.87*	*1.62*
C05	5.40	5.52	5.55	6.22	6.20	6.09	5.83	0.38
C06	6.04	5.93	5.47	6.12	6.18	5.64	5.90	0.28
C07	6.40	6.30	6.40	6.50	6.60	6.50	6.45	0.10
C08	6.00	5.95	5.98	5.88	5.76	5.84	5.90	0.09
C09	6.49	6.51	6.44	7.32	7.16	7.01	6.82	0.39
C10	5.50	5.18	5.17	5.17	5.26	5.22	5.25	0.13
C11	6.46	6.67	6.36	6.39	6.28	6.69	6.48	0.17

Values of laboratory C04 were excluded from evaluation of the certified value.



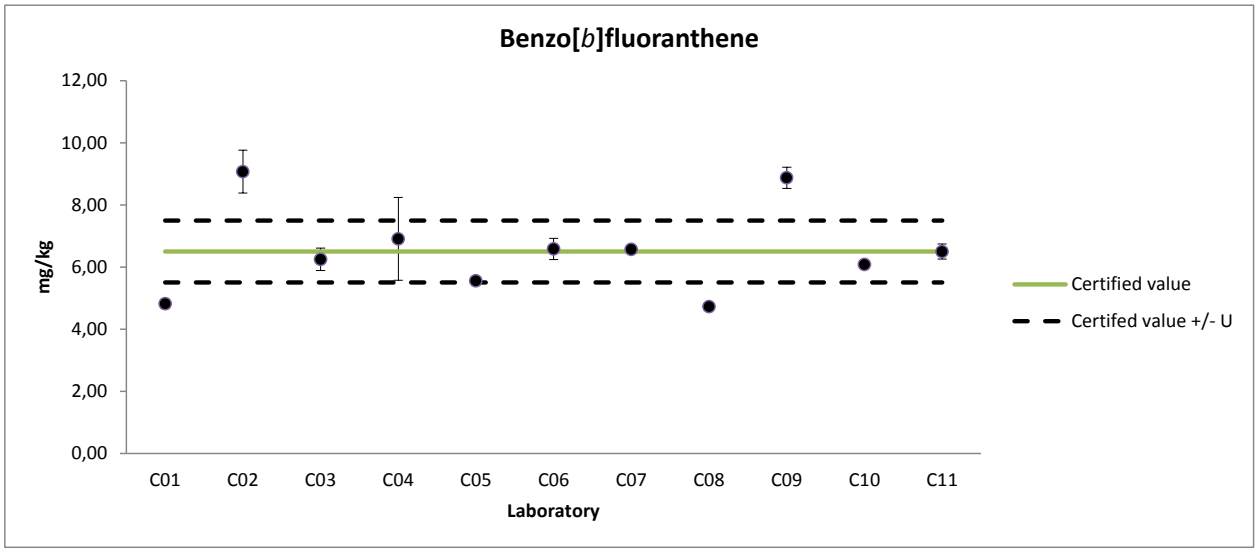
Chrysene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	4.57	4.88	4.15	4.17	4.39	4.65	4.47	0.29
C02	4.86	5.43	4.60	4.81	5.01	5.21	4.99	0.30
C03	6.42	6.83	5.76	5.14	5.40	5.48	5.84	0.65
C04	*6.09*	*6.03*	*5.29*	*7.21*	*5.40*	*7.17*	*6.20*	*0.83*
C05	4.96	5.09	4.44	5.34	5.32	5.54	5.11	0.39
C06	5.76	5.75	5.31	6.08	5.91	5.54	5.73	0.27
C07	5.50	5.50	5.40	5.50	5.70	5.50	5.52	0.10
C08	4.70	4.72	4.77	4.82	4.66	4.68	4.73	0.06
C09	6.60	6.51	6.54	6.26	6.23	6.23	6.40	0.17
C10	5.63	5.49	5.35	5.42	5.35	5.13	5.40	0.17
C11	5.53	6.29	5.80	5.27	4.86	5.33	5.51	0.49

Values of laboratory C04 were excluded from evaluation of the certified value.



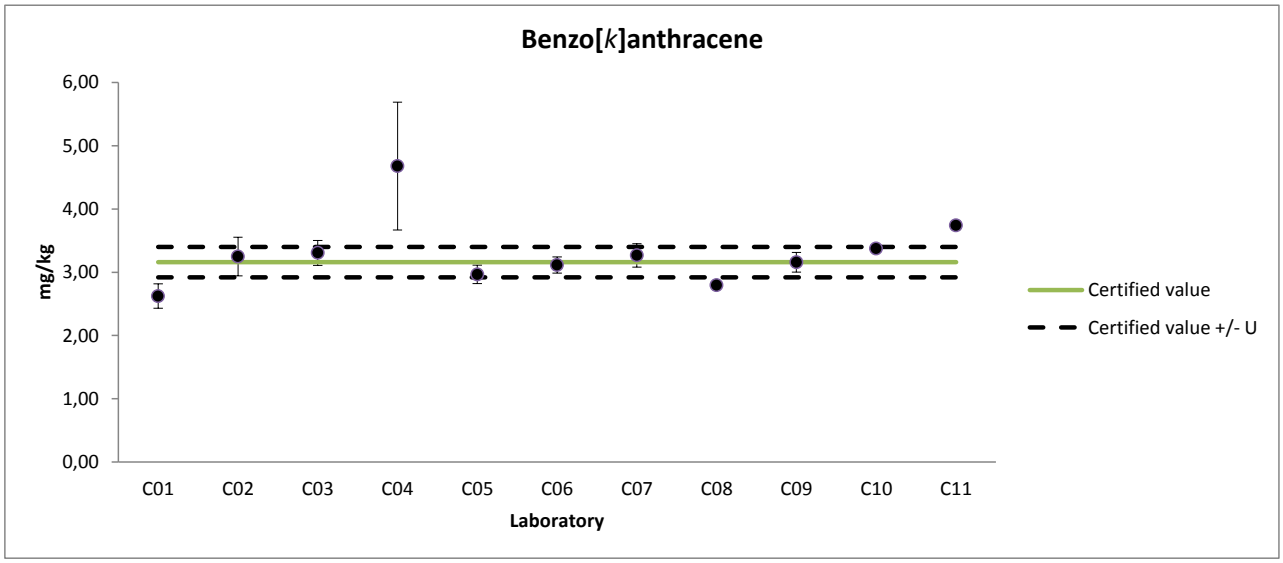
Benzo[*b*]fluoranthene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	4.72	4.89	5.04	4.63	4.88	4.74	4.82	0.15
C02	9.63	9.50	9.80	8.00	8.69	8.80	9.07	0.69
C03	6.66	6.64	6.30	6.18	5.78	5.93	6.25	0.36
C04	*5.20*	*5.20*	*8.00*	*7.53*	*7.61*	*7.91*	*6.91*	*1.33*
C05	5.40	5.65	5.75	5.60	5.45	5.49	5.56	0.13
C06	6.31	6.20	6.87	6.86	6.94	6.31	6.58	0.34
C07	6.70	6.60	6.60	6.60	6.40	6.50	6.57	0.10
C08	4.70	4.72	4.77	4.82	4.66	4.68	4.73	0.06
C09	8.60	8.53	8.57	9.28	9.19	9.05	8.87	0.34
C10	6.29	6.02	5.97	6.03	6.06	6.10	6.08	0.11
C11	6.61	6.91	6.45	6.37	6.51	6.19	6.50	0.24

Values of laboratory C04 were excluded from evaluation of the certified value.



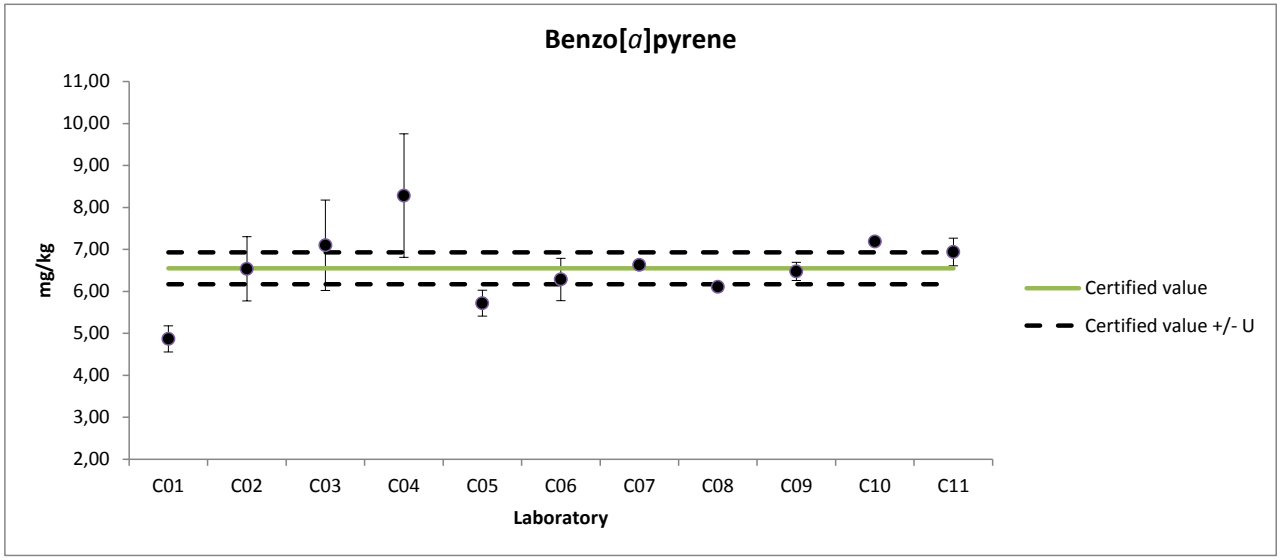
Benzo[*k*]fluoranthene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	2.42	2.75	2.92	2.45	2.68	2.54	2.62	0.19
C02	3.64	3.18	3.59	2.86	3.06	3.17	3.25	0.30
C03	3.54	3.53	3.26	3.08	3.31	3.12	3.31	0.20
C04	*4.40*	*3.45*	*4.48*	*6.54*	*4.56*	*4.62*	*4.68*	*1.01*
C05	2.77	2.84	2.93	3.17	3.05	3.04	2.97	0.15
C06	3.18	3.13	2.97	3.19	3.27	2.95	3.11	0.13
C07	3.00	3.50	3.30	3.30	3.40	3.10	3.27	0.19
C08	2.85	2.81	2.85	2.78	2.74	2.76	2.80	0.05
C09	3.22	3.12	3.44	3.10	3.04	3.03	3.16	0.16
C10	3.47	3.38	3.31	3.33	3.37	3.38	3.37	0.06
C11	3.77	3.67	3.66	3.75	3.85	3.75	3.74	0.07

Values of laboratory C04 were excluded from evaluation of the certified value.



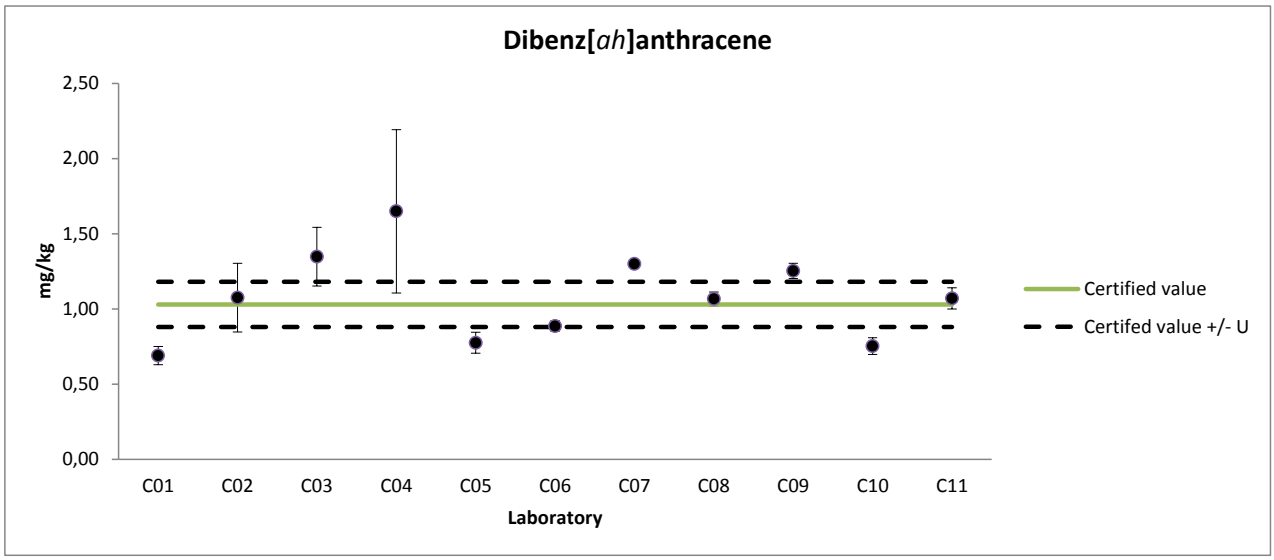
Benzo[*a*]pyrene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	*4.55*	*5.10*	*5.36*	*4.59*	*4.79*	*4.82*	*4.87*	*0.31*
C02	7.32	6.62	7.44	5.42	6.16	6.27	6.54	0.76
C03	8.43	8.54	6.48	6.33	6.51	6.31	7.10	1.08
C04	*7.57*	*6.04*	*8.14*	*9.52*	*8.22*	*10.20*	*8.28*	*1.47*
C05	5.24	5.50	5.66	6.04	5.91	5.97	5.72	0.31
C06	6.29	6.00	5.53	6.72	6.93	6.23	6.28	0.50
C07	6.70	6.60	6.60	6.70	6.60	6.60	6.63	0.05
C08	6.06	6.17	6.20	6.16	5.93	6.13	6.11	0.10
C09	6.81	6.64	6.48	6.40	6.30	6.24	6.48	0.22
C10	7.06	7.17	7.24	7.17	7.27	7.22	7.19	0.07
C11	6.51	7.30	7.11	7.26	6.66	6.80	6.94	0.33

Values of laboratories C01, C04 were excluded from evaluation of the certified value.



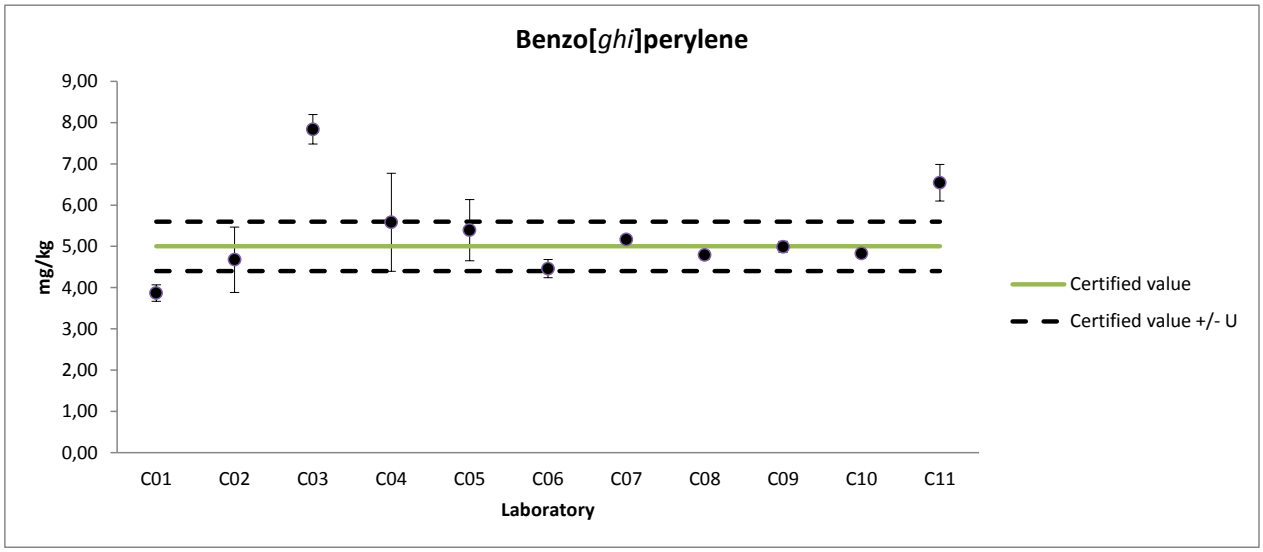
Dibenz[*ah*]anthracene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	0.66	0.75	0.61	0.66	0.77	0.70	0.69	0.06
C02	0.92	1.22	1.19	0.69	1.14	1.30	1.07	0.23
C03	1.11	1.13	1.47	1.35	1.60	1.43	1.35	0.19
C04	*1.42*	*1.17*	*1.37*	*2.53*	*1.30*	*2.12*	*1.65*	*0.54*
C05	0.73	0.77	0.89	0.70	0.75	0.81	0.78	0.07
C06	0.94	0.86	0.86	0.85	0.89	0.92	0.89	0.03
C07	1.30	1.30	1.30	1.30	1.30	1.30	1.30	0.00
C08	1.02	1.01	1.05	1.11	1.08	1.13	1.07	0.05
C09	1.22	1.21	1.20	1.29	1.28	1.32	1.25	0.05
C10	0.70	0.80	0.80	0.72	0.69	0.81	0.75	0.06
C11	1.11	1.09	1.16	1.13	0.98	1.18	1.11	0.07

Values of laboratory C04 were excluded from evaluation of the certified value.



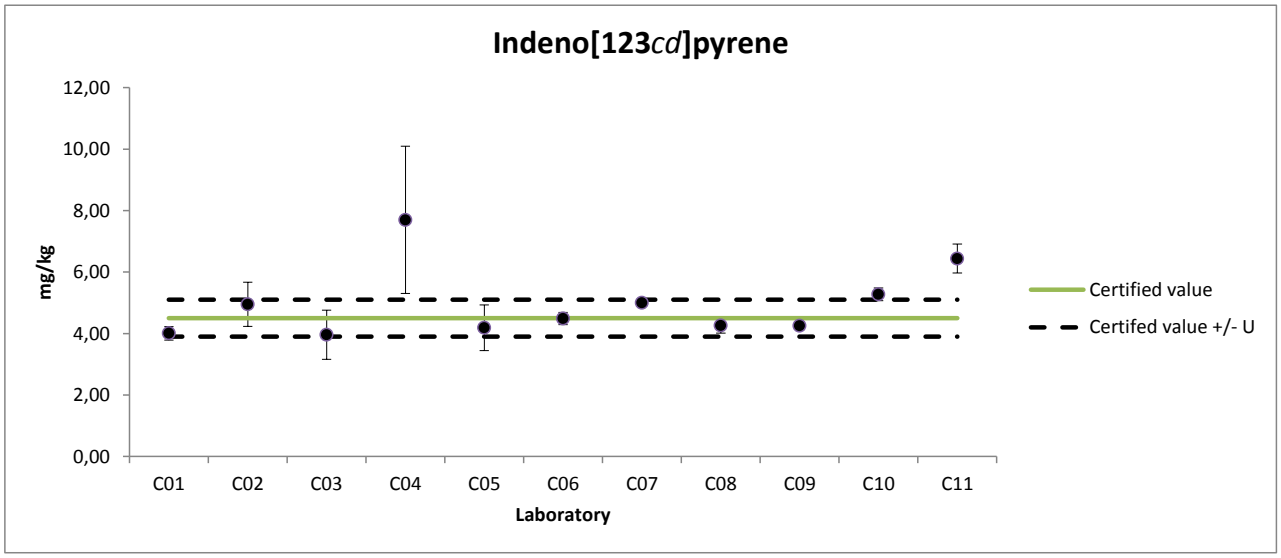
Benzo[*ghi*]perylene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	3.66	4.07	3.59	4.03	3.86	4.00	3.87	0.20
C02	4.92	5.15	5.11	3.07	4.88	4.94	4.68	0.79
C03	*7.60*	*7.37*	*8.05*	*8.27*	*8.12*	*7.61*	*7.84*	*0.36*
C04	*4.85*	*3.57*	*6.60*	*5.78*	*6.70*	*5.99*	*5.58*	*1.19*
C05	4.67	4.45	5.13	6.10	6.01	6.00	5.39	0.74
C06	4.50	4.44	4.09	4.61	4.74	4.38	4.46	0.22
C07	5.20	5.20	5.20	5.20	5.10	5.10	5.17	0.05
C08	4.71	4.66	4.75	4.90	4.80	4.94	4.79	0.11
C09	5.13	5.07	5.11	4.82	4.86	4.96	4.99	0.13
C10	4.93	4.88	4.83	4.65	4.73	4.94	4.83	0.12
C11	6.45	6.33	5.97	7.17	6.96	6.35	6.54	0.44

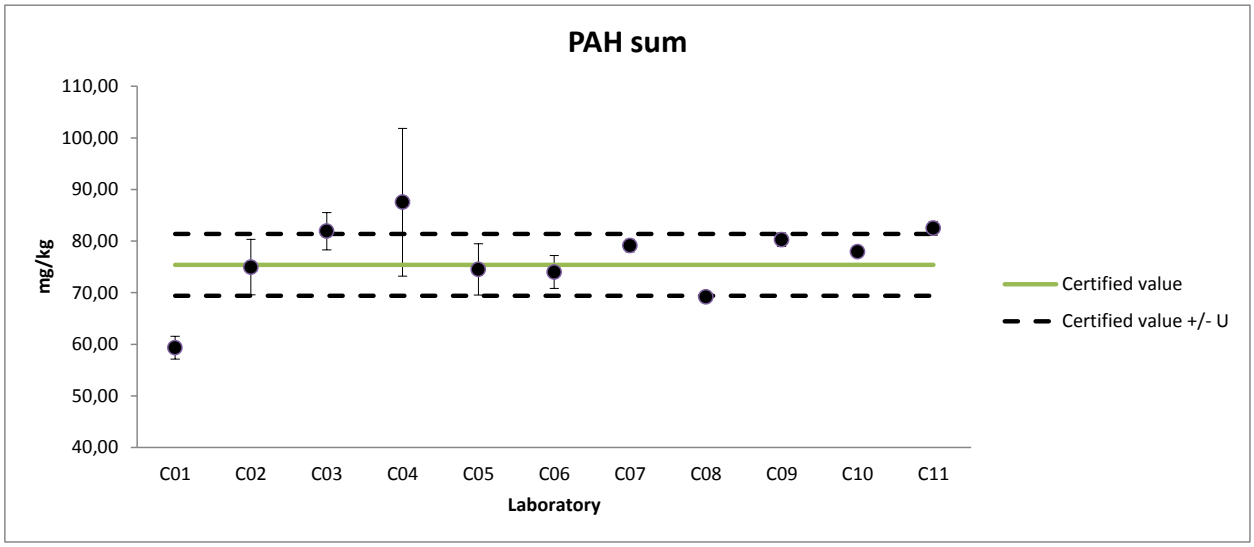
Values of laboratories C03, C04 were excluded from evaluation of the certified value.



Indeno[*123cd*]pyrene								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	3.92	4.33	3.73	3.88	4.18	4.00	4.01	0.22
C02	5.15	5.23	5.44	3.50	5.23	5.14	4.95	0.72
C03	5.08	4.90	3.44	3.45	3.47	3.41	3.96	0.80
C04	*5.81*	*4.24*	*9.70*	*7.33*	*8.53*	*10.58*	*7.70*	*2.39*
C05	3.29	3.43	3.89	4.94	4.78	4.78	4.19	0.74
C06	4.47	4.39	4.28	4.75	4.72	4.34	4.49	0.20
C07	5.00	5.00	5.00	5.10	4.90	5.00	5.00	0.06
C08	4.07	4.02	4.08	4.45	4.30	4.64	4.26	0.25
C09	4.40	4.36	4.36	4.13	4.13	4.14	4.25	0.13
C10	5.48	5.11	5.52	5.08	5.38	5.09	5.28	0.21
C11	*6.79*	*5.90*	*5.85*	*7.01*	*6.60*	*6.46*	*6.44*	*0.47*

Values of laboratories C04, C11 were excluded from evaluation of the certified value.



PAH Sum								
Laboratory	**Replicate determination (mg/kg)**						**Mean (mg/kg)**	**Standard deviation (mg/kg)**
	#1	#2	#3	#4	#5	#6		
C01	56.82	61.11	61.23	56.40	60.82	59.62	59.33	2.19
C02	79.20	78.66	79.30	65.61	72.45	74.45	74.94	5.38
C03	86.07	86.52	80.45	80.27	80.73	77.40	81.90	3.61
C04	*75.63*	*64.21*	*94.38*	*96.07*	*93.99*	*100.87*	*87.52*	*14.32*
C05	68.55	70.05	71.74	78.60	78.23	79.99	74.53	4.97
C06	74.41	72.50	70.02	77.62	77.76	71.71	74.00	3.19
C07	80.25	78.32	79.03	80.92	78.41	77.80	79.12	1.22
C08	69.26	69.16	70.17	69.01	68.23	69.27	69.18	0.62
C09	82.15	80.87	81.09	79.41	79.16	78.87	80.26	1.30
C10	78.91	78.31	78.03	76.85	77.61	77.89	77.93	0.69
C11	82.79	82.84	80.80	83.87	80.91	83.73	82.49	1.34

Values of laboratory C04 were excluded from evaluation of the certified value.