Certification Report

Certified Reference Material

BAM-B001

Polycyclic aromatic hydrocarbons in rubber toy

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Summary

This report describes the preparation, characterisation and certification of the certified reference material (CRM) BAM-B001. BAM-B001 is available as ground rubber from a commercial toy product contaminated with polycyclic aromatic hydrocarbons (PAHs). This CRM is intended to be used for performance control and validation of analytical methods for the determination of PAH in rubber toys. BAM-B001 may also be applicable for other similar consumer products.

Certified Values

Measurand [1)]	Mass fraction [2)] in mg kg^{-1}	Uncertainty [3)] in mg kg^{-1}
Fluorene	1.71	0.22
Phenanthrene	15.4	1.2
Anthracene	2.9	1.1
Fluoranthene	4.3	0.5
Pyrene	11.4	1.1
Benz[*a*]anthracene	2.17	0.22
Chrysene	2.08	0.15
Benzo[*b*]fluoranthene	0.57	0.05
Benzo[*k*]fluoranthene	0.213	0.022
Benzo[*j*]fluoranthene	0.40	0.04
Benzo[*e*]pyrene	1.21	0.16
Benzo[*a*]pyrene	1.41	0.10
Indeno[1,2,3-*cd*]pyrene	0.28	0.06
Benzo[*ghi*]perylene	1.43	0.09

1) PAH congener determined using sample preparation (extraction, clean-up), gas chromatographic separation and mass spectrometric detection applying stable isotopic dilution analysis according to AfPS GS 2019:01 PAK method as specified in Section 3 of this certification report.

2) Unweighted mean value of 3 BAM workplace mean values (total of 98 individual results)

3) Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95%, as defined in the Guide to the expression of uncertainty in measurement (GUM), ISO/IEC Guide 98-3 (2008).

Values for Information (not certified)

Measurand [1)]	Mass fraction [2)] in mg kg^{-1}	Uncertainty [3)] in mg kg^{-1}
Naphthalene	0.09	0.08
Acenaphthylene	1.6	1.6
Acenaphthene	0.63	0.28
Dibenz[*a,h*]anthracene	0.118	0.020

1, 2, 3) See description in table above

Content

List of abbreviations

(if not explained elsewhere)

AfPS	Ausschuss für Produktsicherheit
ANOVA	Analysis of Variance
BVL	Bundesamt für Verbraucherschutz und Lebensmittelsicherheit
CCQM	Consultative Committee on the Quantity of Material
CRM	Certified reference material
DAD	Diode array detection
EI	Electron impact
FLD	Fluorescence detection
GC	Gas chromatography
HPLC	High performance liquid chromatography
ID	Inner diameter
ILC	Interlaboratory comparison study
ISO	International Organization of Standardization
ISTD	Internal standard
k	Coverage factor
LFGB	Lebensmittel- und Futtermittelgesetzbuch
LOQ	Limit of quantification
MS	Mass spectrometry
PAH	Polycyclic aromatic hydrocarbon
PTFE	Polytetrafluoroethylene
SI	International System of Units
SIDA	Stable isotope dilution analysis
SIM	Single Ion Monitoring
SPE	Solid phase extraction

1. Introduction

1.1 Need of reference materials for PAHs in consumer products

Environmental protection, consumers' health as well as food and product safety have gained an increased importance in the last decade. In 2019, imported toys to Germany accounted for over 2.4 billion EUR, a large part of which originated from Asia, especially the People's Republic of China. According to the Rapid Alert System of the European Union most alerts were issued within the toy product category, with chemical risks to health identified as the second highest cause for notification.

Monitoring the chemical composition of toys is therefore a pivotal process in ensuring overall toy safety. Exposing humans to polycyclic aromatic hydrocarbons (PAHs), which can be found in plastic and rubber parts of toys, creates potential health risks. Toddlers and young children constitute a high-risk group due to their mouthing behavior which allows PAHs to enter their body much more easily. Thus, the mass fractions of certain PAHs are restricted in Commission Regulation (EU) No 1272/2013 [1] amending Annex XVII to the REACH-Regulation 1907/2006 including consumer products and toys.

PAHs belong to the priority organic pollutants in environmental matrices as well as in food and consumer products. PAHs can be found in plastic and rubber parts of a wide range of consumer articles including toys. They are present as impurities in some of the raw materials used in the production of such articles, particularly in extender oils and in carbon black. Due to PAHs' negative health effects (e.g. carcinogenic), several standard methods for PAH determination have been developed worldwide. In Germany, the method AfPS GS 2019:01 PAK [2] was developed and validated to control PAHs in consumer/toy products based on gas-chromatography mass-spectrometry (GC-MS). AfPS is applied for PAH testing of consumer products to award the GS mark according to the German Product Safety Law (ProdSG), § 21, Abs. 1 Nr. 3.

Although maximum levels are in force for PAHs, there is no certified reference material (CRM) for the analysis of PAHs in rubber toys available to date. Therefore, reference materials (RM) and especially CRM are required to verify the accuracy of analytical measurements. Thus, a new CRM for PAHs in rubber toy (BAM-B001) was developed at BAM. The produced BAM-B001 is intended to be used for performance control and validation of analytical methods for the determination of PAHs in rubber toys and similar consumer products.

1.2 Strategy of the certification project

Because fortification of matrices with the respective analytes is generally avoided whenever possible, a real-life material, representative for a toy product with regard to PAH contents in the range of the EU maximum level (0.5 mg kg^{-1} for each regulated PAH congener) and real congener pattern was aimed to produce as CRM. Although HPLC-DAD/FLD and GC-MS are equally used for routine PAH determination of environmental samples, GC-MS (using isotopically labelled internal standards) is prescribed for PAHs determination in consumer products according the German AfPS method. Therefore, the AfPS method had to be applied for the certification of the PAH mass fractions of reference material BAM-B001.

According to Commission Regulation (EU) No 1272/2013, a maximum level of 0.5 mg kg^{-1} is in force for each of the following eight PAH congeners: Benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene and dibenz[*a,h*]anthracene. Since July 1st 2020, the German GS mark awarding according to AfPS (2019) requires the determination of seven additional PAH congeners (15-PAH list): naphthalene, phenanthrene, anthracene, pyrene, fluoranthene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene. Until July 1st 2020, the AfPS method (2014) was in force which addressed three additional PAH congeners (18-PAH list): Acenaphthylene, acenaphthene and fluorene. In order to achieve the widest possible applicability, BAM-B001 should be characterised with respect to the 18-PAH list.

Certification of BAM-B001 was planned based on an in-house study at BAM with the participation of two independent workplaces. In order to support BAM's in-house certification strategy, the candidate

reference material should additionally be tested in two interlaboratory comparison studies (ILC). One ILC (ILC-1) with > 50 laboratories from China and Germany was focussed on the eight REACH-regulated PAH congeners. Another ILC (ILC-2) was conducted within the German working group "Consumer products" of BVL §64 LFGB. This certification report describes the preparation, characterisation and certification of reference material BAM-B001. Certification of BAM-B001 was carried out based on ISO 17034 [3] and the relevant ISO-Guides [4, 5].

2. Production of the candidate material

2.1 Procurement and preparation

In a survey of different plastic and rubber toys from German retail markets, certain rubber balls were identified containing relevant PAH contents. After selecting these balls as suitable candidate material, a total of 86 balls (diameter: 11 cm, 166 g) corresponding to about 14.3 kg was procured in various toy stores in Berlin/Germany. Subsequent analytical tests at BAM confirmed, that all procured balls showed similar PAH contents. The following procedure was applied for the preparation of the candidate material (see also Figure 1).

- manual cutting each ball into 32 pieces
- cryo-milling (liquid N_2) to < 8 mm using a cutting mill
- cryo-milling (liquid N_2) to < 2 mm using a centrifugal mill
- sieving the < 2 mm fraction (2 mm sieve) for fabric removal ("sieving 1", Fig. 1)
- cryo-milling (liquid N_2) to < 500 µm using a centrifugal mill
- sieving the < 500 µm fraction (500 µm sieve) for fabric removal ("sieving 2", Fig. 1)
- homogenization of the < 500 µm sieve fraction with drum hoop mixer for 18 hours

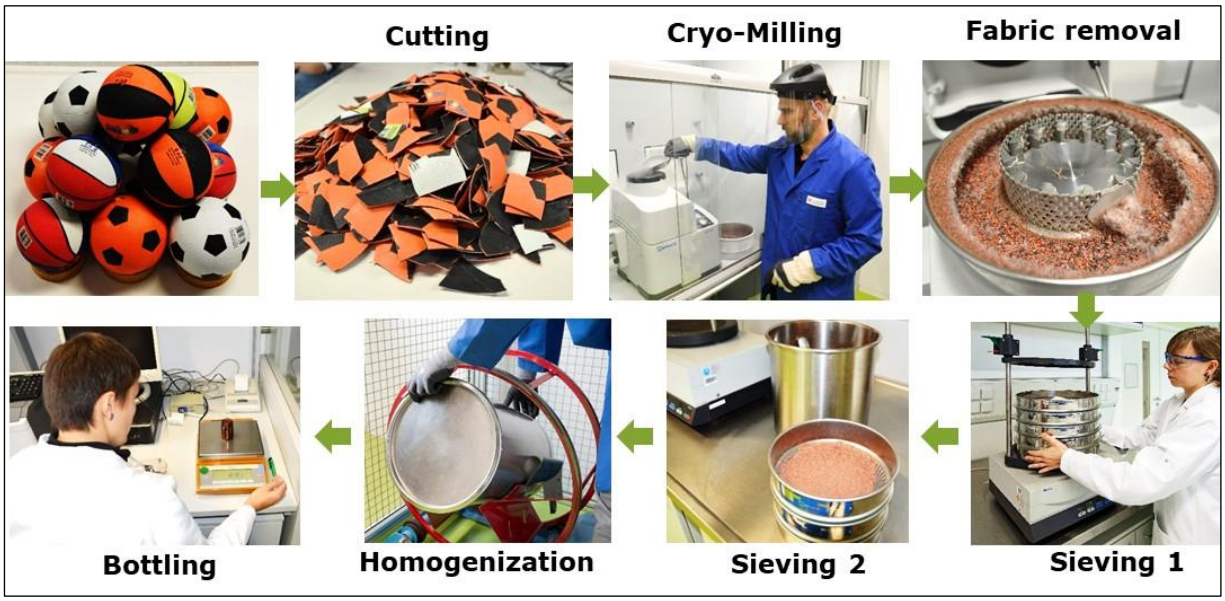

Fig. 1: Preparation of the candidate material BAM-B001 for PAHs in rubber toy

2.2 Bottling of the candidate material

After homogenisation by drum hoop mixing, a total of 9265 g of the candidate material was obtained. In a first step, 115 amber glass bottles were manually filled (12 g each). These samples were intended for the German/Chinese ILC (ILC-1). Afterwards, the remaining material (7882 g) was used to produce 778 units of BAM-B001. The material was bottled into 50 mL amber screw-capped glass bottles containing (10.1 ± 0.1) g of rubber each and numbered in the order of leaving the manual bottling process. The screw caps equipped with PTFE inserts were tightly closed. All units were stored at -20 °C directly after bottling and will be kept in the freezer until dispatch from BAM.

3. Analytical method

Sample preparation was done by using the official AfPS GS 2019:01 PAK method [2]. For in-house certification measurements, an additional sample preparation method was applied, which was successfully used in the CCQM-K146 trial for "Benzo[*a*]pyrene in olive oil". The applied sample preparation techniques of both workplaces (operator 1 and 2) are in detail:

Sample preparation of Operator 1 acc. to AfPS method: All steps of sample preparation were gravimetrically controlled even if volumes are indicated below. 0.5 g of the rubber toy sample were weighed into a 40 mL glass vial with screw cap (PTFE inlet). After adding 20 mL of toluene, the sample was extracted by ultrasonication at 60 °C for 1 hour. When the extract has reached ambient temperature, an aliquot of 0.5 mL extract was transferred into a 1.5 mL HPLC-vial. After adding 100 µL of ISTD-solution (deuterated PAH-mix) to the aliquot, the sample was analysed using *GC-MS 1* system.

Sample preparation of Operator 2 acc. to BAM's in-house method: A sample amount of 0.5 g was weighed into a 22 mL glass vial with screw cap (PTFE inlet). After adding 30 µL of ISTD-solution (deuterated PAH-mix) and 20 mL of toluene, the sample was extracted by ultrasonication at 60 °C for 1 hour. The extract was separated from solid particles by filtration (paper). Glass vial and filter were rinsed with 3x5 mL of toluene and combined with the extract. The latter was evaporated in a Kuderna-Danish flask at 50 °C in a nitrogen stream almost to dryness. The residue was re-dissolved in 1 mL of cyclohexane/ethyl acetate (1:1) and transferred to a 5 mL flask. After rinsing the Kuderna-Danish flask with 3x1 mL of cyclohexane/ethyl acetate (1:1) into the 5 mL flask and filling-up the flask to the mark, the turbid extract was filtered using a 0.22 µm PTFE-filter. A volume of 4 mL of the clear extract was injected into a GPC system (660 x 40 mm, ID = 25 mm; Bio-Beads S-X3, 200-400). The PAH fraction was selected and transferred into a Kuderna-Danish flask and evaporated at 50 °C and 300 mbar almost to dryness. Subsequent evaporation to dryness was completed in a gentle stream of nitrogen. The yellow residue was re-dissolved in 1 mL of petroleum ether and purified by applying this solution to a SPE-cartridge filled with 2 g aluminium oxide (deactivated with 11% water) covered by 0.5 g sodium sulfate. The Kuderna-Danish flask was rinsed with 3x5 mL of petroleum ether, also applied to the SPE-cartridge. The PAHs were eluted from the SPE-cartridge by addition of 10 mL of petroleum ether onto the SPE-cartridge. After adding 1 mL of toluene to the petroleum ether eluate, the solution was evaporated at ambient temperature almost to dryness and adjusted with toluene to 1 mL. The finally prepared sample was transferred to a GC-vial and analysed using *GC-MS 2* system.

GC-MS analysis: Analyses for material characterisation (homogeneity, stability, certification) were conducted using *GC-MS 1* system (Tab. 1). For certification measurements, *GC-MS 2* system was additionally used (Tab. 1).

Tab. 1: GC-MS instrumental parameters used for PAH analysis of BAM-B001

Instr. parameter	***GC-MS 1* system**	***GC-MS 2* system**
GC system	6890N (Agilent)	7890A (Agilent)
Column	Select PAH (Agilent)	DB-17ms (Agilent)
Column dimensions	30 m x 0.25 mm x 0.15 µm ID	60 m x 0.25 mm x 0.25µm ID
Oven program	70°C (1 min) → (85°C/min) 180°C → (3°C/min) 230°C (7 min) → (28°C/min) 280°C (10 min) → (14°C/min) 350°C (3 min)	80°C (1 min) → (5°C/min) 320°C (33 min)
Carrier gas	He 5.0 (2 mL/min)	He 5.0 (2 mL/min)
Injection	5 µL (LVI)	1 µL (splitless)
MS system	MSD 5975B inert XL (Agilent)	MSD 5975C inert XL (Agilent)
Ionisation	70 eV (EI)	70 eV (EI)
Acquisition mode	SIM	SIM

Native PAH analytes and deuterated ISTD were recorded in SIM (single ion monitoring) mode to increase measurement sensitivity and to reduce background noise. For GC-MS parameter see Table 2.

Tab. 2: GC-MS parameter for PAH measurements of BAM-B001. *GC-MS 1* was used for all characterisation analyses, *GC-MS 2* was additionally used for certification measurements of BAM-B001.

Compound	Sum formula	SIM (m/z)	Retention time (min)		Quantified using internal standard
			GC-MS 1	*GC-MS 2*	
Naphthalene	$C_{10}H_8$	128.1	2.97	14.52	D_8-Naphthalene
Acenaphthylene	$C_{12}H_8$	152.1	4.11	22.56	D_8-Acenaphthylene
Acenaphthene	$C_{12}H_{10}$	*)	4.23	23.18	D_{10}-Acenaphthene
Fluorene	$C_{13}H_{10}$	166.1	5.01	25.61	D_{10}-Fluorene
Phenanthrene	$C_{14}H_{10}$	178.1	7.73	30.99	D_{10}-Phenanthrene
Anthracene	$C_{14}H_{10}$	178.1	7.88	31.14	D_{10}-Anthracene
Fluoranthene	$C_{16}H_{10}$	202.1	13.41	37.16	D_{10}-Fluoranthene
Pyrene	$C_{16}H_{10}$	202.1	15.01	38.61	D_{10}-Pyrene
Benz[*a*]anthracene	$C_{18}H_{12}$	228.1	24.56	44.54	D_{12}-Benz[*a*]anthracene
Chrysene	$C_{18}H_{12}$	228.1	25.41	44.91	D_{12}-Chrysene
Benzo[*b*]fluoranthene	$C_{20}H_{12}$	252.1	30.60	49.81	D_{12}-Benzo[*b*]fluoranthene
Benzo[*k*]fluoranthene	$C_{20}H_{12}$	252.1	30.71	49.93	D_{12}-Benzo[*k*]fluoranthene
Benzo[*j*]fluoranthene	$C_{20}H_{12}$	252.1	30.78	51.00	D_{12}-Benzo[*k*]fluoranthene
Benzo[*e*]pyrene	$C_{20}H_{12}$	252.1	32.37	52.72	D_{12}-Benzo[*a*]pyrene
Benzo[*a*]pyrene	$C_{20}H_{12}$	252.1	32.68	52.01	D_{12}-Benzo[*a*]pyrene
Indeno[1,2,3-*cd*]pyrene	$C_{22}H_{12}$	276.1	39.84	62.35	D_{12}-Indeno[1,2,3-*cd*]pyrene
Dibenz[*a,h*]anthracene	$C_{22}H_{14}$	278.1	39.93	59.30	D_{14}-Dibenz[*a,h*]anthracene
Benzo[*ghi*]perylene	$C_{22}H_{12}$	276.1	41.00	62.35	D_{12}-Benzo[*ghi*]perylene
D_8-Naphthalene	$C_{10}D_8$	136.1	2.95	14.42	---
D_8-Acenaphthylene	$C_{12}D_8$	160.1	4.10	22.48	---
D_{10}-Acenaphthene	$C_{12}D_{10}$	164.2	4.22	23.00	---
D_{10}-Fluorene	$C_{13}D_{10}$	176.2	4.96	25.43	---
D_{10}-Phenanthrene	$C_{14}D_{10}$	188.2	7.64	30.85	---
D_{10}-Anthracene	$C_{14}D_{10}$	188.2	7.80	31.03	---
D_{10}-Fluoranthene	$C_{16}D_{10}$	212.2	13.29	37.05	---
D_{10}-Pyrene	$C_{16}D_{10}$	212.2	14.89	38.51	---
D_{12}-Benz[*a*]anthracene	$C_{18}D_{12}$	240.2	34.27	44.41	---
D_{12}-Chrysene	$C_{18}D_{12}$	240.2	25.06	44.81	---
D_{12}-Benzo[*b*]fluoranthene	$C_{20}D_{12}$	264.2	30.47	49.69	---
D_{12}-Benzo[*k*]fluoranthene	$C_{20}D_{12}$	264.2	30.60	49.81	---
D_{12}-Benzo[*a*]pyrene	$C_{20}D_{12}$	264.2	32.52	51.86	---
D_{12}-Indeno[1,2,3-*cd*]pyrene	$C_{22}D_{12}$	288.2	39.73	59.10	---
D_{14}-Dibenz[*a,h*]anthracene	$C_{22}D_{14}$	292.2	39.75	58.98	---
D_{12}-Benzo[*ghi*]perylene	$C_{22}D_{12}$	288.2	40.91	62.06	---

*) m/z = 153 (*GC-MS 1*); m/z = 154 (*GC-MS 2*)

Calibration and Quantification

PAHs were quantified using stable isotope dilution analysis (SIDA) GC-MS, defined as primary ratio method. Most of the PAH analytes were quantified using the corresponding deuterated congener as internal standard (ISTD). Where not possible, the respective ISTD is indicated in Table 2.

For native PAH calibration, the certified standard SRM 2260a (NIST, Gaithersburg, USA) was used containing all relevant PAHs dissolved in toluene. The deuterated internal standards were provided via the PAH-Mix 9 (Dr. Ehrenstorfer GmbH, Germany) dissolved in toluene. Nine-point (*GC-MS 1*) and twelve-point calibrations (*GC-MS 2*) were used for quantification of the measured area ratios. The calibration functions for all PAH analytes were assumed to be linear obtained by regression analysis.

4. Homogeneity study

The analytical method employed for this study was used as described in Section 3 (Operator 1, *GC-MS 1* system). The sample intake for each analysis was 0.5 g and is therefore recommended as minimum sample intake. Since the pre-homogeneity test for the German/Chinese ILC was successful (10 out of 115 bottles tested), a similar result could be expected for this homogeneity study. Twelve units were selected equidistantly from the produced batch of the 778 units numbered in the order of bottling. The selected units were analysed in quadruplet each. All 12 units were extracted under repeatability conditions on one single day (i.e. 12 x 4 = 48 extractions). All extracts were analysed in randomised manner under repeatability conditions in such a way that all 48 extracts were quantified against one calibration. The measurements showed no trend, neither regarding the filling/bottling order nor regarding the GC-MS measurement sequence order. All measurement results of the homogeneity study are summarised in Annex A. Table 3 contains the results of the analysis of variance (ANOVA) together with the estimations of the contributions due to the between-bottle inhomogeneity (u_{bb}).

Tab. 3: Analysis of variance (ANOVA) and estimates for uncertainty contribution due to homogeneity for candidate material BAM-B001

PAH congener	**Mean**[a] mg kg^{-1}	**MS**$_{between}$[b] mg^2 kg^{-2}	**MS**$_{within}$[c] mg^2 kg^{-2}	**F**$_{obs}$[d]	**F**$_{crit}$[d]	**u**$_{bb}$[e] mg kg^{-1}	**u**$_{bb,r}$[f]
Naphthalene	0.0639	0.00001	0.00001	0.8776	2.0666	0	0
Acenaphthylene	0.9647	0.00399	0.00707	0.5642	2.0666	0	0
Acenaphthene	0.7890	0.00226	0.00263	0.8600	2.0666	0	0
Fluorene	1.6892	0.00948	0.00381	2.4846	2.0666	0.03763	0.02228
Phenanthrene	15.8744	0.15350	0.10296	1.4909	2.0666	0.11240	0.00708
Anthracene	2.5201	0.01065	0.01071	0.9947	2.0666	0	0
Fluoranthene	4.5275	0.01136	0.00757	1.5009	2.0666	0.03079	0.00680
Pyrene	11.9476	0.06998	0.05639	1.2409	2.0666	0.05827	0.00488
Benz[*a*]anthracene	2.3173	0.00181	0.00135	1.3381	2.0666	0.01070	0.00462
Chrysene	2.1127	0.00263	0.00181	1.4580	2.0666	0.01438	0.00681
Benzo[*b*]fluoranthene	0.5988	0.00013	0.00013	1.0027	2.0666	0.00029	0.00049
Benzo[*k*]fluoranthene	0.2146	0.00019	0.00033	0.5924	2.0666	0	0
Benzo[*j*]fluoranthene	0.3954	0.00010	0.00016	0.5888	2.0666	0	0
Benzo[*e*]pyrene	1.3079	0.00035	0.00061	0.5779	2.0666	0	0
Benzo[*a*]pyrene	1.4237	0.00037	0.00074	0.4980	2.0666	0	0
Indeno[1,2,3-*cd*]pyrene	0.2728	0.00018	0.00022	0.8407	2.0666	0	0
Dibenz[*a,h*]anthracene	0.1355	0.00041	0.00041	0.9903	2.0666	0	0
Benzo[*ghi*]perylene	1.4340	0.00072	0.00086	0.8402	2.0666	0	0

[a] Mean of the homogeneity study (= mean of bottle means)
[b] Mean of squared deviation between units (from 1-way ANOVA)
[c] Mean of squared deviation within units (from 1-way ANOVA)
[d] Observed F-value (= $MS_{between}/MS_{within}$) and critical F-value (from F-value table; significance level α, α=0.05)
[e] Standard uncertainty between the units: Estimate of inhomogeneity contribution to the total uncertainty
[f] Relative standard uncertainty between the units (u_{bb} / mean of homogeneity study)

The estimates of the inhomogeneity contributions u_{bb} were calculated according to ISO Guide 35 [5]:

$$u_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \qquad \textbf{(1)}$$

n = number of replicate determinations for each unit (n = 4)

According to ISO Guide 35, Equation 1 does not apply if MS_{within} is larger than $MS_{between}$, i.e. the observed F-value is < 1. In this case the uncertainty contribution is set to zero as done for several PAH congeners (Tab. 3). There are three main reasons for this effect (F-value < 1): *i*) a highly homogenous distribution of PAH contents between bottles; *ii*) an elevated inhomogeneity of PAH within bottles (at 0.5 g sample intake) and/or *iii*) a high measurement uncertainty. The latter is rather unlikely due to the use of SIDA GC-MS method. An elevated within-bottle inhomogeneity caused be a low sample intake cannot be completely excluded. On the other hand, a satisfactory repeatability (1.3 - 3.4 %) for PAH contents in a 2 mg/kg range (fluorene, anthracene, benz[*a*]anthracene, chrysene) was observed. Is should be kept in mind that a sample intake of 0.5 g is prescribed according to AfPS GS 2019:01 PAK method [2] and further milling the particles lower than 500 µm was technically not possible due to the temperature sensitive rubber matrix (even with cryo-milling). In summary, the results of the study indicate that the material is sufficiently homogeneous for its intended use.

5. Stability monitoring

5.1 Initial stability study

Experience with temperature-driven deterioration of PAHs exist for various matrices when PAHs are mainly adsorbed on the particle surface (or pores) of soils, sediment or wood. There are no experiences regarding stability of PAHs embedded in a material such as rubber. Selected units of the candidate material were submitted to an isochronous accelerated ageing [6] at temperatures between +4 °C and +60 °C over periods of 1 to 12 months as shown in Table 4. 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 the method described in Section 3 (Operator 1, *GC-MS 1* system) was employed.

Tab. 4: Accelerated ageing of BAM-B001: Exposition temperatures and time periods are displayed for selected units (bottle numbers)

Ageing time (months)	+4 °C	+23 °C	+40 °C	+60 °C	Remark
1	022	091	069	100	*Initial short-term study (for 8 REACH regulated PAH + Indeno[1,2,3-cd]pyrene + Benzo[ghi]perylene)*
2	054	099	048	013	
3	006	037	095	085	
6	093	114	101	---	*Initial long-term study (for all 18 PAHs)*
9	112	103	092	---	
12	105	096	116	---	
12	029 / 076				*Reference samples (-20 °C)*
24	023	---	---	---	*post certification monitoring (+4 °C and samples -20 °C)*
36	055	---	---	---	
48	007	---	---	---	
60	094	---	---	---	

For stability data evaluation a kinetic approach exists [7], which was successfully employed for a variety of organic compounds in food and environmental matrices in the past: From semi-logarithmic plots of measured single values over time, effective deterioration rates k_{eff} are tested against an *Arrhenius* model describing the temperature dependence of the deterioration rates. However, this model failed when the PAH deterioration in the rubber toy material was evaluated because very high recoveries of the PAH congeners were obtained after temperature-dependent ageing over 12 months (Tab. 5).

Tab. 5: Mean recoveries (± standard deviation) of PAHs in rubber toy (BAM-B001) after 12 months at different storage temperatures

PAH congener	Recovery (%)				Remark
	+4 °C	+23 °C	+40 °C	+60 °C	
Naphthalene	100.7 ± 6.8	98.4 ± 6.3	108.7 ± 8.5	---	Long-term study
Acenaphthylene	109.2 ± 5.5	108.8 ± 4.3	99.4 ± 4.9	---	Long-term study
Acenaphthene	82.5 ± 43.3	100.7 ± 33.9	105.6 ± 22.8	---	Long-term study
Fluorene	104.4 ± 2.1	105.1 ± 1.9	104.0 ± 2.6	---	Long-term study
Phenanthrene	100.4 ± 0.9	100.5 ± 0.8	99.8 ± 1.2	---	Long-term study
Anthracene	102.2 ± 1.2	101.7 ± 1.2	100.0 ± 0.9	---	Long-term study
Fluoranthene	100.4 ± 0.8	100.7 ± 0.8	100.4 ± 0.5	---	Long-term study
Pyrene	100.0 ± 0.7	100.4 ± 0.8	99.7 ± 0.5	---	Long-term study
Benz[*a*]anthracene	99.1 ± 2.2	99.9 ± 1.6	99.3 ± 1.8	99.3 ± 1.5	Short- and long-term
Chrysene	99.5 ± 1.7	100.4 ± 2.3	99.3 ± 1.8	98.7 ± 3.0	Short- and long-term
Benzo[*b*]fluoranthene	98.6 ± 2.0	98.8 ± 1.2	98.5 ± 2.0	98.7 ± 2.7	Short- and long-term
Benzo[*k*]fluoranthene	100.1 ± 3.1	99.3 ± 3.0	100.0 ± 3.8	99.0 ± 3.6	Short- and long-term
Benzo[*j*]fluoranthene	104.2 ± 2.9	102.7 ± 3.7	102.6 ± 2.1	101.3 ± 1.9	Short- and long-term
Benzo[*e*]pyrene	99.5 ± 1.8	99.9 ± 1.6	99.3 ± 1.7	99.0 ± 1.8	Short- and long-term
Benzo[*a*]pyrene	99.8 ± 1.9	101.2 ± 2.0	99.7 ± 1.8	100.9 ± 3.6	Short- and long-term
Indeno[1,2,3-*cd*]pyrene	100.6 ± 6.7	103.3 ± 8.0	102.2 ± 8.9	107.0 ± 8.6	Short- and long-term
Dibenz[*a,h*]anthracene	96.5 ± 5.0	96.8 ± 5.0	97.0 ± 6.2	99.1 ± 4.0	Short- and long-term
Benzo[*ghi*]perylene	100.4 ± 2.1	100.7 ± 2.1	100.7 ± 1.4	99.2 ± 1.7	Short- and long-term

Because no trend of the PAH values was observed over storage time, the mean of the following values was calculated and given in Table 5 for each temperature and each PAH congener: 9 values from long-term study (3 time periods 6/9/12 months x 3 replicates per time period), and for the 10 indicated PAH congeners additionally 9 values from short-term study (3 time periods 1/2/3 months x 3 replicates per time period).

As a conclusion from the initial stability testing, storage temperatures of -20 °C, +4°C and even room temperature are sufficient for a desirable minimum shelf life of 5 years. For this reason, an uncertainty contribution due to long-term (in)stability was not considered. Exposure to temperatures higher than room temperature may eventually reduce the time of validity of BAM-B001 especially for low molecular PAH congeners. Therefore, a common user-end expiry date of two years after delivery from storage is established provided the sample is stored equal or lower than +4 °C at the user's site. The stability of the reference material is not affected by short periods of handling at ambient temperature during transport and use. Therefore, BAM-B001 can be shipped at ambient temperature.

5.2 Post-certification monitoring

The initial stability estimation will be updated by periodic measurements of units stored at -20 °C and +4 °C during the availability of the reference material. Recently performed post-certification measurements in June 2020 showed no degradation of the PAH congeners.

6. Certification study

6.1 Design of the study

The assignment of the certified PAH mass fractions of BAM-B001 is based on an in-house study at BAM analysing the candidate material at two independent workplaces using SIDA GC-MS method. A third separate data set was taken from the homogeneity study. To support and to confirm BAM's in-house certification study, the candidate reference material was subject of two ILCs with experienced laboratories.

6.2 In-house-Certification study

For in-house certification, 5 units of the candidate reference material (No. 150, 300, 450, 600, 750) were selected and equally subdivided into part A and B. While the 5 A-bottles were analysed by Operator 1, the 5 B-bottles were analysed by Operator 2. Each operator (workplace) applied their own sample preparation using a separate GC-MS system, individually prepared PAH standards/calibration, and separate data evaluation. The applied sample preparations and the SIDA GC-MS methods for quantification are described in section 3. Five independent replicates were analysed for each unit, resulting in 25 analyses per operator and 50 results for each PAH congener in total. Additionally, 48 results for each PAH congener were obtained from the homogeneity study, so a total of 98 independent analyses/results were obtained for each PAH congener. Table 6 displays the results of all PAH congeners generated for the in-house certification study.

Tab. 6: Results of the three workplaces for the in-house certification study of BAM-B001 (values in mg kg^{-1})

PAH congener	Operator 1		Operator 2		Homogeneity study	
	$Mean_{OP1}$	**SD_{OP1}**	**$Mean_{OP2}$**	**SD_{OP2}**	**$Mean_{Homo}$**	**SD_{Homo}**
Naphthalene	0.043	0.016	0.169	0.056	0.0639	0.0031
Acenaphthylene	0.784	0.067	3.161	0.893	0.9647	0.0797
Acenaphthene	0.755	0.091	0.359	0.020	0.7890	0.0504
Fluorene	1.580	0.034	1.874	0.085	1.6892	0.0717
Phenanthrene	15.530	0.164	14.754	0.302	15.8744	0.3388
Anthracene	2.267	0.032	3.894	0.294	2.5201	0.1034
Fluoranthene	4.289	0.046	4.004	0.054	4.5275	0.0920
Pyrene	11.463	0.080	10.654	0.182	11.9476	0.2441
Benz[*a*]anthracene	2.183	0.014	2.022	0.053	2.3173	0.0382
Chrysene	2.047	0.022	2.083	0.104	2.1127	0.0447
Benzo[*b*]fluoranthene	0.569	0.008	0.554	0.012	0.5988	0.0114
Benzo[*k*]fluoranthene	0.198	0.020	0.227	0.005	0.2146	0.0172
Benzo[*j*]fluoranthene	0.388	0.016	0.417	0.009	0.3954	0.0122
Benzo[*e*]pyrene	1.238	0.012	1.077	0.029	1.3079	0.0234
Benzo[*a*]pyrene	1.423	0.010	1.370	0.021	1.4237	0.0256
Indeno[1,2,3-*cd*]pyrene	0.243	0.011	0.334	0.006	0.2728	0.0145
Dibenz[*a,h*]anthracene	0.112	0.011	0.107	0.004	0.1355	0.0203
Benzo[*ghi*]perylene	1.416	0.022	1.455	0.037	1.4340	0.0288

$Mean_{OP1}$, $Mean_{OP2}$ Mean of 5 bottle means of each operator
$Mean_{Homo}$ Mean of 12 bottle means
SD_{OP1}, SD_{OP2} Standard deviation of 25 single values of each operator
SD_{Homo} Standard deviation of 48 single values from homogeneity study

The results of the in-house certification study are summarized in Table 7.

Tab. 7: Summarized results of the in-house certification study of BAM-B001

PAH congener	x_{char} [a] (mg kg^{-1})	SD [b] (mg kg^{-1})	u_{char} [c] (mg kg^{-1})	No. of independent data sets	Total no. of independent results
Naphthalene	0.0921	0.0674	0.0389	3	98
Acenaphthylene	1.6364	1.3232	0.7640	3	98
Acenaphthene	0.6341	0.2392	0.1381	3	98
Fluorene	1.7143	0.1486	0.0858	3	98
Phenanthrene	15.3863	0.5737	0.3312	3	98
Anthracene	2.8938	0.8755	0.5055	3	98
Fluoranthene	4.2735	0.2621	0.1513	3	98
Pyrene	11.3551	0.6535	0.3773	3	98
Benz[*a*]anthracene	2.1740	0.1478	0.0853	3	98
Chrysene	2.0808	0.0328	0.0189	3	98
Benzo[*b*]fluoranthene	0.5739	0.0230	0.0133	3	98
Benzo[*k*]fluoranthene	0.2133	0.0147	0.0085	3	98
Benzo[*j*]fluoranthene	0.3999	0.0151	0.0087	3	98
Benzo[*e*]pyrene	1.2078	0.1182	0.0682	3	98
Benzo[*a*]pyrene	1.4056	0.0307	0.0178	3	98
Indeno[1,2,3-*cd*]pyrene	0.2834	0.0463	0.0267	3	98
Dibenz[*a,h*]anthracene	0.1181	0.0154	0.0089	3	98
Benzo[*ghi*]perylene	1.4348	0.0195	0.0113	3	98

[a] Mean of workplace (participant) means
[b] Standard deviation of workplace (participant) means
[c] Standard uncertainty of the mean of means acc. to Eq. 2

$$u_{char} = \frac{SD}{\sqrt{N}} \qquad \textbf{(2)}$$

u_{char} Standard uncertainty of the mean of means (uncertainty of characterisation)
SD Standard deviation of workplace (participant) means
N Number of data sets (N=3)

6.3 Uncertainty budget

The combined uncertainty u_{com} of the candidate reference material is calculated acc. to Equation 3.

$$u_{com} = x_{char} \cdot \sqrt{u_{char,r}^2 + u_{bb,r}^2 + u_{pur,r}^2 + u_{hand,r}^2} \qquad \textbf{(3)}$$

x_{char} certified value (mean of workplace (participant) means)
$u_{char,r}$ Uncertainty of characterisation
$u_{bb,r}$ Contribution due to the between-bottle inhomogeneity as recommended in [5, 8]
$u_{pur,r}$ Uncertainty of the native PAH calibration standard SRM 2260a (NIST)
$u_{hand,r}$ Contribution from sample handling (pragmatic approach: 3 % for all PAH congeners)

While u_{char}, u_{bb} and u_{pur} are resulting from measurable contributions, the uncertainty from handling u_{hand} is a combined, rather worst-case estimate for all gravimetric and volumetric sample handling procedures including the calibration uncertainty. Table 8 contains the data to calculate the combined uncertainty u_{com} (example: phenanthrene) and Table 9 summarizes the u_{com} values for all PAHs.

Tab. 7: Uncertainty contributions for calculation of the combined uncertainty (u_{com}) of phenanthrene

Parameter	Characterisation	Homogeneity	Purity	Handling
Mean (mg kg^{-1})	15.3863	15.8744	11.5700	
u (mg kg^{-1})	0.3312	0.1124	0.0400	
u_{rel}	0.0215	0.0071	0.0035	0.0300
u_{com} acc. to eq. 3	**0.5809 mg kg^{-1}**			

Tab. 8: Combined uncertainties of analysed PAHs in BAM-B001

PAH	u_{com} (mg kg^{-1})	PAH	u_{com} (mg kg^{-1})
Naphthalene	0.0390	Chrysene	0.0712
Acenaphthylene	0.7660	Benzo[*b*]fluoranthene	0.0219
Acenaphthene	0.1396	Benzo[*k*]fluoranthene	0.0106
Fluorene	0.1089	Benzo[*j*]fluoranthene	0.0156
Phenanthrene	0.5809	Benzo[*e*]pyrene	0.0774
Anthracene	0.5130	Benzo[*a*]pyrene	0.0488
Fluoranthene	0.2010	Indeno[1,2,3-*cd*]pyrene	0.0281
Pyrene	0.5125	Dibenz[*a,h*]anthracene	0.0096
Benz[*a*]anthracene	0.1086	Benzo[*ghi*]perylene	0.0449

6.4 Interlaboratory comparison studies (ILCs)

The candidate reference material BAM-B001 was subject of two ILCs for different purposes (see below). As secondary use, the ILC-results were used to support and to confirm the outcome of the in-house certification study at BAM.

ILC-1 was conducted for PAHs in rubber toy in the framework of the Sino-German Working group "Product safety" (Toy Safety) under responsibility of the Federal Ministry for Economic Affairs and Energy (BMWi). BAM organised ILC-1 with > 50 expert laboratories from China and Germany focussing on the 8 REACH-regulated PAH congeners (Regulation 1272/2013) and two additional PAHs: Indeno[1,2,3-*cd*]pyrene and Benzo[*ghi*]perylene. The main objective of ILC-1 was to gain a general understanding of the performance in determining PAHs in rubber toys.

ILC-2 was organised by the Working group "Consumer products" of BVL §64 LFGB for method validation (AfPS method). 18 PAH congeners which are relevant for AfPS/GS-mark were subject of analysis including 16 participating laboratories from Germany.

Because both ILCs were not primarily intended to assess the certified PAH mass fractions of BAM-B001 and are partially not 'owned'/organised by BAM (ILC-2, BVL), the participating laboratories are kept anonymous in this report. Participants of the ILCs received one bottle of BAM-B001 and were requested to analyse each bottle in three replicates (ILC-1) and two replicates (ILC-2), respectively. The participants of both ILCs were requested to analyse the candidate material according to AfPS-method [2]. The returned results were evaluated by BAM (ILC-1) and BVL/Quodata (ILC-2). The results of both ILCs are displayed in Table 10 in comparison to BAM's in-house measurement results.

Tab. 10: Results of ILC-1 (Sino-German ILC) and ILC-2 (BVL, §64 LFGB) using AfPS method and BAM's in-house study. Mean ILC-1 (robust mean, *Hampel* estimator), mean ILC-2 (arithmetic mean after outlier elimination); SD_{ILC}: standard deviation of the ILC; ds: number of data sets with quantitative results after outlier elimination.

PAH congener	ILC-1			ILC-2			BAM in-house study	
	Mean	SD_{ILC}	ds	Mean	SD_{ILC}	ds	x_{char}	u_{char}
Naphthalene							0.092	0.039
Acenaphthylene				1.856	0.313	15	1.636	0.764
Acenaphthene				0.472	0.076	14	0.634	0.138
Fluorene				1.452	0.066	12	1.714	0.086
Phenanthrene				15.541	1.324	14	15.386	0.331
Anthracene				3.035	0.224	15	2.894	0.505
Fluoranthene				4.492	0.162	15	4.273	0.151
Pyrene				11.401	0.384	14	11.355	0.377
Benz[*a*]anthracene	2.455	0.156	36	2.871	0.149	16	2.174	0.085
Chrysene	2.488	0.175	36	2.645	0.179	16	2.081	0.019
Benzo[*b*]fluoranthene	0.674	0.061	35	0.649	0.042	16	0.574	0.013
Benzo[*k*]fluoranthene	0.288	0.037	34	0.248	0.021	12	0.213	0.008
Benzo[*j*]fluoranthene	0.429	0.042	34	0.373	0.023	14	0.400	0.009
Benzo[*e*]pyrene	1.220	0.082	36	1.135	0.041	16	1.208	0.068
Benzo[*a*]pyrene	1.433	0.097	35	1.364	0.071	16	1.406	0.018
Indeno[1,2,3-*cd*]pyrene	0.300	0.033	30	0.331	0.033	16	0.283	0.027
Dibenz[*a,h*]anthracene	0.205	0.040	18				0.118	0.009
Benzo[*ghi*]perylene	1.254	0.094	31	1.250	0.071	14	1.435	0.011

A robust statistic was applied to evaluate the results of ILC-1. The *Hampel* estimator was used for the robust mean and the Q-method was applied for determining the robust standard deviation of ILC-1 according to ISO 13528:2015 [9] and DIN 38402-45:2014 [10]. Calculation of statistical evaluation was performed by using ProLab plus software, version 2016.7.28.0 (quodata, Dresden, Germany). The PAH congeners indicated with crossed fields in Table 9 for ILC-1 were not subject of the study.

The results of ILC-2 were statistically evaluated by means of ProLab plus software, using the statistical approaches according to ISO 5725-2 [11] and ASU § 64 LFGB [12]. The two PAH congeners indicated with crossed fields in Table 9 for ILC-2 (naphthalene, dibenz[*a,h*]anthracene) could not be evaluated statistically due to a proportion of < LOQ results of more than 25 %.

The conformity of the ILC results with the BAM in-house values was tested using the (amended) E_n criterion on the difference between the ILC mean x_1 and the BAM in-house value x_2 according to Equation 4:

$$E_n = \frac{|x_1 - x_2|}{2\sqrt{SD_{ILC}^2 + u_{char}^2}} \qquad \textbf{(4)}$$

SD_{ILC} standard deviation of the ILC
u_{char} uncertainty of characterisation (at BAM)

The factor 2 in Eq. 4 converts the standard uncertainties in the denominator into expanded uncertainties. The resulting E_n values were 0.1 to 1.2 for ILC-1 and 0.1 to 1.6 for ILC-2 with one exception slightly exceeding the critical value of E_n=2: benz[*a*]anthracene, E_n 2.03 (ILC-2) but E_n 0.8 for ILC-1.

Conclusion: The results of the E_n criterion indicate that the outcomes of ILCs are consistent with the in-house certification results based on the SIDA GC-MS at BAM.

6.5 Summary of certified values

The certified mass fractions of the PAH congeners (Table 11) are based on the in-house certification results (6.2), which have been confirmed by two ILCs (6.4). The expanded uncertainty (*U*) of the certified values (Table 11) are calculated based on the combined uncertainties (6.3) applying a coverage factor (*k*) of *k*=2. The data of four PAH congeners (naphthalene, acenaphthylene, acenaphthene and dibenz[*a,h*]anthracene) are considered as informative (not certified) due to the reasons indicated in the footnotes of Table 11.

Tab. 11: Certified mass fractions of the PAH congeners of BAM-B001 with respect to raw sample mass

PAH congener	Mass fraction (mg kg^{-1})		Remark
	Certified value	*U*	
Naphthalene	0.09	0.08	informative [a)]
Acenaphthylene	1.6	1.6	informative [b)]
Acenaphthene	0.63	0.28	informative [c)]
Fluorene	1.71	0.22	
Phenanthrene	15.4	1.2	
Anthracene	2.9	1.1	
Fluoranthene	4.3	0.5	
Pyrene	11.4	1.1	
Benz[*a*]anthracene	2.17	0.22	
Chrysene	2.08	0.15	
Benzo[*b*]fluoranthene	0.57	0.05	
Benzo[*k*]fluoranthene	0.213	0.022	
Benzo[*j*]fluoranthene	0.40	0.04	
Benzo[*e*]pyrene	1.21	0.16	
Benzo[*a*]pyrene	1.41	0.10	
Indeno[1,2,3-*cd*]pyrene	0.28	0.06	
Dibenz[*a,h*]anthracene	0.118	0.020	informative [d)]
Benzo[*ghi*]perylene	1.43	0.09	

a) Large uncertainty of BAM's naphthalene value; no confirmation by ILCs possible; PAH contents < 0.2 mg/kg are not quantified according to AfPS GS 2019:01 PAK method.
b) Large uncertainty of BAM's acenaphthylene value; lacking information from ILC-1.
c) Relatively large uncertainty of BAM's acenaphthene value; lacking information from ILC-1.
d) PAH contents < 0.2 mg/kg are not quantified according to AfPS GS 2019:01 PAK method; lacking information from ILC-2.

Rounding: Intermediate results were not rounded; rounding was done for the expanded uncertainties, not for the combined uncertainties. The certified PAH mass fractions and expanded uncertainties in Table 11 are rounded according to DIN 1333 [13].

6.6 Metrological traceability

All certified values refer to the extractable amounts of the PAH congeners applying the AfPS GS 2019:01 PAK method and are conventional to this extent. However, different sample preparation methods have been used such that systematic biases will (at least partially) be cancelled out. In order to ensure traceability of the extractable contents as defined above, the gravimetrically prepared certified calibration standard SRM 2260a (NIST) was employed for the in-house certification study. Traceability was further established by using stable isotope dilution analysis using isotopically labelled PAHs internal standards for GC-MS measurements.

6.7 Commutability

BAM-B001 was produced from a commercial rubber toy product without changes of the matrix. Therefore, the analytical behavior is the same as for a routine sample of rubber toy products. For samples other than rubber (toy) products, the commutability must be re-assessed.

7. Information on the proper use of BAM-B001

7.1 Shelf life

From the initial stability study, a considerably large shelf life well above a period of 5 years at a storage temperature of +4 °C was estimated. Since the dispatch to the end user may occur at any time during this period, the certified properties will be valid for 24 months beginning with the dispatch of the material from BAM. The validity of this information will be maintained by post-certification monitoring.

7.2 Transport and storage

BAM-B001 can be shipped at ambient temperature. On receiving, must be stored at a temperature equal to or lower than +4 °C. The stability of the reference material is not affected by short periods of handling at ambient temperature during transport and use. However, BAM cannot be held responsible for any alteration of the material occurring during handling and storage at the customer's premises, especially of opened samples.

7.3 Instructions for use

This material is intended to be used for performance control and validation of analytical methods for the determination of PAHs in rubber (toy) products. Before taking a subsample, the bottle must have reached ambient temperature. Thereafter, the bottle is to be closed tightly and stored at a temperature equal to or lower than +4 °C. The stability of the reference material is not affected by short periods of handling at ambient temperature during transport and use. However, BAM cannot be held responsible for any alteration of the material occurring during handling and storage at the customer's premises, especially of opened samples.

7.4 Safety instructions

The usual laboratory safety precautions have to be applied. No hazardous effects are to be expected when the material is used under conditions usually adopted for the analysis of consumer products low or moderately contaminated with polycyclic aromatic hydrocarbons. Any contact or use other than the intended one should be avoided. Personnel handling the material must be trained adequately and follow regular laboratory safety precautions.

7.5 Legal notice

Neither BAM, its contractors nor any legal person acting on their behalf:

(a) make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately-owned intellectual property rights; or

(b) assume any liability with respect to, or for damages resulting from the use of any information, material, apparatus, method or process disclosed in this document save for loss or damage arising solely and directly from the negligence of BAM.

8. Information on and purchase of the CRM

The certified reference material BAM-B001 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)

Department 1 – Analytical Chemistry; Reference Materials
Division 1.7 - Organic Trace and Food Analysis
Richard-Willstätter-Str. 11. D-12489 Berlin. Germany
Phone: +49 (0)30 - 8104 2061
Fax: +49 (0)30 – 8104 72061
E-Mail: sales.crm@bam.de

Each unit of BAM-B001 will be distributed together with a certificate containing the certified PAH values and their uncertainties, a material description and instructions for use, storage and safety.

Information on certified reference materials can be obtained from BAM homepage https://www.bam.de and BAM-webshop www.webshop.bam.de.

9. References

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[2] Product Safety Commission (AfPS), German standard method AfPS GS 2019:01 PAK, Testing and assessment of polycyclic aromatic hydrocarbons (PAHs) in the course of awarding the GS mark - Specification pursuant to article 21(1) no. 3 of the Product Safety Act (ProdSG), 2019.

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[11] DIN ISO 5725-2 (2002), Genauigkeit (Richtigkeit und Präzision) von Messverfahren und Messergebnissen; Teil 2: Grundlegende Methode für die Ermittlung der Wiederhol- und Vergleichspräzision eines vereinheitlichten Messverfahrens, Dezember 2002.

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10. Annexes

Annex A: Data of homogeneity testing for PAHs in BAM-B001

A1: Homogeneity measurements for naphthalene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.0642	0.0657	0.0673	0.0650	0.0656	0.0013	2.0%
071	0.0606	0.0650	0.0616	0.0644	0.0629	0.0021	3.4%
141	0.0645	0.0643	0.0608	0.0675	0.0643	0.0027	4.2%
212	0.0580	0.0680	0.0684	0.0623	0.0642	0.0050	7.7%
283	0.0618	0.0701	0.0630	0.0674	0.0656	0.0038	5.9%
354	0.0622	0.0629	0.0668	0.0662	0.0645	0.0023	3.6%
424	0.0590	0.0638	0.0659	0.0641	0.0632	0.0030	4.7%
495	0.0622	0.0640	0.0661	0.0727	0.0662	0.0046	6.9%
566	0.0604	0.0669	0.0620	0.0639	0.0633	0.0028	4.4%
637	0.0616	0.0605	0.0582	0.0637	0.0610	0.0023	3.8%
707	0.0612	0.0652	0.0625	0.0642	0.0633	0.0018	2.8%
778	0.0604	0.0604	0.0638	0.0674	0.0630	0.0033	5.3%
Mean of bottle means:				**0.06391 mg/kg**			

A2: Homogeneity measurements for acenaphthylene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.7251	1.0801	0.8203	0.9884	0.9035	0.1604	17.7%
071	0.7742	1.0068	0.9048	0.9800	0.9165	0.1042	11.4%
141	0.8592	1.0104	0.9443	0.9799	0.9485	0.0653	6.9%
212	0.9042	1.0687	1.0022	0.9825	0.9894	0.0677	6.8%
283	0.9168	1.0020	0.9609	0.9262	0.9515	0.0386	4.1%
354	0.9567	0.9956	0.9894	0.8844	0.9566	0.0510	5.3%
424	1.0003	0.9475	1.0902	1.0304	1.0171	0.0596	5.9%
495	0.9022	0.9379	1.0204	1.0374	0.9745	0.0649	6.7%
566	1.0063	0.8737	0.9507	1.0882	0.9797	0.0904	9.2%
637	0.9723	0.9195	0.9929	1.0522	0.9842	0.0549	5.6%
707	1.0302	0.8647	1.0093	1.0102	0.9786	0.0765	7.8%
778	0.9915	0.8269	1.0439	1.0431	0.9763	0.1026	10.5%
Mean of bottle means:				**0.96469 mg/kg**			

A3: Homogeneity measurements for acenaphthene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.7424	0.8060	0.7893	0.8394	0.7943	0.0404	5.1%
071	0.7768	0.8057	0.7782	0.7389	0.7749	0.0274	3.5%
141	0.7782	0.7998	0.7877	0.7495	0.7788	0.0214	2.8%
212	0.7617	0.8377	0.8082	0.7454	0.7882	0.0424	5.4%
283	0.7529	0.8701	0.8440	0.8427	0.8274	0.0513	6.2%
354	0.7814	0.6274	0.8177	0.8489	0.7688	0.0983	12.8%
424	0.7609	0.7921	0.7325	0.8149	0.7751	0.0360	4.6%
495	0.7228	0.8597	0.7967	0.6040	0.7458	0.1098	14.7%
566	0.8240	0.8103	0.7978	0.8528	0.8212	0.0236	2.9%
637	0.7698	0.7814	0.7726	0.7824	0.7766	0.0063	0.8%
707	0.8048	0.8049	0.7974	0.8229	0.8075	0.0108	1.3%
778	0.8233	0.8059	0.7783	0.8290	0.8091	0.0228	2.8%
				Mean of bottle means:	**0.78898 mg/kg**		

A4: Homogeneity measurements for fluorene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	1.5860	1.6686	1.5832	1.6706	1.6271	0.0491	3.0%
071	1.6007	1.6605	1.5933	1.6532	1.6269	0.0348	2.1%
141	1.7886	1.6703	1.7003	1.6560	1.7038	0.0595	3.5%
212	1.6958	1.8028	1.7302	1.6639	1.7232	0.0596	3.5%
283	1.6388	1.7170	1.7346	1.6993	1.6974	0.0417	2.5%
354	1.6420	1.6421	1.6908	1.6276	1.6506	0.0276	1.7%
424	1.7312	1.6467	1.8370	1.6856	1.7251	0.0822	4.8%
495	1.6441	1.6903	1.6774	1.7022	1.6785	0.0251	1.5%
566	1.7498	1.7132	1.7041	1.7754	1.7356	0.0331	1.9%
637	1.5759	1.6486	1.6660	1.6577	1.6370	0.0414	2.5%
707	1.7590	1.7066	1.9079	1.7638	1.7843	0.0864	4.8%
778	1.6496	1.5210	1.7865	1.7649	1.6805	0.1221	7.3%
				Mean of bottle means:	**1.68918 mg/kg**		

A5: Homogeneity measurements for phenanthrene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	15.6872	15.7838	15.7079	15.7602	15.7348	0.0449	0.3%
071	15.7708	15.8050	15.7595	15.8529	15.7971	0.0419	0.3%
141	16.6126	15.9014	15.7516	16.0135	16.0698	0.3775	2.3%
212	15.7795	16.3620	16.1855	15.8403	16.0418	0.2784	1.7%
283	15.7986	16.8006	15.8122	16.2015	16.1532	0.4703	2.9%
354	15.8405	15.8926	16.3363	15.7834	15.9632	0.2527	1.6%
424	15.7860	15.6987	15.9037	15.7908	15.7948	0.0840	0.5%
495	15.8350	16.1514	15.8532	15.9572	15.9492	0.1451	0.9%
566	15.7651	15.7495	15.7110	16.7325	15.9895	0.4958	3.1%
637	15.6733	15.8412	14.4849	15.6888	15.4220	0.6293	4.1%
707	15.9096	15.7573	15.9043	15.6340	15.8013	0.1320	0.8%
778	15.5996	15.6810	16.0547	15.7688	15.7760	0.1982	1.3%
				Mean of bottle means:	**15.87439 mg/kg**		

A6: Homogeneity measurements for anthracene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	2.474	2.545	2.475	2.494	2.497	0.033	1.3%
071	2.484	2.534	2.477	2.566	2.515	0.042	1.7%
141	2.640	2.536	2.504	2.564	2.561	0.058	2.3%
212	2.253	2.626	2.576	2.237	2.423	0.207	8.5%
283	2.521	2.658	2.529	2.601	2.578	0.065	2.5%
354	2.555	2.480	2.599	2.517	2.538	0.051	2.0%
424	2.532	2.507	2.554	2.546	2.535	0.021	0.8%
495	2.519	2.578	2.233	2.576	2.477	0.164	6.6%
566	2.546	2.520	2.502	2.767	2.584	0.124	4.8%
637	2.503	2.528	2.200	2.531	2.441	0.161	6.6%
707	2.583	2.508	2.579	2.544	2.553	0.035	1.4%
778	2.501	2.488	2.594	2.577	2.540	0.053	2.1%
Mean of bottle means:				**2.52007 mg/kg**			

A7: Homogeneity measurements for fluoranthene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	4.423	4.448	4.416	4.544	4.458	0.059	1.3%
071	4.548	4.537	4.541	4.548	4.543	0.006	0.1%
141	4.688	4.541	4.533	4.592	4.589	0.071	1.5%
212	4.553	4.684	4.582	4.470	4.572	0.088	1.9%
283	4.549	4.795	4.467	4.560	4.593	0.141	3.1%
354	4.485	4.539	4.609	4.460	4.523	0.066	1.5%
424	4.528	4.508	4.533	4.544	4.528	0.015	0.3%
495	4.548	4.646	4.499	4.502	4.549	0.069	1.5%
566	4.450	4.551	4.509	4.805	4.579	0.157	3.4%
637	4.487	4.567	4.258	4.430	4.435	0.131	3.0%
707	4.486	4.423	4.491	4.494	4.473	0.034	0.8%
778	4.496	4.429	4.548	4.477	4.488	0.049	1.1%
Mean of bottle means:				**4.52749 mg/kg**			

A8: Homogeneity measurements for pyrene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	11.7225	11.8695	11.9051	11.9425	11.8599	0.0964	0.8%
071	11.7980	11.8955	11.9231	11.9535	11.8925	0.0673	0.6%
141	12.5298	11.9000	11.9112	11.9473	12.0720	0.3058	2.5%
212	11.7906	12.3048	12.2194	11.8887	12.0509	0.2496	2.1%
283	11.9803	12.5653	11.8891	12.2208	12.1639	0.3020	2.5%
354	12.0605	11.8801	12.1483	11.8094	11.9746	0.1568	1.3%
424	11.8817	11.8697	12.0352	11.8908	11.9194	0.0777	0.7%
495	11.8160	12.1927	11.9941	11.9783	11.9953	0.1543	1.3%
566	11.8889	11.8984	11.7167	12.5531	12.0143	0.3688	3.1%
637	11.6827	11.9222	11.0319	11.9299	11.6416	0.4224	3.6%
707	12.0171	11.9009	11.9603	11.7885	11.9167	0.0978	0.8%
778	11.6702	11.8122	12.1330	11.8659	11.8703	0.1936	1.6%
Mean of bottle means:				**11.94762 mg/kg**			

A9: Homogeneity measurements for benz[*a*]anthracene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	2.2952	2.2955	2.2769	2.3076	2.2938	0.0126	0.6%
071	2.3077	2.3219	2.3268	2.3193	2.3190	0.0081	0.4%
141	2.4129	2.3113	2.3025	2.3355	2.3405	0.0502	2.1%
212	2.3227	2.3874	2.3582	2.3180	2.3466	0.0326	1.4%
283	2.2935	2.4228	2.3122	2.3608	2.3473	0.0578	2.5%
354	2.3163	2.2672	2.3640	2.2995	2.3118	0.0403	1.7%
424	2.2932	2.3033	2.2966	2.3079	2.3002	0.0066	0.3%
495	2.2986	2.3419	2.3127	2.3294	2.3206	0.0190	0.8%
566	2.3163	2.2992	2.2839	2.4410	2.3351	0.0718	3.1%
637	2.2830	2.3156	2.2459	2.2892	2.2834	0.0287	1.3%
707	2.3229	2.2767	2.3181	2.2895	2.3018	0.0223	1.0%
778	2.2879	2.2928	2.3414	2.3095	2.3079	0.0242	1.0%
			Mean of bottle means:	**2.31734 mg/kg**			

A10: Homogeneity measurements for chrysene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	2.0815	2.0795	2.0720	2.1063	2.0849	0.0149	0.7%
071	2.0954	2.1083	2.0967	2.0918	2.0980	0.0072	0.3%
141	2.2227	2.1235	2.0921	2.1500	2.1471	0.0557	2.6%
212	2.1046	2.1627	2.1431	2.1387	2.1373	0.0242	1.1%
283	2.1212	2.2722	2.1035	2.1273	2.1560	0.0781	3.6%
354	2.1127	2.0758	2.1352	2.0742	2.0995	0.0297	1.4%
424	2.0866	2.1364	2.1074	2.0731	2.1009	0.0275	1.3%
495	2.1098	2.1622	2.0874	2.1735	2.1332	0.0413	1.9%
566	2.0660	2.0988	2.0866	2.2401	2.1229	0.0793	3.7%
637	2.0692	2.0888	2.0718	2.0848	2.0787	0.0096	0.5%
707	2.1164	2.0840	2.1377	2.0794	2.1044	0.0277	1.3%
778	2.0644	2.0619	2.1322	2.1011	2.0899	0.0334	1.6%
			Mean of bottle means:	**2.11272 mg/kg**			

A11: Homogeneity measurements for benzo[*b*]fluoranthene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.5889	0.5924	0.6299	0.5977	0.6022	0.0188	3.1%
071	0.5997	0.5961	0.5946	0.5894	0.5950	0.0043	0.7%
141	0.6102	0.5872	0.5853	0.5882	0.5927	0.0117	2.0%
212	0.5942	0.6051	0.6064	0.5879	0.5984	0.0089	1.5%
283	0.5984	0.6265	0.6029	0.5970	0.6062	0.0137	2.3%
354	0.6147	0.6010	0.6144	0.6062	0.6091	0.0067	1.1%
424	0.6018	0.5946	0.5893	0.5947	0.5951	0.0051	0.9%
495	0.5945	0.6043	0.6002	0.6047	0.6009	0.0047	0.8%
566	0.6020	0.5851	0.5850	0.6165	0.5972	0.0152	2.5%
637	0.5839	0.6021	0.5773		0.5878	0.0128	2.2%
707	0.6109	0.5916	0.5919	0.5946	0.5973	0.0092	1.5%
778	0.5859		0.6084	0.6175	0.6039	0.0163	2.7%
			Mean of bottle means:	**0.59881 mg/kg**			

A12: Homogeneity measurements for benzo[*k*]fluoranthene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.2346	0.2275	0.2121	0.1972	0.2178	0.0167	7.7%
071	0.1950	0.2122	0.2424	0.1974	0.2118	0.0218	10.3%
141	0.2006	0.2165	0.2333	0.2053	0.2139	0.0146	6.8%
212	0.2293	0.2094	0.1918	0.2458	0.2191	0.0235	10.7%
283	0.2322	0.2185	0.2441	0.2159	0.2277	0.0131	5.7%
354	0.2320	0.2018	0.2204	0.2132	0.2169	0.0127	5.9%
424	0.1993	0.1877	0.2227	0.2054	0.2038	0.0146	7.2%
495	0.2323	0.2605	0.2021	0.1963	0.2228	0.0297	13.3%
566	0.2333	0.1967	0.2011	0.2196	0.2127	0.0169	8.0%
637	0.2016		0.2235		0.2125	0.0155	7.3%
707	0.2114	0.2235	0.2046	0.2109	0.2126	0.0079	3.7%
778	0.1869	0.2098	0.1910	0.2263	0.2035	0.0182	8.9%
Mean of bottle means:				**0.21458 mg/kg**			

A13: Homogeneity measurements for benzo[*j*]fluoranthene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.3840	0.3927	0.4172	0.3892	0.3958	0.0147	3.7%
071	0.3905	0.4007	0.3983	0.4019	0.3979	0.0051	1.3%
141	0.4201	0.3884	0.3871	0.3923	0.3970	0.0156	3.9%
212	0.3634	0.4085	0.4128	0.3931	0.3945	0.0223	5.7%
283	0.3909	0.4183	0.3913	0.4220	0.4056	0.0168	4.1%
354	0.3904	0.3934	0.4143	0.4004	0.3996	0.0107	2.7%
424	0.3883	0.3894	0.3851	0.3933	0.3890	0.0034	0.9%
495	0.3806	0.3920	0.4010	0.3861	0.3899	0.0087	2.2%
566	0.3829	0.3961	0.3926	0.4206	0.3981	0.0161	4.0%
637	0.3831	0.4003	0.3769	0.3919	0.3881	0.0102	2.6%
707	0.3871	0.4046	0.3961	0.3874	0.3938	0.0083	2.1%
778	0.3890	0.3939	0.4088	0.3924	0.3960	0.0087	2.2%
Mean of bottle means:				**0.39544 mg/kg**			

A14: Homogeneity measurements for benzo[*e*]pyrene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	1.2858	1.3003	1.3181	1.3037	1.3020	0.0133	1.0%
071	1.3001	1.2974	1.3059	1.2932	1.2991	0.0053	0.4%
141	1.3597	1.3020	1.2871	1.3005	1.3123	0.0323	2.5%
212	1.3173	1.3430	1.3234	1.2976	1.3203	0.0187	1.4%
283	1.2848	1.3686	1.2886	1.3185	1.3151	0.0387	2.9%
354	1.3127	1.2870	1.3346	1.2909	1.3063	0.0220	1.7%
424	1.2911	1.2852	1.3117	1.2841	1.2930	0.0128	1.0%
495	1.2901	1.3291	1.3024	1.3019	1.3059	0.0165	1.3%
566	1.3163	1.3093	1.3020	1.3722	1.3250	0.0321	2.4%
637	1.2714	1.3108	1.2939	1.3680	1.3110	0.0413	3.1%
707	1.3064	1.2819	1.3078	1.2966	1.2982	0.0119	0.9%
778	1.3043	1.2886	1.3341	1.2994	1.3066	0.0195	1.5%
Mean of bottle means:				**1.30790 mg/kg**			

A15: Homogeneity measurements for benzo[*a*]pyrene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	1.4187	1.4097	1.4428	1.4257	1.4242	0.0140	1.0%
071	1.4171	1.4114	1.4219	1.4175	1.4170	0.0043	0.3%
141	1.4820	1.4110	1.4037	1.4287	1.4313	0.0354	2.5%
212	1.4284	1.4432	1.4445	1.4223	1.4346	0.0110	0.8%
283	1.3987	1.4885	1.4116	1.4502	1.4373	0.0406	2.8%
354	1.4238	1.3928	1.4497	1.4161	1.4206	0.0235	1.7%
424	1.3990	1.4108	1.4197	1.4096	1.4098	0.0085	0.6%
495	1.4087	1.4432	1.4220	1.4198	1.4234	0.0144	1.0%
566	1.4176	1.4269	1.4112	1.4965	1.4381	0.0395	2.7%
637	1.3917	1.4134	1.3731	1.4879	1.4165	0.0504	3.6%
707	1.4149	1.3978	1.4228	1.4130	1.4121	0.0104	0.7%
778	1.4040	1.4076	1.4583	1.4080	1.4195	0.0260	1.8%
				Mean of bottle means:	**1.42370 mg/kg**		

A16: Homogeneity measurements for indeno[1,2,3-*cd*]pyrene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.3209	0.2601	0.3203	0.2614	0.2907	0.0345	11.9%
071	0.2907	0.2712	0.2917	0.2630	0.2791	0.0143	5.1%
141	0.2908	0.2546	0.2794	0.2662	0.2727	0.0157	5.8%
212	0.2703	0.2754	0.2791	0.2691	0.2735	0.0046	1.7%
283	0.2617	0.2781	0.2678	0.2826	0.2726	0.0095	3.5%
354	0.2746	0.2663	0.2728	0.2762	0.2725	0.0044	1.6%
424	0.2632	0.2669	0.2629	0.2670	0.2650	0.0023	0.9%
495	0.2687	0.2718	0.2633	0.2664	0.2675	0.0036	1.3%
566	0.2651	0.2740	0.2626	0.2746	0.2691	0.0061	2.3%
637	0.2626	0.2793	0.2595	0.2673	0.2672	0.0087	3.3%
707	0.2685	0.2796	0.2670	0.2622	0.2693	0.0073	2.7%
778	0.2680	0.3117	0.2639	0.2525	0.2740	0.0259	9.5%
				Mean of bottle means:	**0.27277 mg/kg**		

A17: Homogeneity measurements for dibenz[*a,h*]anthracene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	0.2003	0.1301	0.1755	0.1241	0.1575	0.0366	23.3%
071	0.1503	0.1252	0.1534	0.1315	0.1401	0.0139	9.9%
141	0.1438	0.1208	0.1355	0.1308	0.1327	0.0096	7.2%
212	0.1353	0.1307	0.1371	0.1202	0.1308	0.0076	5.8%
283	0.1283	0.1392	0.1235	0.1426	0.1334	0.0090	6.7%
354	0.2108	0.1278	0.1353	0.1333	0.1518	0.0395	26.0%
424	0.1298	0.1287	0.1184	0.1225	0.1249	0.0054	4.3%
495	0.1288	0.1351	0.1256	0.1247	0.1286	0.0047	3.7%
566	0.1299	0.1395	0.1257	0.1272	0.1306	0.0062	4.7%
637	0.1184	0.1444	0.1280	0.1154	0.1266	0.0131	10.3%
707	0.1176	0.1511	0.1267	0.1231	0.1296	0.0148	11.4%
778	0.1233	0.1902	0.1312	0.1155	0.1400	0.0340	24.3%
				Mean of bottle means:	**0.13555 mg/kg**		

A18: Homogeneity measurements for benzo[*ghi*]perylene; all values in mg kg^{-1}

Bottle-No.	#1	#2	#3	#4	Mean	SD	RSD
001	1.4915	1.4230	1.4652	1.4281	1.4520	0.0324	2.2%
071	1.4363	1.4032	1.4424	1.4117	1.4234	0.0189	1.3%
141	1.5032	1.4026	1.4122	1.4281	1.4365	0.0457	3.2%
212	1.4441	1.4515	1.4430	1.4282	1.4417	0.0097	0.7%
283	1.4192	1.4993	1.4266	1.4617	1.4517	0.0367	2.5%
354	1.4413	1.4017	1.4852	1.4271	1.4388	0.0350	2.4%
424	1.4067	1.4265	1.4235	1.4155	1.4180	0.0089	0.6%
495	1.4164	1.4605	1.4319	1.4267	1.4339	0.0189	1.3%
566	1.4100	1.4393	1.4053	1.4982	1.4382	0.0427	3.0%
637	1.4056	1.4363	1.3910	1.4078	1.4102	0.0189	1.3%
707	1.4182	1.4369	1.4335	1.3893	1.4195	0.0217	1.5%
778	1.4116	1.4837	1.4584	1.4228	1.4441	0.0331	2.3%
Mean of bottle means:				**1.43401 mg/kg**			

Annex B: Data of certification measurements for PAHs in BAM-B001

B1: Certification measurements of Operator 1 (*GC-MS 1* system; A-bottles); mass fractions are given in mg kg^{-1}

Repl	1					2					3					4					5				
Bottle	150	300	450	600	750	150	300	450	600	750	150	300	450	600	750	150	300	450	600	750	150	300	450	600	750
NAP	0.040	0.048	0.046	0.046	0.051	0.031	0.029	0.029	0.028	0.043	0.033	0.027	0.048	0.047	0.024	0.048	0.046	0.089	0.046	0.029	0.048	0.031	0.048	0.041	0.091
ACY	0.618	0.693	0.753	0.794	0.776	0.798	0.728	0.724	0.782	0.670	0.744	0.772	0.789	0.888	0.840	0.796	0.816	0.759	0.788	0.759	0.870	0.831	0.872	0.883	0.852
ACE	0.903	0.656	0.676	0.867	0.752	0.788	0.847	0.659	0.690	0.786	0.696	0.866	0.863	0.669	0.554	0.684	0.714	0.899	0.724	0.767	0.758	0.747	0.692	0.736	0.878
FLU	1.533	1.548	1.592	1.551	1.566	1.581	1.581	1.647	1.554	1.569	1.655	1.592	1.539	1.521	1.602	1.580	1.584	1.603	1.596	1.580	1.566	1.610	1.530	1.602	1.614
PHE	15.31	15.39	15.44	14.99	15.33	15.51	15.49	15.47	15.54	15.54	15.53	15.55	15.56	15.54	15.49	15.58	15.56	15.74	15.57	15.72	15.76	15.74	15.62	15.67	15.63
ANT	2.192	2.232	2.273	2.256	2.243	2.266	2.246	2.235	2.262	2.236	2.208	2.253	2.260	2.274	2.275	2.285	2.282	2.305	2.281	2.292	2.305	2.309	2.301	2.321	2.285
FLT	4.205	4.216	4.236	4.298	4.314	4.273	4.246	4.358	4.268	4.243	4.352	4.250	4.274	4.279	4.250	4.294	4.295	4.325	4.264	4.313	4.310	4.312	4.393	4.337	4.319
PYR	11.29	11.40	11.36	11.40	11.33	11.44	11.47	11.41	11.50	11.45	11.45	11.46	11.45	11.60	11.48	11.35	11.46	11.53	11.51	11.52	11.54	11.62	11.53	11.56	11.49
BEA	2.204	2.183	2.207	2.170	2.167	2.188	2.178	2.171	2.193	2.182	2.183	2.177	2.190	2.158	2.193	2.153	2.172	2.187	2.176	2.192	2.175	2.212	2.188	2.185	2.179
CHR	2.035	2.052	2.034	2.078	2.047	2.020	2.042	2.062	2.025	2.035	2.027	2.060	2.103	2.080	2.067	2.037	2.011	2.065	2.022	2.062	2.052	2.031	2.048	2.031	2.052
BBF	0.573	0.566	0.571	0.558	0.561	0.561	0.560	0.571	0.574	0.587	0.566	0.563	0.568	0.569	0.564	0.571	0.566	0.580	0.574	0.595	0.568	0.568	0.562	0.569	0.568
BKF	0.166	0.211	0.187	0.177	0.214	0.201	0.171	0.193	0.184	0.203	0.186	0.208	0.201	0.185	0.179	0.178	0.221	0.227	0.192	0.232	0.241	0.184	0.193	0.228	0.187
BJF	0.403	0.376	0.365	0.375	0.387	0.399	0.376	0.398	0.401	0.367	0.386	0.399	0.400	0.392	0.395	0.397	0.409	0.361	0.388	0.418	0.390	0.403	0.360	0.367	0.376
BEP	1.218	1.229	1.239	1.225	1.219	1.230	1.239	1.238	1.226	1.224	1.226	1.247	1.243	1.240	1.246	1.239	1.229	1.244	1.231	1.257	1.252	1.257	1.252	1.252	1.250
BAP	1.431	1.434	1.446	1.423	1.410	1.420	1.428	1.431	1.419	1.430	1.408	1.429	1.413	1.421	1.425	1.410	1.402	1.421	1.419	1.437	1.415	1.433	1.417	1.424	1.429
INP	0.243	0.231	0.235	0.230	0.240	0.242	0.238	0.249	0.255	0.270	0.238	0.244	0.248	0.232	0.242	0.232	0.247	0.243	0.245	0.274	0.242	0.237	0.250	0.241	0.237
DBA	0.106	0.105	0.106	0.107	0.107	0.111	0.109	0.121	0.127	0.140	0.108	0.107	0.103	0.107	0.101	0.110	0.112	0.118	0.125	0.144	0.110	0.108	0.102	0.107	0.109
BEP	1.429	1.438	1.430	1.392	1.368	1.394	1.437	1.450	1.422	1.448	1.408	1.426	1.439	1.412	1.404	1.411	1.388	1.428	1.412	1.445	1.417	1.393	1.416	1.378	1.409

Repl: Replicate

NAP: Naphthalene; ACY: Acenaphthylene; ACE: Acenaphthene; FLU: Fluorene; PHE: Phenanthrene; ANT: Anthracene; FLT: Fluoranthene; PYR: Pyrene; BEA: Benz[*a*]anthracene; CHR: Chrysene; BBF: Benzo[*b*]fluoranthene; BKF: Benzo[*k*]fluoranthene; BJF: Benzo[*j*]fluoranthene; BEP: Benzo[*e*]pyrene; BAP: Benzo[*a*]pyrene; INP: Indeno[1,2,3-*cd*]pyrene; DBA: Dibenz[*a,h*]anthracene; BEP: Benzo[*ghi*]perylene

B2: Certification measurements of Operator 2 (*GC-MS 2* system; B-bottles); mass fractions are given in mg kg^{-1}

Repl	1					2					3					4					5				
Bottle	150	300	450	600	750	150	300	450	600	750	150	300	450	600	750	150	300	450	600	750	150	300	450	600	750
NAP	0.230	0.257	0.091	0.116	0.118	0.248	0.235	0.107	0.109	0.142	0.244	0.201	0.154	0.115	0.188	0.264	0.193	0.170	0.101	0.168	0.160	0.224	0.127	0.137	0.126
ACY	5.273	4.480	2.638	2.410	2.638	4.133	4.211	2.151	2.390	3.080	4.499	3.621	3.176	2.492	2.612	4.479	3.986	2.528	2.375	2.694	2.659	3.087	2.310	2.632	2.464
ACE	0.328	0.393	0.382	0.351	0.344	0.350	0.381	0.334	0.346	0.365	0.363	0.375	0.346	0.356	0.347	0.361	0.358	0.358	0.338	0.383	0.370	0.408	0.346	0.342	0.339
FLU	1.965	1.947	1.835	1.793	1.828	1.977	2.011	1.780	1.776	1.917	1.999	1.938	1.849	1.813	1.806	1.972	1.985	1.815	1.784	1.839	1.965	1.913	1.760	1.797	1.780
PHE	15.33	14.93	14.58	14.64	14.72	14.86	15.02	13.84	14.46	15.18	14.87	14.96	14.60	14.73	14.56	14.89	15.02	14.45	14.58	14.80	14.96	15.03	14.43	14.86	14.56
ANT	4.546	4.376	3.887	3.714	3.712	4.075	4.295	3.585	3.673	3.900	4.125	4.080	3.675	3.671	3.653	4.104	4.259	3.588	3.594	3.663	4.303	3.948	3.650	3.652	3.625
FLT	4.048	4.088	3.954	4.000	4.005	3.942	4.026	3.912	4.006	4.040	3.938	3.931	3.971	4.056	4.012	4.020	3.944	3.910	4.012	4.090	4.063	3.997	4.024	4.076	4.036
PYR	10.95	10.79	10.33	10.72	10.75	10.79	10.87	10.21	10.53	10.91	10.78	10.64	10.55	10.41	10.65	10.56	10.78	10.56	10.60	10.85	10.65	10.48	10.55	10.81	10.66
BEA	2.064	2.083	2.119	2.002	2.063	2.002	2.007	1.991	2.032	2.060	2.009	2.060	2.016	2.052	2.040	2.019	2.004	2.040	2.043	1.978	2.035	1.830	2.035	2.000	1.965
CHR	2.041	2.051	2.492	2.117	2.119	1.994	2.047	2.172	2.040	2.020	2.023	2.066	1.963	2.082	2.106	1.983	2.223	2.043	2.005	2.139	2.070	2.090	2.013	2.075	2.091
BBF	0.554	0.558	0.542	0.552	0.544	0.556	0.571	0.562	0.545	0.562	0.553	0.552	0.547	0.548	0.541	0.542	0.556	0.552	0.548	0.549	0.553	0.602	0.543	0.560	0.549
BKF	0.225	0.239	0.220	0.227	0.222	0.231	0.238	0.234	0.223	0.229	0.226	0.229	0.228	0.226	0.222	0.225	0.227	0.228	0.222	0.226	0.227	0.228	0.230	0.229	0.223
BJF	0.406	0.434	0.400	0.417	0.408	0.413	0.432	0.402	0.411	0.421	0.416	0.421	0.421	0.421	0.410	0.410	0.416	0.426	0.412	0.420	0.416	0.429	0.427	0.424	0.405
BEP	1.103	1.072	1.021	1.111	1.128	1.084	1.074	1.028	1.089	1.095	1.103	1.068	1.074	1.112	1.045	1.057	1.050	1.076	1.071	1.059	1.081	1.055	1.080	1.140	1.058
BAP	1.361	1.380	1.321	1.365	1.381	1.377	1.360	1.348	1.355	1.390	1.378	1.392	1.398	1.364	1.339	1.353	1.367	1.405	1.361	1.375	1.374	1.409	1.355	1.393	1.351
INP	0.340	0.337	0.322	0.334	0.324	0.334	0.347	0.338	0.331	0.338	0.344	0.333	0.334	0.335	0.326	0.322	0.335	0.339	0.332	0.333	0.335	0.339	0.335	0.333	0.333
DBA	0.101	0.108	0.099	0.107	0.103	0.101	0.110	0.109	0.100	0.105	0.116	0.104	0.108	0.110	0.104	0.103	0.109	0.110	0.111	0.104	0.104	0.113	0.109	0.104	0.112
BEP	1.453	1.453	1.391	1.474	1.465	1.437	1.451	1.446	1.399	1.458	1.456	1.418	1.455	1.476	1.520	1.452	1.429	1.491	1.489	1.564	1.425	1.456	1.427	1.458	1.423

Repl: Replicate

NAP: Naphthalene; ACY: Acenaphthylene; ACE: Acenaphthene; FLU: Fluorene; PHE: Phenanthrene; ANT: Anthracene; FLT: Fluoranthene; PYR: Pyrene; BEA: Benz[*a*]anthracene; CHR: Chrysene; BBF: Benzo[*b*]fluoranthene; BKF: Benzo[*k*]fluoranthene; BJF: Benzo[*j*]fluoranthene; BEP: Benzo[*e*]pyrene; BAP: Benzo[*a*]pyrene; INP: Indeno[1,2,3-*cd*]pyrene; DBA: Dibenz[*a,h*]anthracene; BEP: Benzo[*ghi*]perylene