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Polycyclic aromatic hydrocarbons (PAHs) – Method for the determination of semi-volatile PAHs in workplace air using high performance liquid chromatography (HPLC)

Air Monitoring Method – Translation of the German version from 2017

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Polycyclic aromatic hydrocarbons (PAHs) – Method for the determination of semi-volatile PAHs in workplace air using high performance liquid chromatography (HPLC)

Air Monitoring Methods

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Abstract

This analytical method is a validated measurement procedure for the determination of six semi-volatile polycyclic aromatic hydrocarbons (PAHs) from the EPA list (US Environmental Protection Agency) such as benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene, indeno[1,2,3-cd]pyrene and also benzo[*e*]pyren in workplace air averaged over the sampling period after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a PTFE filter, which is inserted in a GSP sampling system. The collected PAH components are extracted with a mixture of acetonitrile/methanol and analysed by means of high performance liquid chromatography (HPLC) with fluorescence detection. The quantitative determination of the PAHs is based on calibration functions obtained by means of multiple-point calibrations. The limit of quantification for an individual PAH is in the range from 0.0012 to 0.0043 µg/m^3.

Joint Publication of the Analytical Subcommittee of the Chemistry Board of Experts of the Expert Committee Raw Materials and Chemical Industry of the German Social Accident Insurance and the working group “Air Analyses” of the Permanent Senate Commission of the Deutsche Forschungsgemeinschaft for the Investigation of Health Hazards of Chemical Compounds in the Work Area.

Keywords

polycyclic aromatic hydrocarbons; PAH; benzo[b]fluoranthene; benzo[k]fluoranthene; benzo[a]pyrene; dibenzo[a,h]anthracene; benzo[ghi]perylene; indeno[1,2,3-cd]pyrene; benzo[e]pyrene; air analysis; workplace measurement; hazardous substances; air sampling; workplace monitoring; measurement method; PTFE filter; high performance liquid chromatography; HPLC; fluorescence detection

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Polycyclic aromatic hydrocarbons (PAHs) – Method for the determination of semi-volatile PAHs in workplace air using high performance liquid chromatography (HPLC)

Method number	1
Application	Air analysis
Analytical principle	High performance liquid chromatography (HPLC)
Completed in	May 2017

Summary

This measurement method permits the determination of six semi-volatile polycyclic aromatic hydrocarbons (PAHs) listed by the EPA (US Environmental Protection Agency), such as benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-cd]pyrene as well as benzo[*e*]pyrene in the workplace air. The method is suitable for monitoring the currently valid acceptance concentration of 70 ng/m^3 or tolerance concentration of 700 ng/m^3 for benzo[*a*]pyrene.

Sampling is performed by drawing a defined volume of air through a PTFE filter located in a GSP sampling system using a flow regulated pump. The collected PAH components are extracted from the PTFE filter with acetonitrile/methanol and then analysed by means of high performance liquid chromatography (HPLC) and fluorescence detection. The quantitative determination is based on calibration functions obtained by multiple-point calibrations with external standards.

Characteristics of the method

Reproducibility:	Standard deviation (rel.):	s = 2.4 to 6.3%
Expanded uncertainty:	For all investigated PAHs:	U = 22.1 to 24.7%

in the concentration range from 0.0083 to 2.8 µg/m^3 depending on the individual PAHs and with at least n = 6 determinations (this applies to both the reproducibility and the expanded uncertainty).

Limit of quantification (LOQ):	Benzo[*e*]pyrene	0.0039 µg/m^3
	Benzo[*b*]fluoranthene	0.0014 µg/m^3
	Benzo[*k*]fluoranthene	0.0012 µg/m^3
	Benzo[*a*]pyrene	0.0016 µg/m^3
	Dibenzo[*a,h*]anthracene	0.0043 µg/m^3
	Benzo[*ghi*]perylene	0.0020 µg/m^3
	Indeno[1,2,3-cd]pyrene	0.0023 µg/m^3
	for an air sample volume of 1200 L (1.2 m^3)	
Mean recovery:	Benzo[*e*]pyrene	97.8%
	Benzo[*b*]fluoranthene	98.8%
	Benzo[*k*]fluoranthene	99.3%
	Benzo[*a*]pyrene	98.6%
	Dibenzo[*a,h*]anthracene	100.0%
	Benzo[*ghi*]perylene	100.2%
	Indeno[1,2,3-cd]pyrene	98.6%
Sampling recommendations:	Sampling period:	at least 2 h
	Air sample volume:	1.2 m^3 (1200 L)
	Flow rate:	600 L/h (10 L/min)

Description of the substances

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are predominantly released into the environment as a result of incomplete combustion of organic material. Forest fires represent the main source of emission in nature; anthropogenic sources are combustion engines, power stations and incineration plants in particular. Depending on their vapour pressure, PAHs in the atmosphere occur in the gaseous state or bound to particles. Furthermore, considerable amounts of PAHs can also be found in tars and pitches and during the processing of such materials they are released in the gaseous state, adsorbed onto particles or in form of dust into the surrounding air.

Many PAHs have mutagenic or carcinogenic effects, whereby the toxicity is in part only activated when certain PAH components are metabolised in the human body. Detailed information on the toxicity of PAHs can be found in the toxicological-occupational health documentation of the MAK values [1, 2]. In the List of MAK and BAT Values PAHs have been assigned to Section III "Carcinogenic Substances" (pyrolysis products derived from organic material). The PAH components benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene and indeno[1,2,3-cd]pyrene are also assigned to Carcinogen Category 2 [3].

Benzo[*a*]pyrene is used as the indicator component for PAH exposure at the workplace. Up until 2005, the TRK (technical reference concentration) value for benzo[*a*]pyrene was set at 2 µg/m^3 or 5 µg/m^3 for the manufacture and loading of strands of pitch as well as in the oven area of coking plants [4, 5]. An ERR (Exposure-Risk Relationship) was set for handling benzo[*a*]pyrene in 2011 [6]. The tolerance concentration currently is 700 ng/m^3 and the acceptance concentration is 70 ng/m^3. The establishment of the ERR is based on existing data on activities in industrial sectors such as coking plants, coal gasification and liquification, aluminium production, manufacture of graphite and carbon electrodes, tar distillation and processing as well as chimney cleaning [7]. Further information on PAHs can be found in the IARC monographs [8].

Contents

1 General principles

This measurement method permits the determination of six semi-volatile polycyclic aromatic hydrocarbons (PAHs) listed by the EPA (US Environmental Protection Agency), such as benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-cd]pyrene as well as benzo[*e*]pyrene in the workplace air. The method is suitable for monitoring the currently valid acceptance concentration of 70 ng/m^3 or tolerance concentration of 700 ng/m^3 for benzo[*a*]pyrene.

Sampling consists of a flow-regulated pump drawing a defined volume of air through a PTFE filter located in a GSP sampling system, which includes a 10 L/min intake cone. The minimum sampling period is 2 hours at a flow rate of 10 L/min, whereby an air sample volume of 1.2 m^3 is collected. For sample preparation the PTFE filter, loaded with PAH components, is transferred into a sample vial, covered with acetonitrile/methanol (60/40% (v/v)) and extraction is performed in the ultrasonic bath. The analysis is carried out by means of high performance liquid chromatography and fluorescence detection. The quantitative determination is based on calibration functions obtained by multiple-point calibrations with external standards.

2 Equipment, chemicals and solutions

2.1 Equipment

- Pump for personal sampling, suitable for a flow rate of 10 L/min, GSM/SG10 type, e.g. from Leschke Messtechnik GmbH, 15230 Frankfurt an der Oder, Germany
- Personal sampling system: sampling head (GSP) for the inhalable fraction with an intake cone suitable for 10 L/min, supplied by Analyt-MTC GmbH, 79379 Müllheim, Germany
- Filter cassettes for the GSP sampling system
- High performance liquid chromatograph (HPLC) with a column oven and a fluorescence detector, e.g. from Agilent 1100/1200 FLD
- Separation column, e.g. MZ PAH C18, from MZ-Analysentechnik GmbH, 55120 Mainz, Germany
- Ultrapure water system
- Ultrasonic bath
- Laboratory shaker
- Volumetric flasks, 1, 2 and 5 mL
- Measuring cylinder
- Microlitre syringes, gas-tight, 10 to 500 µL
- Vials made of amber glass (7 mL) with screw caps and rubber/PTFE seals
- Autosampler vials made of glass (1.5 mL) with crimp caps and rubber/PTFE septa
- Disposable filters, pore size 0.45 µm, e.g. Chromafil Xtra PTFE 45/25
- PTFE filters, e.g. Gelman Zefluor ∅ 37 mm, 2 µm

2.2 Chemicals

- PAH Stock Solution 1, 20 to 200 µg/mL, e.g. Supelco 49156 in acetonitrile/methanol (9:1)
- PAH Stock Solution 2, 100 to 200 µg/mL, e.g. Dr. Ehrenstorfer PAH Mix 61 in acetone/methanol (1:1), supplied by LGC Standards, 46485 Wesel, Germany
- Benzo[*e*]pyrene Stock Solution 1, 100 µg/mL, e.g. from Sigma-Aldrich 36962 in cyclohexane
- Benzo[*e*]pyrene Stock Solution 2, 100 µg/mL, e.g. Dr. Ehrenstorfer XA20645000AL, supplied by LGC Standards
- Acetonitrile, suitable for HPLC, e.g. Baker, Order No. 9017
- Methanol, suitable for HPLC, e.g. Baker, Order No. 8402

2.3 Solutions

Solvent used for the preparation of measurement solutions and as a desorption agent for sample preparation:

Acetonitrile/water (60/40% (v/v)) (specific resistance of the water ≥ 18.2 MΩ × cm at 25 °C). *The solvent and desorption agent respectively must be freshly prepared every working day.*

Standard solutions

PAH Standard Solution 1 containing all the PAHs:

50 µL of PAH Stock Solution 1 and 40 µL of Benzo[*e*]pyrene Stock Solution 1 are each pipetted into a 2 mL volumetric flask using a microlitre syringe. The volumetric flask is subsequently filled to the mark with acetonitrile/methanol (60/40% (v/v)). The concentration of the individual PAH components is in the range of 0.50 to 5.0 µg/mL. The concentration of benzo[*a*]pyrene is 1.25 µg/mL.

PAH Standard Solution 2 containing all the PAHs:

25 µL of PAH Stock Solution 2 and 50 µL of Benzo[*e*]pyrene Stock Solution 2 are each pipetted into a 5 mL volumetric flask using a microlitre syringe. The volumetric flask is then filled to the mark with acetonitrile/methanol (60/40% (v/v)). The concentration of the individual PAH components are in the range of 0.5 to 1 µg/mL. The concentration of benzo[*a*]pyrene is 0.5 µg/mL.

The PAH standard solutions containing all the PAHs are stable for at least 3 months when stored at −18 °C.

PAH calibration solutions:

Further intermediate dilutions are prepared from Standard Solution 1 containing all the PAHs – depending on the respective PAH components – using microlitre syringes. These dilutions are then used to prepare the calibration solutions together with acetonitrile/methanol (60/40% (v/v)) in 1 mL volumetric flasks. The dosing

Table 1 Dosing scheme for the preparation of the benzo[a]pyrene calibration solutions

Calibration Solution No.	Intermediate dilution of PAH Standard Solution 1	Volume of the intermediate dilution/1 mL [µL]	Concentration [µg/mL]
1	1 : 10	10	0.00125
2	1 : 10	20	0.00250
3	1 : 10	30	0.00375
4	1 : 10	40	0.00500
5	1 : 10	50	0.00625
6	1 : 10	60	0.00750
7	1 : 10	70	0.00875
8	1 : 10	80	0.0100
9	1 : 10	90	0.0113
10	1 : 10	100	0.0125

scheme for the preparation of ten benzo[*a*]pyrene calibration solutions is shown in Table 1. For this purpose an intermediate dilution at a ratio of 1:10 is prepared using Standard Solution 1 containing all the PAHs.

Control solutions

PAH control solution for the precision:

A sample, whose concentration lies in the mean range of the calibration for all PAH components, is used as a control solution for the precision. The concentration of benzo[*a*]pyrene is 0.00750 µg/mL.

PAH control solution for the accuracy:

120 mL of PAH Standard Solution 2 containing all the PAHs are pipetted into a 10 mL volumetric flask using a microlitre syringe. The volumetric flask is subsequently filled to the mark with acetonitrile/methanol (60/40% (v/v)). This is equivalent to a concentration of benzo[*a*]pyrene of 0.006 µg/mL.

The calibration and control solutions for the precision and accuracy are stable for at least 1 month when stored at –18 °C.

Eluents for the chromatography:

Eluent A:	Acetonitrile/water (65/35% (v/v)) (specific resistance of the water ≥18.2 MΩ × cm at 25 °C) *Eluent A must be freshly prepared every working day.*
Eluent B:	Acetonitrile

3 Sampling and sample preparation

A PTFE filter is inserted into the GSP sampling system and the system is connected to the flow-regulated pump at the beginning of sampling. The GSP system is fitted with a 10 L/min intake cone corresponding to the flow rate. At a recommended sampling period of 2 hours this is equivalent to an air sample volume of approx. 1200 litres (1.2 m^3). The important parameters for the determination of the concentration of the individual PAH component in air are documented in the sampling record. After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discard the sample [9]. The filter cassette with the loaded PTFE filter is sealed with the supplied caps.

The PTFE filter is transferred into a 7 mL amber glass vial and covered with 2 mL of acetonitrile/methanol (60/40% (v/v)) for sample preparation. The sample vessel is sealed, treated in the ultrasonic bath for 60 minutes and then shaken for 60 minutes on a laboratory shaker. A disposable syringe is used to withdraw sample liquid from the supernatant solution of the prepared sample. The sample is filtered through a disposable filter into a 1.5 mL autosampler vial and analysed.

4 Operating conditions for the HPLC

The analytical measurements are performed with a combination of instruments comprising a HPLC system with a binary pump, column oven, degasser and autosampler, as well as a fluorescence detector (FLD).

Apparatus:	High performance liquid chromatograph (HPLC), e.g. Agilent 1100				
Separation column:	Material:	Stainless steel			
	Length:	250 mm			
	Internal diameter (ID):	2.1 mm			
	Column packing:	MZ PAH C18			
	Particle size:	5 µm			
Column temperature:	25 °C				
Eluent:	A: Acetonitrile in ultrapure water (65/35% (v/v))				
	B: Acetonitrile				
Gradient:	0 to 7 min:		100% A		
	7 to 19 min: →		100% B		
	19 to 37 min:		100% B		
	Reconditioning: > 37 min: →		100% A		
Flow rate:	0.3 mL/min				
Injection volume:	12 µL				
Detector:	Fluorescence detector (FLD):				
	Ex:		260 nm		
	Em:	FLD A:	502 nm		
		FLD B:	400 nm		
		FLD C:	430 nm		
		FLD D:	452 nm		
	PMT:		11	after 27.0 min:	13

5 Analytical determination

12 µL of the prepared sample solution are injected into the liquid chromatograph by means of the autosampler and analysed in a duplicate determination under the conditions described in Section 4. If the measured concentrations are above the calibration range, then a suitable dilution of the sample under investigation must be prepared with acetonitrile/methanol (60/40% (v/v)) and analysis must be carried out again.

Four examples of chromatograms of a standard solution obtained under the conditions described above are shown in Figure 1. Furthermore, the wavelengths of the signals used for the evaluation are also listed.

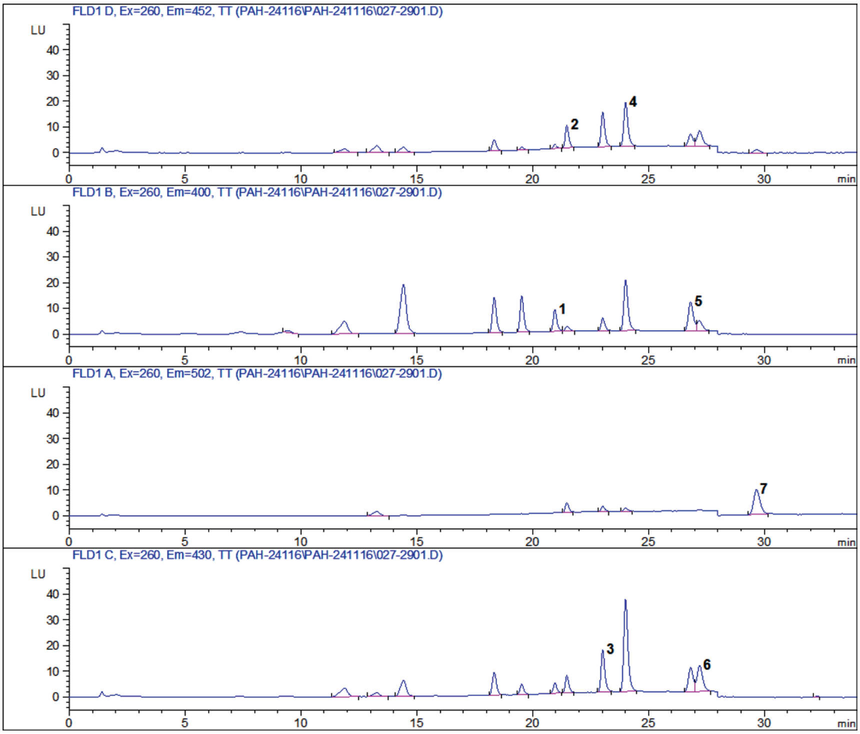

Figure 1 Example of chromatograms for the liquid chromatographic separation of the PAHs in the concentration range from 0.003 to 0.03 µg/mL; the concentration of benzo[*a*]pyrene is 0.00750 µg/mL (for chromatographic conditions see Section 4)

1	Benzo[*e*]pyrene	FLD B: Ex 260 nm, Em 400 nm
2	Benzo[*b*]fluoranthene	FLD D: Ex 260 nm, Em 452 nm
3	Benzo[*k*]fluoranthene	FLD C: Ex 260 nm, Em 430 nm
4	Benzo[*a*]pyrene	FLD D: Ex 260 nm, Em 452 nm
5	Dibenzo[*a,h*]anthracene	FLD B: Ex 260 nm, Em 400 nm
6	Benzo[*ghi*]perylene	FLD C: Ex 260 nm, Em 430 nm
7	Indeno[1,2,3-cd]pyrene	FLD A: Ex 260 nm, Em 502 nm

6 Calibration

The calibration solutions described in Section 2.3 are used to obtain the calibration functions. 12 µL of the calibration solutions are injected into the liquid chromatograph in each case and analysed in the same manner as the sample solutions. The resulting peak areas of a PAH component are plotted versus its corresponding concentration. The calibration functions are linear in the investigated concentration ranges.

Immediately after each calibration two control solutions (determination in parallel) are analysed in order to check the accuracy. The accuracy of the calibration is deemed satisfactory if the content of the PAH components in the control solution deviate by no more than ± 5% from the respective theoretical concentration.

Two control samples for the precision (determination in parallel) are analysed each working day to check the calibration functions. The precision of the calibration is deemed satisfactory if the content of the PAH components in the control solution deviate by no more than ± 5% from the respective theoretical concentration. The calibration must be performed anew if the analytical conditions change or the quality control results indicate that this is necessary.

7 Calculation of the analytical result

The concentration of the PAHs in the workplace air is calculated from the concentrations of the individual PAHs in the measured solution by the data evaluation unit. For this purpose the data evaluation unit uses the calibration functions calculated as part of the calibration.

The concentrations of the PAHs in the workplace air are calculated from the measured concentrations, taking the dilutions and the air sample volume into account. The mass concentrations ρ (µg PAH per m^3 of air) present in the workplace air are obtained from Equation (1) as follows:

$$\rho = \frac{(F - a) \cdot 2}{b \cdot V_{air}} \tag{1}$$

where:

ρ is the mass concentration of a PAH component in the ambient air in µg/m^3

F is the peak area

a is the y-intercept of the calibration function

b is the slope of the calibration curve [$F \times mL/\mu g$]

2 is the conversion factor for the desorption volume in mL

V_{air} is the air sample volume in m^3

8 Reliability of the method

The characteristics of the method were determined as stipulated in EN 482 [10] and EN 13890 [11]. The limits of quantification of the PAH components were calculated from 10-point calibrations according to DIN 32645 [12].

8.1 Reproducibility and expanded uncertainty

The reproducibility was determined by using microlitre syringes to spike six or ten PTFE filters each with defined masses of PAHs. Then 1200 L of ambient air was drawn through the filters and the samples were prepared and analysed as described in Sections 3, 4 and 5. In the case of benzo[*a*]pyrene a concentration range of a third of the acceptance concentration up to twice of the tolerance concentration was investigated. The results are summarised in Table 2.

Table 2 Relative standard deviations and expanded uncertainties *U*

PAH	Concentration [µg/m³]	Number of determinations n	Standard deviation (rel.) [%]	Expanded uncertainty *U* [%]
Benzo[*e*]pyrene	0.033	10	6.3	24.7
	0.33	10	4.3	24.3
	0.67	10	5.5	24.0
	2.8	6	2.7	24.6
Benzo[*b*]fluoranthene	0.0083	10	6.0	23.6
	0.083	10	5.1	23.2
	0.17	10	5.1	23.2
	2.8	6	2.5	23.6
Benzo[*k*]fluoranthene	0.0083	10	6.0	23.0
	0.083	10	5.3	22.8
	0.17	10	4.2	22.9
	1.4	6	2.4	23.1
Benzo[*a*]pyrene	0.021	10	5.2	22.9
	0.21	10	4.0	22.2
	0.42	10	3.2	22.1
	1.4	6	3.2	22.4
Dibenzo[*a,h*] anthracene	0.083	10	4.5	22.5
	0.83	10	3.6	22.4
	1.7	10	3.1	22.3
	2.8	6	4.7	22.6
Benzo[*ghi*]perylene	0.033	10	6.3	23.5
	0.33	10	5.1	23.1
	0.67	10	5.0	23.1
	2.8	6	4.5	23.4
Indeno[1,2,3-cd] pyrene	0.021	10	3.3	22.4
	0.21	10	4.5	22.3
	0.42	10	3.2	24.1
	1.4	6	3.7	22.9

Table 3 Mean recoveries throughout the entire concentration range

PAH	Concentration range [µg/m³]	Mean recovery [%]
Benzo[*e*]pyrene	0.033–2.8	97.8
Benzo[*b*]fluoranthene	0.0083–2.8	98.8
Benzo[*k*]fluoranthene	0.0083–1.4	99.3
Benzo[*a*]pyrene	0.021–1.4	98.6
Dibenzo[*a,h*]anthracene	0.083–2.8	100.0
Benzo[*ghi*]perylene	0.033–2.8	100.2
Indeno[1,2,3-*cd*]pyrene	0.021–1.4	98.6

Table 4 Limits of quantification calculated from 10-point calibrations

PAH	Concentration range	Limit of quantification (LOQ)	
	[µg/mL]	[µg/mL]	[µg/m^3]*
Benzo[*e*]pyrene	0.006–0.06	0.0023	0.0039
Benzo[*b*]fluoranthene	0.0015–0.015	0.00084	0.0014
Benzo[*k*]fluoranthene	0.001–0.01	0.00072	0.0012
Benzo[*a*]pyrene	0.00125–0.0125	0.00098	0.0016
Dibenzo[*a,h*]anthracene	0.0045–0.045	0.0026	0.0043
Benzo[*ghi*]perylene	0.002–0.02	0.0012	0.0020
Indeno[1,2,3-*cd*]pyrene	0.0025–0.025	0.0014	0.0023

* for an air sample volume of 1.2 m^3

The expanded uncertainty was estimated taking all the relevant influencing factors according to EN 13890 [11] into consideration and calculated using the IFA software for calculation of the uncertainty [13]. The results of the individual PAH components are shown in Table 2.

8.2 Recovery

The recoveries were determined for four concentrations from the data obtained during determination of the reproducibility in the minimum measurement range (see Table 6 in the Appendix). They are in the range of 95% ≤ recovery ≤ 105% for all PAH components. Based on the data obtained the mean recoveries listed in Table 3 do not have to be taken into consideration in the calculation of the analytical results.

8.3 Limit of quantification

Determination of the limits of quantification for the individual PAH components is carried out according to DIN 32645 [12] from 10-point calibrations for the substance-specific concentration ranges documented in Table 4 with a statistical certainty of P = 99.5% and k = 3. The limits of quantification listed in Table 4 were based on an air sample volume of 1200 litres (1.2 m^3).

8.4 Storage stability

Storage stability was determined by using microlitre syringes to spike six or ten PTFE filters for three concentrations each with a defined mass of PAHs. Then 1200 L of ambient air was drawn through the filters and these were prepared and analysed as described in Sections 3, 4 and 5. In the case of benzo[*a*]pyrene a concentration range of a third of the acceptance concentration up to twice the tolerance concentration was checked.

Initially samples were stored at room temperature, protected from light for 7 days and then for a further 7 days in the refrigerator at 4 °C. After a storage period of 14 days no significant losses could be detected. The results are summarised in Table 5.

Table 5 Recovery (concentration-related) and results for the storage stability

PAH	Concentration [µg/m³]	Number of determinations n	Mean recovery [%]	Mean recovery after storage [%]
Benzo[*e*]pyrene	0.033	10	97.1	96.7
	0.33	10	97.9	–
	0.67	10	98.8	96.6
	2.8	6	97.3	95.7
Benzo[*b*]fluoranthene	0.0083	10	98.2	98.7
	0.083	10	99.0	–
	0.17	10	99.4	96.7
	2.8	6	98.6	98.4
Benzo[*k*]fluoranthene	0.0083	10	99.0	96.3
	0.083	10	99.6	–
	0.17	10	99.0	97.7
	1.4	6	99.4	100.3
Benzo[*a*]pyrene	0.021	10	97.2	97.6
	0.21	10	98.9	–
	0.42	10	99.4	98.3
	1.4	6	99.1	98.7
Dibenzo[*a,h*] anthracene	0.083	10	101.0	96.3
	0.83	10	98.9	–
	1.7	10	99.4	96.2
	2.8	6	100.9	99.8
Benzo[*ghi*]perylene	0.033	10	102.0	96.7
	0.33	10	100.9	–
	0.67	10	99.4	97.0
	2.8	6	98.8	97.2
Indeno[1,2,3-cd] pyrene	0.021	10	98.9	96.1
	0.21	10	98.5	–
	0.42	10	99.5	97.2
	1.4	6	97.6	96.2

8.5 Blank values

Blank values of unused PTFE filters were checked by preparing and analysing ten filters from four different manufacturing batches as described in Sections 3, 4 and 5. No blank values were detected for the PTFE filters.

8.6 Interference

The analytical procedure by means of high performance liquid chromatography and fluorescence detection is specific and robust under the conditions stated here. No interference was observed.

9 Discussion

This measurement method described here permits the selective and sufficiently sensitive determination in workplace air of six semi-volatile PAH components listed by the EPA (US Environmental Protection Agency), such as benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*] perylene and indeno[1,2,3-cd]pyrene as well as benzo[*e*]pyrene with limits of quantification in the range of 0.0012 to 0.0043 µg/m^3.

At workplaces where PAH components bound to complex matrices occur, it is advisable to either extend the duration of extraction with acetonitrile/methanol (60/40% (v/v)) during sample preparation (see Section 3) to at least 24 hours or alternatively to carry out an extraction using toluene, in order to ensure complete capture of all PAH components in this way.

If required, other semi-volatile PAH components may be determined with the measurement method presented here. In this case the analytical performance characteristics as well as the chromatographic conditions must be checked and adapted accordingly.

10 Appendix: Precision and accuracy by means of comparative measurements

The precision and accuracy of the measurement method was checked by comparative measurements. For this purpose a PAH standard solution was diluted and a total of 12 PTFE filters were each spiked with 50 µL of this solution. Then six filters were prepared in the laboratory of the developer of the method (IFA – *Institute for Occupational Safety and Health of the German Social Accident Insurance*) and six filters in the laboratory of the examiner of the method (BGN – *German Social*

Table 6 Results of the comparative measurements of the spiked solution

PAH	Theoretical concentration [ng/mL]	Laboratory 1 (IFA)*		Test laboratory (BGN)**	
		Concentration detected [ng/mL]	Recovery [%]	Concentration detected [ng/mL]	Recovery [%]
Benzo[*b*]fluoranthene	12	11.9	99.5	11.9	99.0
Benzo[*k*]fluoranthene	6	6.0	100.2	6.0	100.7
Benzo[*a*]pyrene	6	5.9	98.7	5.9	98.7
Dibenzo[*a,h*]anthracene	12	11.9	99.5	11.6	96.6
Benzo[*ghi*]perylene	12	11.8	98.3	11.8	98.4
Indeno[1,2,3-cd]pyrene	6	5.9	98.8	6.0	99.3

* Institute for Occupational Safety and Health of the German Social Accident Insurance; ** German Social Accident Insurance Institution for the foodstuffs industry and the catering trade

Table 7 Results of the comparative measurements of the spiked filters

PAH	Spiked mass [ng/ filter]	Laboratory 1 (IFA)*			Test laboratory (BGN)**		
		Mass detected [ng/ filter]	Recovery [%]	STD (rel.) [%]	Mass detected [ng/ filter]	Recovery [%]	STD (rel.) [%]
Benzo[*b*]fluoranthene	24	23.5	97.8	1.0	23.2	96.9	1.3
Benzo[*k*]fluoranthene	12	12.2	101.7	0.9	11.9	99.4	0.7
Benzo[*a*]pyrene	12	11.6	96.7	1.0	11.6	96.3	1.0
Dibenzo[*a,h*] anthracene	24	23.2	96.8	1.5	24.2	100.8	0.5
Benzo[*ghi*]perylene	24	23.6	98.2	2.9	24.3	101.1	1.4
Indeno[1,2,3-cd] pyrene	12	11.8	98.3	2.6	11.7	97.7	0.2

* Institute for Occupational Safety and Health of the German Social Accident Insurance; ** Institution for the foodstuffs industry and the catering trade

Accident Insurance Institution for the foodstuffs industry and the catering trade) and analysed according to their respective in-house methods. In addition to comparison of the calibration, the spiking solutions used in both laboratories were analysed. The results of the comparative measurements of the spiking solutions including the standard deviations (rel. STD) are listed in Table 6 and those for the filters in Table 7.

The precisions of both laboratories showed deviations of < 3%. The recoveries for all PAH components were in the range of 96 to 102%. The maximum deviation of the measurement results between both the test laboratories was approx. 4%.

References

[1] Hartwig A (ed.) (2012) Polycyclic aromatic hydrocarbons (PAH) (translation of German version 2008). The MAK-Collection Part I: Occupational Toxicants, Vol. 27. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb0223orge0027a/pdf

[2] Hartwig A (ed.) (2012) Polycyclic aromatic hydrocarbons, carcinogenic (PAH) (translation of German version 1984). The MAK-Collection Part I: Occupational Toxicants, Vol. 27. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb0223orge0027b/pdf

[3] DFG – Deutsche Forschungsgemeinschaft (2017) List of MAK and BAT Values 2017. Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 53. Wiley-VCH, Weinheim, Germany, http://onlinelibrary.wiley.com/book/10.1002/9783527812127

[4] TRGS 900 (2006) Arbeitsplatzgrenzwerte, BArbBl. Heft 1/2006 pp. 41-55, recently revised and supplemented: GMBl 2017 pp. 919-922 [No. 50] (30.11.2017), https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-900.pdf?__blob=publicationFile&v=3

[5] TRGS 551 (2015) Teer und andere Pyrolyseprodukte aus organischem Material, GMBl 2015 pp. 1066-1083 [No. 54] (06.10.2015) revised and supplemented: GMBl 2016 pp. 8-10 [No. 1] (27.01.2016), http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/TRGS-551.html

[6] TRGS 910 (2014) Risk-related concept of measures for activities involving carcinogenic hazardous substances. Technical Rule for Hazardous Substances. Last amended: GMBl 2016 No. 31 pp. 606-609 (29.07.2016), corrected: GMBl 2016 No. 40 p. 791 (07.10.2016) (not up-to-date and inofficial version; mandatory is the current German version) https://www.baua.de/EN/Service/Legislative-texts-and-technical-rules/Rules/TRGS/TRGS-910.html;jsessionid=0522398F0FE311F37072D4644E3DC6BF.s1t1

[7] Explanatory to the exposure-risk relationship for benzo[a]pyrene in BekGS 910 (2011), https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/910/910-benzo-a-pyren.pdf?__blob=publicationFile&v=2

[8] World Health Organisation (WHO) (2010) International agency for research on cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 92, Some Non-heterocyclic Polyaromatic Hydrocarbons and Some Related Exposures, http://monographs.iarc.fr/ENG/Monographs/vol92/mono92.pdf

[9] ISO 13137 (2013) Workplace atmospheres – Pumps for personal sampling of chemical and biological agents – Requirements and test methods. Beuth Verlag, Berlin, Germany

[10] EN 482 (2015) Workplace exposure – General requirements for the performance of procedures for the measurement of chemical agents. Beuth Verlag, Berlin, Germany

[11] EN 13890 (2010) Workplace exposure – Procedures for measuring metals and metalloids in airborne particles – Requirements and test methods. Beuth Verlag, Berlin, Germany

[12] DIN 32645 (2008) Chemical analysis – Decision limit, detection limit and determination limit under repeatability conditions – Terms, methods, evaluation. Beuth Verlag, Berlin, Germany

[13] Heckmann P and Breuer D (2017) IFA method for calculating expanded measurement uncertainty, http://www.dguv.de/ifa/praxishilfen/hazardous-substances/software-berechnung-der-erweiterten-messunsicherheit-nach-ifa/index.jsp