Polycyclic aromatic hydrocarbons (PAH) (particle-bound)

Application	Air analysis
Analytical principle	Capillary gas chromatography
Completed in	October 1987

Summary

Particle-bound polycyclic aromatic hydrocarbons (PAH) are collected on glass fibre or silver membrane filters and subsequently desorbed with organic solvents. After column chromatographic prepurification they are determined by means of capillary gas chromatography with a flame ionization detector (FID/GC).
Quantitative determination is carried out by the internal standard method.

Precision
(without sampling): Standard deviation (rel.) s = 3–20 %
(cf. Tab. 1)
Mean variation u = 8–45 %
(cf. Tab. 1)
in a concentration range from 10 to 320 µg PAH per mL extracted volume, where n = 10 determinations

Detection limit: 0.15 µg/m^3 air (for each compound) (a sample volume of 1 m^3)
In many cases in which samples are contaminated with other compounds a detection limit of only 0.5 µg/m^3 can be achieved.

	Personal sampling	Stationary
Recommended sampling time:	4–8 h	1 h (or less)
Recommended sample volume:	480–960 L	22.5 m^3 (or less)

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are crystalline substances with very low vapour pressures at room temperature. As animal experiments have shown that some PAHs are carcinogenic, no MAK values are given for these compounds. They are discussed in Section III of the List of MAK Values [1] under Pyrolysis Products of Organic Materials. The TRK value for benzo[a]pyrene (1990) is given as (TRGS 100 [2], TRGS 402 [3]) 2 µg/m^3 and 5 µg/m^3 for the production, loading and unloading of pencil pitch and near the ovens in cokes plants (TRgA 126 [4]). For general information about PAHs see TRgA 551 [5] and [6].
Polycyclic aromatic hydrocarbons can always be produced when organic material is subjected to pyrolysis. The term pyrolysis is defined as the thermal treatment of an organic material in the absence of oxygen or as incomplete combustion. In addition to PAHs, other substances with low boiling points can be produced and also high boiling substances which do not decompose on evaporation.

Authors: *W, Riepe, K. G. Liphard*
Examiners: *U. Knecht*

Polycyclic aromatic hydrocarbons (PAH) (particle-bound)

Application	Air analysis
Analytical principle	Capillary gas chromatography
Completed in	October 1987

Contents

1 General principles
2 Equipment and chemicals
2.1 Equipment
2.2 Chemicals
3 Sample collection and preparation
4 Operating conditions for capillary gas chromatography
5 Analytical determination
6 Calibration
7 Calculation of the analytical results
8 Reliability of the method
8.1 Preliminary remark
8.2 Precision
8.3 Detection limit
8.4 Sources of error
9 Discussion of the method
10 References

1 General principles

The particle-bound polycyclic aromatic hydrocarbons (PAH) are collected on glass fibre or silver membrane filters and subsequently desorbed with organic solvents. After column chromatographic prepurification they are determined by means of capillary gas chromatography (FID/GC) with a flame ionization detector.
Quantitative determination is carried out by the internal standard method.

2 Equipment and chemicals

2.1 Equipment

Gas chromatograph equipped with a glass or a fused silica capillary, flame ionization detector, integrator or data processing system

Capillary column to separate the polycyclic aromatic hydrocarbons, e.g. Sil 5, SE 30, OV 1, OV 101, SE 52, SE 54

Dust collectors for stationary sampling and for personal sampling of workplace air, with a suction velocity of 1.25 m/s ±10 %

Sampling pump

Personal sampling: glass fibre filters (free of binding agents) or silver membrane filters, pore size 0.8 µm, each of diameter 37 or 25 mm

Stationary sampling: glass fibre filters (free of binding agents) 0.8 µm pore size, 150 mm diameter

Soxhlet apparatus or ultrasonic bath, suitable for extraction with about 60 mL of solvent

Rotary evaporator

Chromatography column (length 14 cm, inner diameter 1.4 cm) for sample preparation

Dropping funnel

100 mL round-bottomed flask

5–50 mL flasks with a basal extension containing about 0.5 mL, graduated if possible, for preparation of the samples for separation by capillary gas chromatography

Injection syringe for gas chromatography

2.2 Chemicals

Animal experiments have conclusively shown that most of the polycyclic aromatic hydrocarbons are carcinogenic to a greater or lesser degree. Thus, skin contact or the risk of ingestion or inhalation must be strictly avoided when handling either samples and extracts which may contain PAHs or the polycyclic aromatic reference substances.

Extraction agent:
Cyclohexane, analytical grade, or toluene, analytical grade

Solvent for prepurification:
Ethanol (abs.), analytical grade
n-Pentane, analytical grade
Toluene, analytical grade

All solvents should be distilled over a fractionating column with a sufficient number of plates and used fresh. A blank test ensures that no interfering substances are present.

Column packing:
Servachrom XAD-2 (styrene-divinylbenzene-copolymer) 150–200 µm (e.g. Serva)

Internal standard:
e.g. Indeno[1,2,3-cd]fluoranthene

Reference standards	
fluoranthene	FLU
pyrene	PYR
benzo[b]naphthol[2,1-d]thiophene	BNT
cyclopenta[cd]pyrene	CPP
benz[a]anthracene	BaA
chrysene	CHR
triphenylene	TRI
benzo[b]fluoranthene	BbF
benzo[j]fluoranthene	BjF
benzo[k]fluoranthene	BkF
benzo[e]pyrene	BeP
benzo[apyrene	BaP
perylene	PER
indeno[1,2,3-cd]pyrene	IND
dibenz[ah]anthracene	DBahaA
benzo[ghi]perylene	BghiP
anthanthrene	ANT
coronene	COR

Suppliers:
- Commission of the European Communities
  Community Bureau of Reference BCR, Brussels
- Aldrich

3 Sample collection and preparation

Sampling is carried out with a dust collector which samples the total dust content of the air. The quantity of air to be sampled depends on factors such as workplace conditions and the concentration of airborne dust. In general, the sample volume should not be less than 1 m^3.
The following sampling conditions have proved suitable:

Personal sampling:

Pumping capacity	120 L/h
Sampling time	4–8 h

Stationary sampling:

Pumping capacity	22.5 m^3/h
Sampling time	1 h

During sampling or measurement the provisions of TRGS 401 [3] must always be adhered to.

If the air flow rate is too high, loss of the more volatile compounds through evaporation must be expected [7, 8]. Sensitive substances like benzo[a]pyrene can also be degraded by oxidation. Glass, quartz fibre, PTFE or silver membrane filters can be used. This method permits the quantitative determination only of compounds containing four or more rings and having boiling points above about 370 °C. In the exceptional case when highly volatile compounds are to be detected, an adsorbent resin must be connected after the filter (e.g. XAD-2 or Tenax).

If the filters are not immediately processed, it is advisable to store the exposed filters in sealed containers (e. g. in Petri dishes) in a refrigerator to eliminate loss due to evaporation or decomposition reactions. During long-term storage, losses due, e. g., to catalytic effects cannot be excluded.

Normally, about 60 mL of cyclohexane or toluene and the internal standard are added and the exposed filter is extracted in a Soxhlet apparatus for six hours or in an ultrasonic bath for one hour. The amount of internal standard added depends on the expected sample concentrations. If necessary, they should be determined in preliminary investigations. As a rule, the concentration of the standards should be in the range from one to five times the concentration of benzo [a] pyrene.

The extract is concentrated almost to dryness in a rotary evaporator at 30–40 °C (water pump). Total desiccation causes loss through sublimation and must be strictly avoided. If interfering compounds are present, a preliminary purification is necessary. This will presumably be the case at the majority of workplaces.

The preliminary purification is carried out, e.g., by column chromatography on XAD-2-resin [9]. A column of 1.4 cm inner diameter is filled with XAD-2-resin (150–200 µm) to a depth of 9 cm and conditioned with ethanol. A round-bottomed flask is connected below and a dropping funnel above the column, both with ground glass joints. This combination is a sealed system with no contact with the ambient air.

The extract is dissolved in about 200–1000 µL of ethanol and loaded onto the column. Then 25 mL of ethanol are added to the column to remove the polar components, followed by 10 mL of n-pentane to remove the non-polar and non-aromatic compounds. Another 10 mL ethanol is required for reconditioning. The eluates from these procedures are discarded. The fraction containing the PAHs is eluted first with 12 mL of toluene and then with 10 mL of ethanol. It is collected in a flask with a basal extension and then concentrated until it is almost dry (about 20–50 µL). The column is reconditioned with 20 mL of toluene followed by 25 mL of ethanol. Before the actual analysis procedure begins, the column must be conditioned by carrying out about ten chromatographic analyses of a calibration mixture because otherwise the recovery rate is too low.

4 Operating conditions for capillary gas chromatography

After the extraction or any necessary preliminary purification, the samples to be investigated are analyzed by means of capillary gas chromatography. The following set of parameters is typical.

Capillary column:	Length:	25 m
	Inner diameter:	0.25 mm
	Stationary phase:	Sil 5
Detector:	Flame ionization detector	
Temperatures:	Column:	Start at 140 °C
		Rate: 5 °C/min
		up to 300 °C, then isothermal
	Injection block:	300 °C
	Detector:	310 °C
Carrier gas:	Helium:	0.09 MPa
Detector gas:	Air:	0.2 Mpa
	Hydrogen:	0.1 MPa
Make-up gas:	Nitrogen:	0.13 MPa
Injection volume:	1–5 µL	

Hydrogen can be used as a carrier gas instead of helium for a more rapid analysis. In low concentration ranges the splitless or on column injection mode must be used. Fig. 1 shows a typical gas chromatographic separation of PAHs.

5 Analytical determination

Under the conditions described above a volume of 1–5 µL is taken from the extraction solution and analyzed under the above conditions.
For the FID-signal intensities corresponding to the components to be analyzed, the peak areas are determined by means of an integrator (cf. Section 6).
Identification of the analytes in the chromatograms is carried out by comparing the retention times with those of reference substances or by addition of reference substances to the sample.

6 Calibration

In the capillary gas chromatographic separation and detection with a FID-detector, the responses of the PAH compounds are not all the same as that of the internal standard. Therefore calibration is necessary for quantitative determinations. For this purpose a standard solution with given concentrations of each component is analyzed by means of capillary gas chromatography with the same instrument settings as are used in the analysis. The calibration coefficients are determined by comparing the peak areas and masses.

7 Calculation of the analytical results

The mass of the PAH in the samples is calculated from the ratio of the internal standard peak area to the peak area of the PAH, the mass of the internal standard and the calibration factors.
The concentration of the PAH in the air sample in µg/m^3 is calculated from the following equation:

$$\rho_{PAH} = \frac{X}{V_z}$$

Legend: X Mass of the PAH (µg)
V_z Sample volume (m^3)
ρ_{PAH} Concentration of the PAH in air in µg/m^3

8 Reliability of the method

8.1 Preliminary remark

Parameters like precision and detection limit of the whole procedure cannot be determined because it is impossible to prepare a test gas containing PAHs. For this reason, only the analytical method without the sampling process can be evaluated. Sampling, however, is the greatest source of error.

8.2 Precision

In order to determine the precision, 10 200 µL aliquots were taken from the sample and prepurified by column chromatography. The eluates were concentrated almost to dryness with a rotary evaporator and then analyzed by means of capillary gas chromatography. The components listed below were determined quantitatively:

fluoranthene
pyrene
benz[a]anthracene
chrysene/triphenylene
benzofluoranthenes
benzo[e]pyrene
benzo[a]pyrene
perylene
indeno[1,2,3-cd]pyrene
dibenz[a,h] anthracene
dibenzo[ghi]perylene
anthanthrene

For the resulting precision see Tab. 1. Because of insufficient separation of the individual benzofluoranthenes, only the sum of the isomers is given.
The analyses were carried out using a Hewlett Packard gas chromatograph 5170 A. The operating conditions are described in Section 4. A volume of 1 µL was injected in splitless mode. A typical chromatogram is shown in Fig. 1. For each of the 12 compounds which were investigated, Tab. 1 lists the following parameters: mean values from 10 determinations (µg PAH per mL of the initial solution), standard deviation, relative standard deviation and range.

8.3 Detection limit

In capillary gas chromatographic determination of PAHs the detection limits and the corresponding standard deviations are known to be influenced by numerous factors so that no universally applicable values can be quoted. Investigations have indicated that a concentration of 3 ng per µL injected volume is necessary for quantification. Errors arising from sampling and sample treatment have not been taken into consideration in this estimate.
With a sample air volume of 1 m^3 and a final solution volume of 50 µL a theoretical detection limit of 0.15 $\mu g/m^3$ for each individual substance can be achieved. In practice, however, this detection limit frequently remains unattainable and an actual detection limit of 0.5 $\mu g/m^3$ can be expected.

8.4 Sources of error

The following compounds can be clearly separated using gas chromatography.

fluoranthene
pyrene
benzo[b]naphtho[2,1-d]thiophene
cyclopenta[cd]pyrene
benz[a]anthracene
chrysene/triphenylene
benzofluoranthenes
benzo[e]pyrene
benzo[a]pyrene
perylene
indeno[1,2,3-cd]pyrene
dibenz[a,h] anthracene
picene
benzo[ghi]perylene
anthanthrene
coronene

The separation of the individual benzofluoranthenes is unsatisfactory in most cases. Therefore only the sum of their isomers should be given. A separation of chrysene from

triphenylene cannot be carried out with the capillaries mentioned. These compounds are also given as a sum. Around room temperature the PAHs have such low vapour pressures that they do not usually occur as gaseous components but bound to particles, e.g. to suspended dust. A temperature increase above 50 °C causes vaporization of the PAHs. In such cases, or when there is reason to believe that gaseous PAH is present, an adsorber resin (e. g. XAD-2 or Tenax) must be installed after the filter.
Interference during sampling and sample treatment has already been described (cf. Section 3).

9 Discussion of the method

The method described permits the determination of particle-bound PAHs. The suction velocity of the sampling devices must be set at 1.25 m/s. Losses are caused by the use of higher air flow rates or long storage times.
Although the analytical procedure and the required equipment is described here, newcomers to capillary gas chromatography or organic trace analysis are warned against its use.
For the initial examinination of a workplace, it may be necessary to confirm the results of the gas chromatographic analysis by means of gas chromatography/mass spectrometry:

Apparatus:
Gas chromatograph 5170 A equipped with a flame ionization detector from Hewlett Packard.

10 References

[1] *Deutsche Forschungsgemeinschaft:* Maximale Arbeitsplatzkonzentrationen und Biologische Arbeitsstofftoleranzwerte 1987. Mitteilung XXIII der Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe. VCH Verlagsgesellschaft, Weinheim 1987.
[2] TRGS 100: Auslöseschwelle für gefährliche Stoffe. In: Technische Regeln und Richtlinien des BMA zur Verordnung über gefährliche Stoffe. Bek. des BMA vom 8. 10. 1986, Bundesarbeitsblatt 11/1986, pp. 91–92.
[3] TRGS 402: Ermittlung und Beurteilung der Konzentrationen gefährlicher Stoffe in der Luft in Arbeitsbereichen. In: Technische Regeln und Richtlinien des BMA zur Verordnung über gefährliche Stoffe. Bek. des BMA vom 8. 10. 1986, Bundesarbeitsblatt 11/1986, pp. 92–96.
[4] TRgA 126: Auslöseschwelle für Benzo[a]pyren. In: Technische Regeln und Richtlinien des BMA zur Verordnung über gefährliche Stoffe. Bek. des BMA vom 28. 2. 1986, Bundesarbeitsblatt 4/1986, pp. 61–63.
[5] TRgA 551: Pyrolyseprodukte aus organischem Material. In: Technische Richtlinien des BMA zur Verordnung über gefährliche Stoffe. Bek. des BMA vom 25. 7. 1984, Bundesarbeitsblatt 9/1984, pp. 49–52.
[6] *WHO.* International Agency for Research of Cancer. Polynuclear aromatic compounds. Part 1, Chemical environmental and experimental data. Lyon: IARC 1983 (IARC monographs Vol. 32).
[7] *R. Tomingas:* Remarks on the sampling for polycyclic aromatic hydrocarbons from the atmosphere. Fresenius Z. Anal. Chem. *297,* 97–101 (1979).

[8] *W. Funcke, J. König* and *F. Pott:* Lufstaubsammeleinrichtungen zur quantitativ optimalen Abscheidung von polycyclischen aromatischen Kohlenwasserstoffen. VDI-Bericht 358, Luftverunreinigung durch polycyclische aromatische Kohlenwasserstoffe - Erfassung und Bewertung. VDI-Verlag, Düsseldorf 1980, pp. 121–126.
[9] *T. Spitzer:* Clean-up of polynuclear aromatic hydrocarbons from air particulate matter on XAD-2. J. Chromatogr. *237,* 273–278 (1982).

Authors: *W. Riepe, K. G. Liphard*
Examiner: *U. Knecht*

Table 1. Parameters for evaluation of the method.

PAH	Mean value µg PAH per mL	Abs. standard deviation µg/mL	Rel. standard deviation %	Range %
fluoranthene	108	11	10	23
pyrene	87	7	8	18
benz [a] anthracene	145	11	8	17
chrysene/triphenylene	169	8	5	10
benzofluoranthenes	320	11	3	8
benzo [e] pyrene	163	9	6	12
benzo [a] pyrene	99	4	4	9
perylene	18	3	11	25
indeno[l,2,3-cd]pyrene	60	8	13	30
dibenz [a,h] anthracene	23	3	17	38
benzo [ghi] perylene	47	8	17	38
anthanthrene	10	2	20	45

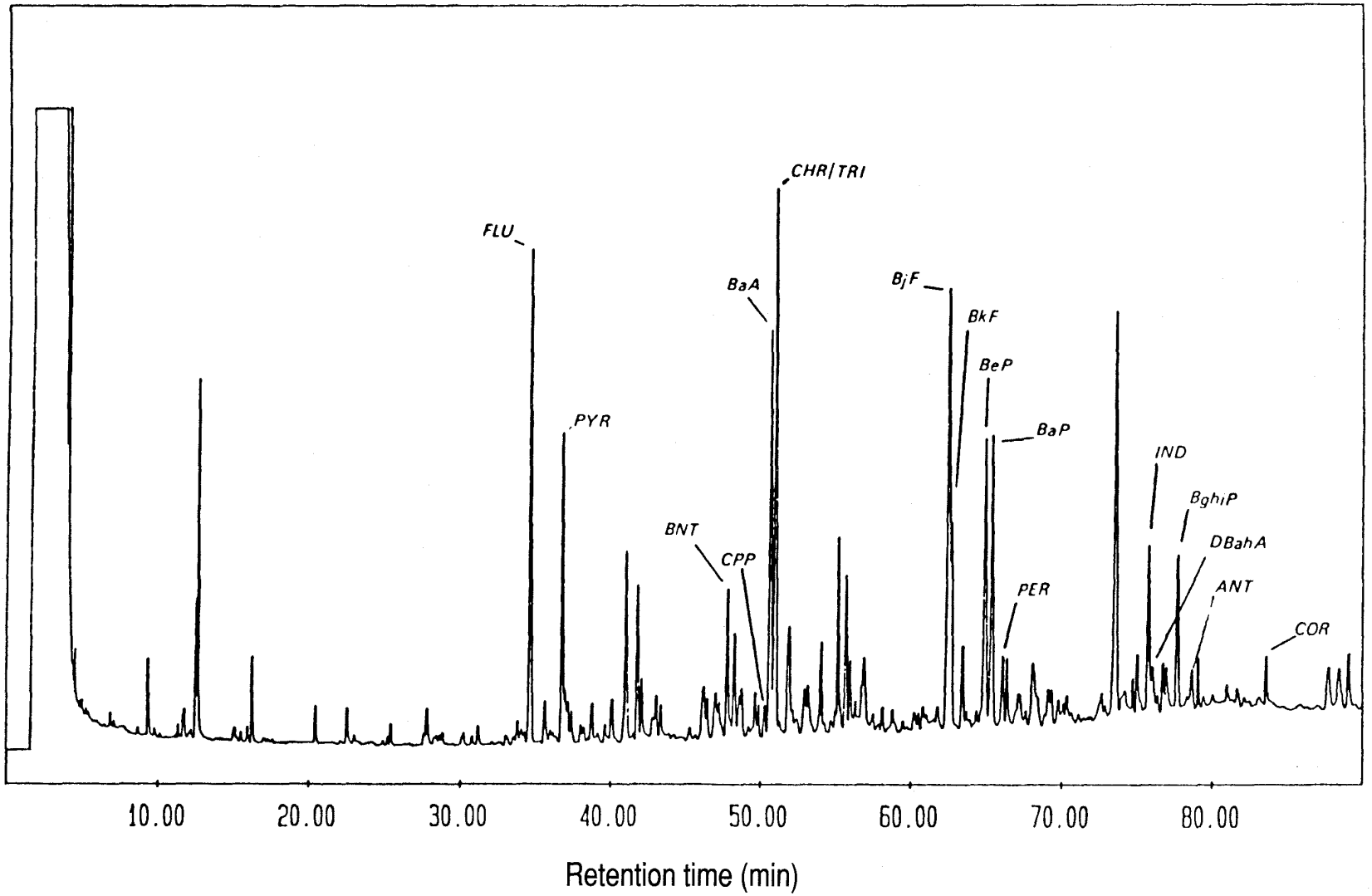

Fig. 1. Extract of airborne dust from a workplace: Gas chromatogram from a 25 m Sil 5 fused silica capillary.