Formulae: Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 5506, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 3: 15 January 1998

OSHA : Table 3
NIOSH: Table 3
ACGIH: Table 3

PROPERTIES: Table 1

Compounds

acenaphthene	benzo[ghi]perylene	fluorene
acenaphthylene	benzo[a]pyrene	indeno[1,2,3-cd]pyrene
anthracene	benzo[e]pyrene	naphthalene
benz[a]anthracene	chrysene	phenanthrene
benzo[b]fluoranthene	dibenz[a,h]anthracene	pyrene
benzo[k]fluoranthene	fluoranthene	

NAMES & SYNONYMS: Polycyclic aromatic hydrocarbons, PAHs; also see Table 2.

SAMPLING

SAMPLER: FILTER + SORBENT TUBE (37-mm, 2-µm, PTFE + washed XAD-2, 100 mg/50 mg)

FLOW RATE: 2 L/min

VOL-MIN: 200 L
-MAX: 1000 L

SHIPMENT: transfer filters to culture tubes; wrap sorbent and culture tubes in Al foil; ship @ 0 °C

SAMPLE STABILITY: unknown; protect from heat and UV light

FIELD BLANKS: 3 to 10 field blanks per set
MEDIA BLANKS: 6 to 10 media blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, FLUORESCENCE/UV DETECTION

ANALYTE: compounds listed above

EXTRACTION: 5 mL acetonitrile; ultrasonic bath, 30 to 60 minutes

INJECTION VOLUME: 10 to 50 µL

MOBILE PHASE: acetonitrile/water gradient @ ambient temperature, 1 mL/min

COLUMN: 250 x 4.6-mm, reversed-phase, 5-µm C_{18}

DETECTOR: UV @ 254 nm; fluorescence @ 340 nm (excitation), 425 nm (emission)

CALIBRATION: standards in acetonitrile

RANGE: see EVALUATION OF METHOD

ESTIMATED LOD: see EVALUATION OF METHOD

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: This method is applicable to samples that can be extracted with acetonitrile. This method is not applicable to samples that require a different extraction solvent or contain large amounts of highly adsorptive particulate matter, e.g., fly ash or diesel soot; also, this method is not applicable to asphalt fume samples.

INTERFERENCES: Any compound that elutes at the same HPLC retention time may interfere. Heat, ozone, NO_2, or UV light may cause sample degradation.

OTHER METHODS: This revises P&CAM 206 and 251 [1]. Method 5515 uses the same sampling technique, with gas chromatographic measurement [2]. Method 5800 uses the same sampling technique, and a flow-injection method to determine total polycyclic aromatic compounds at two different sets of fluorescent wavelengths [3].

REAGENTS:

1. Water, distilled, deionized, degassed.
2. Acetonitrile, HPLC grade, degassed.
3. PAH test mixture,* a liquid standard containing the PAHs except benzo[e]pyrene (EPA 610 Polynuclear Aromatic Hydrocarbons, Supelco, Cat. No. 4-8743; or equivalent).
4. Benzo[e]pyrene,* solid (Supelco, Cat. No. 44-2475; or equivalent).

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
   a. Filter. 37-mm, 2-µm pore size, PTFE membrane filter laminated to PTFE, (Zefluor, Pall Gelman Sciences, Cat. No. P5PJ037; SKC Inc., Cat. No. 225-17-07; or equivalent filter), cellulose spacer ring, 37-mm OD, 32-mm ID, (SKC Inc., Cat. No. 225-23; or equivalent) in a 37-mm cassette filter holder.
      NOTE: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
   b. Sorbent tube, washed XAD-2 resin (front = 100 mg; back = 50 mg) (ORBO 43, Supelco, Cat. No. 2-0258; or equivalent), connected to filter with minimum length of PVC tubing. Plastic caps are required after sampling.
      NOTE: If pressure drop is excessive or pump fails, use a larger diameter sorbent tube with XAD-2 resin (ORBO 42 Large, Supelco, Cat. No. 2-0264U; or equivalent).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Refrigerant, bagged.
5. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
6. Forceps.
7. Syringe filters, 0.45-µm, 25-mm, PTFE (Acrodisc-CR, Pall Gelman Sciences, Cat. No. 4219; or equivalent).
8. Pipet, 5-mL.
9. Syringe or micropipets, 1- to 100-µL.
10. Ultrasonic bath.
11. HPLC, with gradient capability, fluorescence (excitation @ 340 nm, emission @ 425 nm) and UV (254 nm) detectors in series, electronic integrator, and a 250 x 4.6-mm C_{18} column (Vydac 201TP, The Separations Group, Hesperia, CA, Cat. No. 201TP54; or equivalent).
12. Volumetric flasks, 10- and 100-mL.
13. Recommendation: lighting in laboratory should be incandescent or UV-shielded fluorescent.

SPECIAL PRECAUTIONS: Treat all polynuclear aromatic hydrocarbons as carcinogens. Samples and unused standards are considered toxic waste. Dispose of in an appropriate manner. Counter tops and equipment should be checked regularly with a "black light" for fluorescence as an indicator of contamination by PAHs.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Take personal samples at 2 L/min for a total sample size of 200 to 1000 L.
3. Immediately after sampling, transfer the filter carefully with forceps to a culture tube. Hold filter at edge to avoid disturbing the collected sample. Cap the tube and wrap in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes by sublimation.
4. Cap the sorbent tube and wrap in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAHs; therefore, recommend using yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Extract PAH from filters.
   a. Add 5.0 mL of acetonitrile to each culture tube containing a filter. Similarly, add 5.0 mL of acetonitrile to each culture tube containing the media and reagent blanks. Cap the tubes.
   b. Place capped tubes in an ultrasonic bath for 30 to 60 min.
8. Desorb PAH from sorbent.
   a. Score each sorbent tube with a file in front of the front (larger) sorbent section. Break tube at score line.
   b. Transfer front glass wool plug and front sorbent section to a culture tube. Transfer back sorbent section, and the middle glass wool plug to a second culture tube.
   c. Add 5.0 mL acetonitrile to each culture tube. Cap the tubes.
   d. Place capped tubes in an ultrasonic bath for 30 to 60 min.
9. Filter all sample extracts through an 0.45-µm syringe filter.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    NOTE: If a benzo[e]pyrene standard is needed, weigh desired amount and add to a known volume of the PAH test mixture.
    a. Dilute aliquots of thePAH test mixture (containing benzo[e]pyrene if needed) with acetonitrile in 10-mL volumetric flasks. The concentration range should cover most of the PAH concentrations in the samples.
    b. During analysis, intersperse working standards with samples and blanks.
    c. Prepare calibration graphs (peak area vs. µg of each PAH per sample).
11. Recovery and desorption efficiency.
    a. Determine recovery (R) from filters and desorption efficiency (DE) from sorbent tubes at least once for each lot of filters and sorbent tubes used in the range of interest.
       (1) Filters. Using a microliter syringe or a micropipette, spike four filters at each of five concentration levels with a mixture of the analytes. Allow the filters to dry in the dark overnight. Analyze the filters (steps 7, 9, and 13 through 15). Prepare graphs of R vs. amounts found.
       (2) Sorbent tubes. Transfer an unused front sorbent section to a culture tube. Prepare a total of 24 culture tubes in order to measure DE at five concentration levels plus blank in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight. Desorb and analyze (steps 8, 9, and 13 through 15). Prepare graphs of DE vs. amounts found.
    b. Check R and DE at two levels for each sample set, in duplicate. Repeat determination of R or DE graphs if checks do not agree to within ±5% of R or DE graph.
12. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

13. Set HPLC according to manufacturer's instructions, conditions on page 5506-1, and steps 14 and 15.
14. Inject sample aliquot (10 to 50 µL). Start mobile phase gradient:
    a. Linear gradient from 60% acetonitrile/40% deionized water to 100% acetonitrile at 1 mL/min over 20 min.
    b. Hold at 100% acetonitrile for 20 min.
    c. Linear gradient to initial condition, 5 min.
15. Measure peak areas for each analyte using the appropriate detector as specified in Table 1.
    NOTE 1: The order of elution for the PAHs appears in Table 4.
    NOTE 2: If peak area is above the calibration range, dilute with acetonitrile, reanalyze, and apply dilution factor in calculations.
    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary.

CALCULATIONS:

16. Read the mass, µg (corrected for R or DE) of each analyte found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blank filter (B) and front sorbent (B_f) and back sorbent (B_b) sections from the calibration graphs.
17. Calculate concentration, C (mg/m^3), as the sum of the particulate concentration and the vapor concentration in the actual air volume sampled, V (L).

$$C = \frac{\left(W + W_f + W_b - B - B_f - B_b\right)}{V}, \ mg/m^3$$

NOTE 1: $\mu g/mL \equiv mg/m^3$

NOTE 2: W_f and W_b include analyte originally collected on the filter as particulate, then volatilized during sampling. This can be a significant fraction for many PAHs (e.g., anthracene, fluoranthene, fluorene, naphthalene, phenanthrene).

EVALUATION OF METHOD:

The UV detector is used to analyze for some PAHs (see Table 1), and the remaining PAHs are analyzed by a fluorescent detector, which gave better sensitivity for some PAHs. The ranges of the limit of detection (LOD) and the limit of quantitation (LOQ) values for the 17 PAHs are reported in Table 4 [4]. The LOD and LOQ values varied because of differences in the detectors used and the concentrations of the standards. Therefore, it is important that the LOD and LOQ values be determined for each set of samples. The LOQs are the lower end of the analytical ranges. The upper end of the analytical ranges were not determined.

This method was evaluated by means of a user check [5]. An independent laboratory prepared spiked filters and sorbent tubes for a recovery and desorption efficiency study (see Table 4). For the filters, except naphthalene, the recovery results were greater than or equal to 75%. Since naphthalene is fairly volatile under ambient conditions, this may account for the poor recovery results. For the sorbent tubes, only four of the 17 analytes had desorption efficiencies that were greater than or equal to 75%. During the user check, the sorbent tubes were extracted by adding 5 mL acetonitrile and were allowed to stand for 30 minutes with occasional swirling. In more recent quality control experiments, the desorption efficiencies were often better for some analytes (see Table 4) [4]. These results were achieved using an ultrasonic bath for 30 to 60 minutes. The results indicated the importance of preparing media spikes for recovery and desorption efficiency studies for each set of samples; moreover, the results reenforce this need when using new lots of media.

REFERENCES:

[1] NIOSH [1977]. Total particulate aromatic hydrocarbons: Method P&CAM 206. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-A.

[2] NIOSH [1994]. Polynuclear aromatic hydrocarbons by GC: Method 5515. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] NIOSH [1998]. Polycyclic aromatic compounds: Method 5800. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM®), 4th ed., 2nd Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-119.

[4] NIOSH unpublished data.

[5] User Check Report for Method 5506, Analytical Report for NIOSH Sequence 4170 (NIOSH, DPSE, MRSB, unpublished, March 16, 1984).

[6] Handbook of Chemistry and Physics, 78th ed. [1997], Boca Raton, FL: CRC Press.

[7] IARC [1983]. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans: polynuclear aromatic compounds, Part 1, chemical, environmental and experimental data. Vol. 32. Lyon, France: World Health Organization, International Agency for Research on Cancer.

[8] Lenga RE, Votoupal KL, eds. [1993]. The Sigma-Aldrich library of regulatory and safety data, Volume 1. Sigma-Aldrich Company.

[9] NIOSH [1998]. Registry of toxic effects of chemical substances data base. Cincinnati, OH: National Institute for Occupational Safety and Health. Unpublished data base.

[10] NIOSH [1997]. NIOSH pocket guide to chemical hazards. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 97-140.

[11] ACGIH [1997]. 1997 TLVs® and BEIs®, Threshold limit values for chemical substances and physical agents, Biological exposure Indices. Cincinnati, OH: American Conference of Governmental Industrial Hygienists (ACGIH).

[12] NIOSH [1992]. NIOSH recommendations for occupational safety and health, compendium of policy documents and statements. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-100.

METHOD REVISED BY:

L. D. Olsen, B. R. Belinky, C. E. Neumeister, L. B. Jaycox, and D. D. Dollberg, NIOSH/DPSE.

TABLE 1. FORMULAS AND PHYSICAL PROPERTIES.

COMPOUND (by M.W.)	FORMULA	WEIGHT	DETECTOR	MELTING POINT (°C)	BOILING POINT (°C)	REFERENCE
1. NAPHTHALENE	$C_{10}H_8$	128.17	UV	80.2	218	[6]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	UV	92.5	280	[6]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	UV	93.4	279	[6]
4. FLUORENE	$C_{13}H_{10}$	166.22	UV	115	295	[6]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	UV	215	340	[6]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	UV	99.2	340	[6
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	FL	108	384	[6]
8. PYRENE	$C_{16}H_{10}$	202.26	FL	151	404	[6]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	FL	167	435	[7]
10. CHRYSENE	$C_{18}H_{12}$	228.29	UV	258	448	[6]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	FL	168	--	[7]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	FL	217	480	[6]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	FL	177	495	[6, 8]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	FL	178	311	[6]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	FL	278	--	[7]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	FL	164	--	[7]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	FL	270	524	[7, 8]

TABLE 2. SYNONYMS, CAS AND RTECS NUMBERS.

COMPOUND (alphabetically)	SYNONYMS, CAS and RTECS Numbers*
1. ACENAPHTHENE	CAS # 83-32-9; RTECS # AB1000000
2. ACENAPHTHYLENE	acenaphthalene; CAS # 208-96-8; RTECS # AB1254000
3. ANTHRACENE	CAS # 120-12-7; RTECS # CA9350000
4. BENZ[a]ANTHRACENE	1,2-benzanthracene; benzo[b]phenanthrene; 2,3-benzophenanthrene; tetraphene; CAS # 56-55-3; RTECS # CV9275000
5. BENZO[b]FLUORANTHENE	3,4-benzofluoranthene; 2,3-benzofluoranthene; benz[e]acephenanthrylene; B(b)F; CAS # 205-99-2; RTECS # CU1400000
6. BENZO[k]FLUORANTHENE	11,12-benzofluoranthene; CAS # 207-08-9; RTECS # DF6350000
7. BENZO[ghi]PERYLENE	1,12-benzoperylene; CAS # 191-24-2; RTECS # DI6200500
8. BENZO[a]PYRENE	3,4-benzopyrene; 6,7-benzopyrene; B(a)P; BP; CAS # 50-32-8; RTECS # DJ3675000
9. BENZO[e]PYRENE	1,2-benzopyrene; 4,5-benzopyrene; B(e)P; CAS # 192-97-2; RTECS # DJ4200000
10. CHRYSENE	1,2-benzophenanthrene; benzo[a]phenanthrene; CAS # 218-01-9; RTECS # GC0700000
11. DIBENZ[a,h]ANTHRACENE	1,2,5,6-dibenzanthracene; CAS # 53-70-3; RTECS # HN2625000
12. FLUORANTHENE	benzo[jk]fluorene; CAS # 206-44-0; RTECS # LL4025000
13. FLUORENE	CAS # 86-73-7; RTECS # LL5670000
14. INDENO[1,2,3-cd]PYRENE	2,3-phenylenepyrene; CAS # 193-39-5; RTECS # NK9300000
15. NAPHTHALENE	naphthene; CAS # 91-20-3; RTECS # QJ0525000
16. PHENANTHRENE	CAS # 85-01-8; RTECS # SF7175000
17. PYRENE	benzo[def]phenanthrene; CAS # 129-00-0; RTECS # UR2450000

* Data from [6, 8, and 9].

TABLE 3. EXPOSURE LIMITS*.

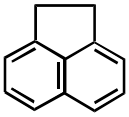
COMPOUND	OSHA†	NIOSH†	ACGIH‡
1. ANTHRACENE	0.2 mg/m^3	--	
2. BENZ[a]ANTHRACENE	--	--	suspect human carcinogen
3. BENZO[b]FLUORANTHENE	--	--	suspect human carcinogen
4. BENZO[a]PYRENE	0.2 mg/m^3	--	suspect human carcinogen
5. CHRYSENE	0.2 mg/m^3	potential occupational carcinogen§	animal carcinogen
6. NAPHTHALENE	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
7. PHENANTHRENE	0.2 mg/m^3	--	--
8. PYRENE	0.2 mg/m^3	--	--

* This table only includes the compounds with established exposure limit values.
† Information from [10].
‡ Information from [11].
§ Information from [12].

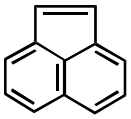
TABLE 4. LOD AND LOQ VALUES, AND RECOVERY DATA.

COMPOUND (by elution order)	Range of values*		Recoveries (%)†	
	LOD (µg per sample)	LOQ (µg per sample)	Filters	Sorbent tubes
1. NAPHTHALENE	0.20 - 0.80	0.39 - 2.6	49.6	68.5
2. ACENAPHTHYLENE	0.090 - 2.0	0.28 - 6.6	98.2	98.2
3. ACENAPHTHENE	0.20 - 5.0	0.58 - 16.	--	--
4. FLUORENE	0.030 - 0.30	0.099 - 0.26	95.0	95.0
5. PHENANTHRENE	0.0070 - 0.060	0.023 - 0.19	99.0, 90.4*	84.0, 92.5*, 82.6*
6. ANTHRACENE	0.0010 - 0.090	0.023 - 0.30	81.8, 94.4*	72.8, 96.2*, 72.9*
7. FLUORANTHENE	0.0020 - 0.090	0.0066 - 0.30	94.9, 90.4*	73.0, 93.5*, 81.7*
8. PYRENE	0.0010 - 0.30	0.0036 - 0.99	94.4, 76.1*	84.9, 77.0*, 75.9*
9. BENZ[a]ANTHRACENE	0.0010 - 0.090	0.0042 - 0.30	86.6, 92.7*	62.4, 95.0*, 72.3*
10. CHRYSENE	0.0070 - 0.20	0.023 - 0.37	94.6, 89.9*	62.7, 89.8*, 74.0*
11. BENZO[e]PYRENE	0.0060 - 0.80	0.020 - 2.6	110	48.3
12. BENZO[b]FLUORANTHENE	0.0030 - 0.20	0.011 - 0.66	94.8	64.2
13. BENZO[k]FLUORANTHENE	0.0020 - 0.040	0.0054 - 0.13	103	53.2
14. BENZO[a]PYRENE	0.0020 - 0.10	0.0051 - 0.33	101, 88.1*	50.4, 91.6*, 68.4*
15. DIBENZ[a,h]ANTHRACENE	0.0040 - 0.60	0.014 - 2.0	76.5	61.0
16. BENZO[ghi]PERYLENE	0.0030 - 0.50	0.011 - 1.7	76.5	61.0
17. INDENO[1,2,3-cd]PYRENE	0.0090 - 0.20	0.027 - 0.66	91.6	36.5

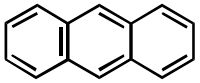
* Data from [4].
† Data from [5]



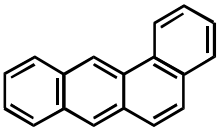
ACENAPHTHENE



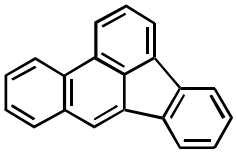
ACENAPHTHYLENE



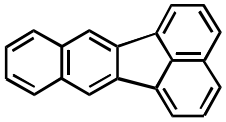
ANTHRACENE



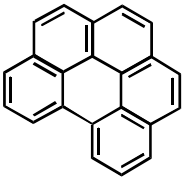
BENZ[a]ANTHRACENE



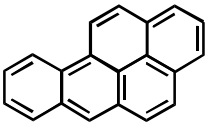
BENZO[b]FLUORANTHENE



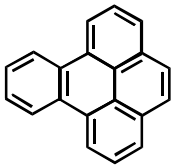
BENZO[k]FLUORANTHENE



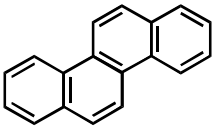
BENZO[g h i]PERYLENE



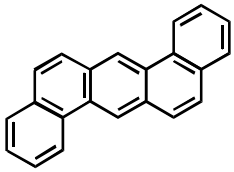
BENZO[a]PYRENE



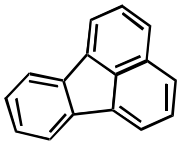
BENZO[e]PYRENE



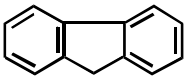
CHRYSENE



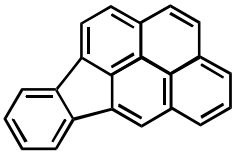
DIBENZ[a,h]ANTHRACENE



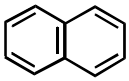
FLUORANTHENE



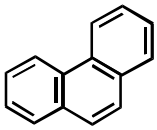
FLUORENE



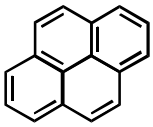
INDENO[1,2,3-c d]PYRENE



NAPHTHALENE



PHENANTHRENE



PYRENE

Figure 1. Structure of the PAHs.