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

METHOD: 5515, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

NIOSH: Table 3
OSHA :

PROPERTIES: Table 1

COMPOUNDS:

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

SYNONYMS: PAH; PNA; also see Table 2.

SAMPLING

SAMPLER: FILTER + SORBENT (2-µm, 37-mm 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 radiation

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 to 10

AREA SAMPLES: 8 replicates on preweighed filters for solvent selection

ACCURACY

RANGE STUDIED, ACCURACY, BIAS, and OVERALL PRECISION ($\hat{S}_{rT}$): not measured

MEASUREMENT

METHOD: GAS CHROMATOGRAPHY, CAPILLARY COLUMN, FID

ANALYTE: compounds above

EXTRACTION: 5 mL organic solvent appropriate to sample matrix (step 7)

INJECTION VOLUME: 4 µL; 10:1 split

COLUMN: 30 m x 0.32-mm ID, fused silica capillary, 1-µm DB-5

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 250 °C
-PROGRAM: 130 to 290 °C @ 4 °C/min

GASES-CARRIER: He @ 1 mL/min
-MAKEUP: He @ 20 mL/min

LOD: ca. 0.3 to 0.5 µg per sample [1]

CALIBRATION: external standards in toluene

RANGE, LOD, and PRECISION ($\hat{S}_r$): EVALUATION OF METHOD

APPLICABILITY: The working range for B[a]P is 3 to 150 µg/m^3 for a 400-L air sample. Specific sample sets may require modification in filter extraction solvent, choice of measurement method, and measurement conditions.

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

OTHER METHODS: This revises P&CAM 183 [2]. The spectrophotometric methods, P&CAM 184 and 186 [2], have not been revised. Method 5506 (HPLC) uses the same sampling technique and is more sensitive.

REAGENTS:

1. Filter extraction solvent: acetonitrile, benzene,* cyclohexane, methylene chloride,* or other appropriate solvents, pesticide grade (step 7).
2. Toluene, pesticide grade.
3. Water, distilled, deionized.
4. PAH reference standards,* appropriate to the PAH-containing matrix sampled.
5. Calibration stock solution, 0.25 mg/mL.* Check purity of each PAH reference standard by GC/FID, HPLC/fluorescence and/or melting point. Purify, if necessary, by recrystallization. Weigh 25 mg of each PAH into a 100-mL volumetric flask; dilute to volume with toluene. Stable six months if refrigerated and protected from light.
6. Helium, prepurified.
7. Hydrogen, dry.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter. PTFE-laminated membrane filter, 2-µm pore size, 37-mm diameter (Gelman Zefluor, Membrana, Pleasantown, CA, or equivalent), backed by a spacer (37-mm OD, 32-mm ID) cut from a cellulose support pad or SKC #225-23, in cassette filter holder.
      NOTE 1: If sampling is to be done in bright sunlight, use opaque or foil-wrapped cassettes to prevent sample degradation.
      NOTE 2: Take filters to be preweighed from the filter package and allow to equilibrate 24 h with laboratory atmosphere before taring.
   b. Sorbent tube, connected to filter with minimum length PVC tubing. Plastic caps are required after sampling. Washed XAD-2 resin (front = 100 mg; back = 50 mg) (Supelco ORBO 43 or equivalent). Pressure drop at 2 L/min airflow 1.6 to 2 kPa (15 to 20 cm H_2O).
2. Personal sampling pump capable of operating for 8 h at 2 L/min, with flexible connecting tubing.
3. Aluminum foil.
4. Vial, scintillation, 20-mL, glass, PTFE-lined cap.
5. Refrigerant, bagged.
6. Culture tubes, PTFE-lined screw cap, 13-mm x 100-mm.
7. Forceps.
8. Filters, 0.45-µm, PTFE (for filtering sample solutions).
9. Pipet, 5-mL.
10. Syringes or micropipets, 1- to 100-µL.
11. Ultrasonic bath.
12. Gas chromatograph with FID, electronic integrator, and capillary column (page 5515-1).
13. Volumetric flasks, 10- and 100-mL.
14. Lighting in laboratory: incandescent or UV-shielded fluorescent.

SPECIAL PRECAUTIONS: Treat benzene, methylene chloride, and all polynuclear aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination by PAH.

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. Take a concurrent set of eight replicate area samples at 2 to 4 L/min on preweighed, 2-µm PTFE filters in an area of highest expected PAH concentration.
   NOTE: The area samples are needed for solvent selection (step 7).
3. Immediately after sampling, transfer the filter carefully with forceps to a scintillation vial. Hold filter at edge to avoid disturbing the deposit. Cap the scintillation vial and wrap it in aluminum foil.
   NOTE: This step is necessary to avoid loss of analytes due to sublimation and degradation by light.
4. Cap the sorbent tube and wrap it in aluminum foil.
5. Ship to laboratory in insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: UV light may degrade PAH. Use yellow, UV-absorbing shields for fluorescent lights or use incandescent lighting.

6. Refrigerate samples upon receipt at laboratory.
7. Determine optimum extraction solvent.
   a. Allow the preweighed area filter samples to equilibrate 24 h with the laboratory atmosphere.
   b. Weigh the area filters. Determine total weight collected on each.
   c. Extract the first pair of area filters with acetronitrile, the second with benzene, the third with cyclohexane, and the fourth with methylene chloride, according to step 8.
      NOTE: Use alternate solvents, if appropriate. PAH of interest may be entrained within, and adsorbed by, particulate matter collected on the filter. It is necessary to determine the solvent which maximizes recovery of the PAH from each sample matrix. For example, methylene chloride [3,4] and benzene:ethanol (4:1 v/v) [5] have been recommended for extraction of PAH from diesel exhaust particulate.
   d. Analyze the extracts for the PAH of interest (steps 10 through 18). Normalize the total mass of PAH found to the mass of sample collected.
   e. Choose the solvent which gives the highest recovery of PAH of interest. Use the solvent chosen to extract the personal filter samples.
8. Extract filters.
   a. Add 5.0 mL of the solvent chosen in step 7 to each scintillation vial containing a filter. Start media and reagent blanks at this step.
   b. Cap and let stand 15 to 20 min in an ultrasonic bath.
      NOTE: Soxhlet extraction may be required when large amounts of highly adsorptive particulate matter (e.g., fly ash or diesel soot) are present.
9. Desorb PAH from sorbent.
   a. Score each sorbent tube with a file in front of the primary (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 toluene to each culture tube. Cap the culture tubes.
d. Allow samples to stand for 30 min. Swirl occasionally.

10. Filter all sample extracts through an 0.45-µm membrane filter.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards.
    a. Dilute aliquots of calibration stock solution with toluene in 10-mL volumetric flasks (e.g., to 5, 1, 0.2, 0.05, and 0.005 µg/mL).
    b. Intersperse working standards and samples in the measurements.
    c. Prepare calibration graphs (peak area vs. µg of each PAH per sample).
12. 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 micropipette, spike four filters at each of five concentration levels with calibration stock solution. Allow the filters to dry in the dark overnight. Analyze the filters (steps 8, 10, and 14 through 16). Prepare graphs of R vs. amounts found.
            NOTE: This step may not be used for some highly adsorptive particulate matrices for which calibration by the method of standard additions may be more accurate.
        (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 blanks in quadruplicate. Using a microliter syringe or micropipette, add calibration stock solution directly to sorbent. Cap culture tubes and allow to stand overnight in the dark. Analyze (steps 9, 10, and 14 through 16). 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 and DE graphs if checks do not agree to within ±5% of DE graph.
13. Analyze at least three field blanks for each sample medium.

MEASUREMENT:

14. Set GC according to manufacturer's recommendations and to the conditions on page 5515-1.
15. Inject sample aliquot. Start temperature program.
16. Measure peak areas.
    NOTE 1: Approximate retention times appear in Table 4.
    NOTE 2: If peak area is above the calibration range, dilute with appropriate solvent, reanalyze, and apply dilution factor in calculations.
    NOTE 3: If sample has many interferences, additional sample cleanup may be necessary. Many cleanup procedures have been published. Liquid-liquid partitioning between cyclohexane and nitromethane [6,7] is widely used, but other techniques may be more appropriate for specific samples.

CALCULATIONS:

17. 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.
18. Calculate concentration, C (mg/m^3), in air as the sum of the particulate concentration and the vapor concentration using the actual air volume sampled, V (L).

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

EVALUATION OF METHOD:

Owing to large interferences that occured while utilizing NIOSH Method P&CAM 206 for samples collected during asphalt roofing operations, the gas chromatographic capillary column method was developed. The GC method has been evaluated using several hundred field filter and sorbent tube sampling trains. To date, no statistical studies have been initiated. Overall, standard spiked filters and sorbent tubes have yielded reproducible measurement calibration graphs. The method has been applied to the following sources with semi-quantitative results using three separate particulate extraction solvents (benzene, cyclohexane, acetonitrile): aluminum reduction facilities, asphalt fume, coal gasification plants, coal liquefaction plants, coal tar pitch, coke oven emissions, creosote treatment facilities, diesel exhaust, graphite electrode manufacturing, petroleum pitch, and roofing tearoff operations.

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Table 1. Formulae and physical properties.

COMPOUND (by M.W.)	EMPIRICAL FORMULA	MOLECULAR WEIGHT	MELTING POINT (°C)*	BOILING POINT (°C)*	REF.
1. NAPHTHALENE	$C_{10}H_8$	128.17	80.2	218	[10]
2. ACENAPHTHYLENE	$C_{12}H_8$	152.20	92-93	265-275	[11]
3. ACENAPHTHENE	$C_{12}H_{10}$	154.21	96.2	279	[11]
4. FLUORENE	$C_{13}H_{10}$	166.22	116	293-295	[10]
5. ANTHRACENE	$C_{14}H_{10}$	178.23	218	340	[10]
6. PHENANTHRENE	$C_{14}H_{10}$	178.23	100	340	[10]
7. FLUORANTHENE	$C_{16}H_{10}$	202.26	110	384*	[10], [12]
8. PYRENE	$C_{16}H_{10}$	202.26	156	393	[10]
9. BENZ[a]ANTHRACENE	$C_{18}H_{12}$	228.29	162-167	435	[10]
10. CHRYSENE	$C_{18}H_{12}$	228.29	255-256	448	[10]
11. BENZO[b]FLUORANTHENE	$C_{20}H_{12}$	252.32	168	--	[10]
12. BENZO[k]FLUORANTHENE	$C_{20}H_{12}$	252.32	217	480	[11]
13. BENZO[a]PYRENE	$C_{20}H_{12}$	252.32	179	495	[10]
14. BENZO[e]PYRENE	$C_{20}H_{12}$	252.32	178-179	--	[10]
15. BENZO[ghi]PERYLENE	$C_{22}H_{12}$	276.34	273	--	[10]
16. INDENO[1,2,3-cd]PYRENE	$C_{22}H_{12}$	276.34	161.5-163	530	[9]
17. DIBENZ[a,h]ANTHRACENE	$C_{22}H_{14}$	278.35	267	524	[10]

*Many of these compounds will sublime.

Table 2. Synonyms.

COMPOUND (alphabetically)	SYNONYMS
1. ACENAPHTHENE	CAS# 83-32-9; RTECS# AB1000000
2. ACENAPHTHYLENE	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; Idryl; CAS# 206-44-0; RTECS# LL4025000
13. FLUORENE	o-biphenylenemethane; 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

Table 3. Exposure Limits.

COMPOUND (alphabetically)	OSHA	NIOSH	ACGIH
1. ACENAPHTHENE	--	--	--
2. ACENAPHTHYLENE	--	--	--
3. ANTHRACENE	0.2 mg/m^3	--	--
4. BENZ[A]ANTHRACENE	--	--	--
5. BENZO[B]FLUORANTHENE	--	--	suspect carcinogen
6. BENZO[K]FLUORANTHENE	--	--	--
7. BENZO[GHI]PERYLENE	--	--	--
8. BENZO[A]PYRENE	0.2 mg/m^3 (benzene sol.)	0.1 mg/m^3 (cyclohexane sol.)	suspect carcinogen
9. BENZO[E]PYRENE	--	--	--
10. CHRYSENE	0.2 mg/m^3 (benzene sol.)	lowest feasible, carcinogen	suspect carcinogen
11. DIBENZ[A,H]ANTHRACENE	--	--	--
12. FLUORANTHENE	--	--	--
13. FLUORENE	--	--	--
14. INDENO[1,2,3-CD]PYRENE	--	--	--
15. NAPHTHALENE	10 ppm	10 ppm; STEL 15 ppm	10 ppm; STEL 15 ppm
16. PHENANTHRENE	0.2 mg/m^3	--	--
17. PYRENE	--	--	--

Table 4. Approximate PAH retention times.

COMPOUND	RETENTION TIME (min)*
1. NAPHTHALENE	not available
2. ACENAPHTHALENE	7.66
3. ACENAPHTHENE	8.37
4. FLUORENE	10.5
5. PHENANTHRENE	15.0
6. ANTHRACENE	15.3
7. FLUORANTHENE	21.4
8. PYRENE	22.6
9. BENZ[a]ANTHRACENE	29.4
10. CHRYSENE	29.6
11. BENZO[e]PYRENE	36.4
12. BENZO[b]FLUORANTHENE	35.1
13. BENZO[k]FLUORANTHENE	35.2
14. BENZO[a]PYRENE	36.2
15. DIBENZ[a,h]ANTHRACENE	43.9
16. BENZO[ghi]PERYLENE	45.6
17. INDENO[1,2,3-cd]PYRENE	43.6

*NOTE: Actual retention times will vary with individual columns and column age.