

POLYCHLOROBENZENES

5517

(1) C ₆ H ₃ Cl ₃	MW: (1) 181.45	CAS: (1) 120-82-1	RTECS: (1) DC2100000
(2) C ₆ H ₂ Cl ₄	(2) 215.89	(2) 95-94-3	(2) DB9450000
(3) C ₆ HCl ₅	(3) 250.34	(3) 608-93-5	(3) DA6640000

METHOD: 5517, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA : no PEL

PROPERTIES: Table 1

NIOSH: (1) C 5 ppm, Group III Pesticides;

(2) & (3) no REL

ACGIH: (1) C 5 ppm; (2) & (3) no TLV

SYNONYMS: (1) 1,2,4-trichlorobenzene
 (2) 1,2,4,5-tetrachlorobenzene
 (3) pentachlorobenzene

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + SOLID SORBENT TUBE (PTFE filter + XAD-2, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, ⁶³ Ni ECD
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	compounds above
VOL-MIN:	3 L	DESORPTION:	2 mL hexane; 30 min ultrasonic agitation
-MAX:	12 L	INJECTION VOLUME:	2 µL
SHIPMENT:	separate filter and sorbent tube	TEMPERATURE-INJECTION:	220 °C
SAMPLE STABILITY:	at least 13 days @ 25 °C [1]	-DETECTOR:	300 °C
FIELD BLANKS:	2 to 10 field blanks per set	-COLUMN:	160 °C
ACCURACY		GASES-CARRIER:	nitrogen, 30 mL/min
RANGE STUDIED:	Table 2	-PURGE:	nitrogen, 90 mL/min
BIAS:	Table 2	COLUMN:	2.0 m x 2-mm ID nickel, 10 % Carbowax 20M-TPA on 80/100-mesh Chromosorb WAW
OVERALL PRECISION (Ŝ_{r,t}):	Table 2	CALIBRATION:	standard solutions of analytes in hexane
ACCURACY:	Table 2	RANGE:	0.02 to 500 µg per sample [1]
		ESTIMATED LOD:	0.001 µg/mL in hexane [1]

APPLICABILITY: The working range is 0.002 to greater than 30 mg/m³ for each analyte for a 10-L air sample. Linear range of the detector is limited but samples are diluted prior to measurement.

INTERFERENCES: Using chromatographic conditions given above, 1,2,3,5-tetrachlorobenzene coelutes with 1,2,4,5-tetrachlorobenzene.

OTHER METHODS: This revises P&CAM 343 [2].

REAGENTS:

1. Hexane, distilled in glass.*
2. Pentachlorobenzene, 98%.*
3. 1,2,4,5-Tetrachlorobenzene, 98%.*
4. 1,2,4-Trichlorobenzene, 99%.*
5. Calibration stock solution, 100 mg/mL.
Dilute accurately weighed 500-mg portions of each analyte to 5 mL with hexane. Store in air tight container. Stock solution in stable indefinitely.
6. Amberlite, XAD-2, 20/50 mesh. Cleanse by Soxhlet extraction for 4 h with 4:1 (v/v) acetone/methanol, 4 h with hexane, and drying overnight at 70 to 100 °C under vacuum.

NOTE: During method evaluation, the capacity of cleansed bulk Amberlite XAD-2 was much higher than that of Amberlite XAD-2 obtained from some commercially available sorbent tubes.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Two-stage sampler:
 - a. Filter: PTFE filter, 13-mm, 5- μ m pore size, unlaminated (Millipore, SKC, Inc., or equivalent) in stainless steel holder, Swinny-type (Millipore, SKC, or equivalent).
 - b. Sorbent tube: glass, 7 cm long, 6.4-mm OD, 4-mm ID, flame sealed with plastic caps, containing two sections of cleansed Amberlite XAD-2 (front = 100 mg; back = 50 mg), separated and held in place by 4-mm silanized glass wool plugs. Tubes are commercially available (SKC, Inc. or equivalent).
 - c. Assembly: To outlet (male luer tip) of filter holder, attach a short (ca. 1.5") piece of PTFE tubing, 6-mm OD, 4-mm ID. Attach sorbent tube to PTFE tube on filter holder with a short piece or flexible tubing. Seal inlet of filter holder and outlet of sorbent tube with PTFE tape plastic caps.
2. Personal sampling pump, 0.01 to 0.2 L/min, flexible connecting tubing.
3. Gas chromatograph, ⁶³Ni electron capture detector, integrator, and column (see page 5517-7).
4. Vials, 5-mL, PTFE-lined caps.
5. Syringe, 10- μ L, readable to 0.1 μ L.
6. Volumetric flasks, 5-mL, and convenient sizes for making dilutions.
7. Pipets, 2-mL, and convenient sizes for making dilutions.
8. Ultrasonic bath.
9. Balance, readable to 1 mg.
10. PTFE tape.

SPECIAL PRECAUTIONS: Hexane (flash point = -22 C) is highly flammable. Prepare samples and standards in well-ventilated hood.

Chlorinated benzenes may irritate skin, eyes, and mucous membranes. Avoid inhalation and contact.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
NOTE: The filter stage permits measurement of exposures to polychlorobenzene aerosols. If it is known that such exposure is not likely, the filter may be omitted.
2. Remove caps from sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.

3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for total sample size of 3 to 12 L.
4. Separate filter from sorbent tube and seal both with PTFE tape and caps. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place filter in one vial, front glass wool plug and sorbent section in another vial, and rear sorbent section and enclosing glass wool plugs in third vial.
6. Add 2.0 mL hexane to each vial. Cap each vial.
7. Allow to stand 30 min with ultrasonic agitation.
8. Wash inside surfaces of filter holder with 2 to 3 mL hexane. Transfer washings to 5-mL volumetric flask and dilute to mark with hexane.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the linear range of the detector.
 - a. Prepare working standards by serial dilution of the calibration stock solution.
 - b. Analyze together with samples and blanks (steps 12 and 13).
 - c. Prepare calibration graph for each analyte (peak height or area vs. $\mu\text{g}/\text{mL}$ analyte).
10. Determine desorption efficiency (DE) over range of interest at least once for each lot of filters and sorbent used. Prepare three samplers at each of five levels plus three media blanks.
 - a. Prepare known concentrations of the analytes in hexane.
 - b. Inject a 5- μL aliquot directly onto the filter of an assembled sampler with a microliter syringe while drawing 12 L of analyte-free air through the sampler at 0.2 L/min.
 - c. Separate filter holder and sorbent tube, seal, and allow to stand overnight.
 - d. Desorb (steps 5 through 8) and analyze together with working standards (steps 12 and 13).

NOTE: Significant amounts should be found on the filters and holders only at the higher loadings. See EVALUATION OF METHOD.
 - e. Prepare graph of DE vs. μg of each analyte recovered. DE is the sum of amounts recovered from filter, holder, and sorbent sections divided by the amount taken.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5517-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE 1: Under these conditions, approximate t_{R} s are: 1,2,4-trichlorobenzene, 2.0 min; 1,2,4,5-tetrachlorobenzene, 3.3 min; pentachlorobenzene, 7.5 min.

NOTE 2: If peak area is above range of working standards, dilute with hexane, reanalyze and apply appropriate dilution factor in calculations.
13. Measure peak height or area.

CALCULATIONS:

14. Determine the concentration, $\mu\text{g/mL}$, for each analyte, and multiply by the desorption volume, mL, and the dilution factor, if any, to calculate the mass, μg , recovered.
15. Add the amounts recovered from filter, filter holder, sorbent front (W_f), and sorbent back (W_b) sections to determine the mass found in a field sample (W) or the average sampler blank (B), and correct for DE.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
16. Calculate concentration, C , of each analyte in air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{mg} / \text{m}^3$$

EVALUATION OF METHOD:

P&CAM 343 was issued on August 31, 1981 [2]. A two-stage sampler was tested using 10- to 12-L samples at 28 to 30 °C and >80% RH over the ranges 0.002 to 100 mg/m^3 for 1,2,4-trichlorobenzene, 0.003 to 31 mg/m^3 for 1,2,4,5-tetrachlorobenzene, and 0.008 to 22 mg/m^3 for pentachlorobenzene for this issue of Method 5517 [1,2]. The average recoveries were 0.957 for 1,2,4-trichlorobenzene, 1.014 for 1,2,4,5-tetrachlorobenzene, and 0.968 for pentachlorobenzene, with concentrations independently verified by collection in impingers. These biases were insignificant at a 0.05 significance level. For levels of 0.02, 0.1, 0.4, 0.5, 25, and 500 μg per sample, the average desorption efficiencies were 0.908 for 1,2,4-trichlorobenzene, 0.901 for 1,2,4,5-tetrachlorobenzene, and 0.917 for pentachlorobenzene. At 25 μg , only pentachlorobenzene was observed in significant amounts on the filter and holder (4.7% of the total amount recovered). However, at 500 μg , the average contribution from the filter and holder to the totals were 7.2% for 1,2,4-trichlorobenzene, 55.2% for 1,2,4,5-tetrachlorobenzene, and 67.9% for pentachlorobenzene. The use of polypropylene filter holders was rejected because even at the 500-ng level, polypropylene filter holders retained 14% of the 1,2,4-trichlorobenzene, 34% of the 1,2,4,5-tetrachlorobenzene, and 45% of the pentachlorobenzene. After storage for several days, this might not be recoverable. Polystyrene holders did not appear to retain chlorobenzenes, but were not available in the 13-mm size.

The capacity of the 100-mg sorbent section for 1,2,4-trichlorobenzene, the most volatile of the analytes, was 24 L for a concentration of 45 mg/m^3 at 40 °C and >80% RH. The test atmosphere also contained 1,2,4,5-tetrachlorobenzene at 22 mg/m^3 and pentachlorobenzene at 15 mg/m^3 . Capacities for the latter two analytes were not specifically determined, but were greater than 24 L. A storage stability study found no significant losses after 13-day storage in the dark at room temperature for 2.5-L samples containing 35 ng 1,2,4-trichlorobenzene, 63 ng 1,2,4,5-tetrachlorobenzene, and 43 ng pentachlorobenzene.

The configuration of the two-stage sampler has been simplified.

REFERENCES:

- [1] Dillon, H. K., and M. L. Bryant. Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene; and Polychlorinated Terphenyls: Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene, NIOSH Contract No. 210-79-0102, Southern Research Institute, Birmingham, AL (1981).

- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 343, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

METHOD WRITTEN (REVISED) BY:

R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0102.

TABLE 1. PROPERTIES.

Name	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure @ 25 °C		Density @ 20 °C (g/mL)	mg/m ³ per ppm @ NTP
			(mm Hg)	(kPa)		
1,2,4-Trichlorobenzene	16.95	213.5	0.291	0.039	1.454	7.42
1,2,4,5-Tetrachlorobenzene	139.5-140.5	243-246	<0.1	<0.0133	1.858 ^a	8.83
Pentachlorobenzene	86	277			1.834 ^b	10.23

^a Solid @ 22 °C.

^b Solid @ 6.5 °C.

TABLE 2. ACCURACY

Name	Range Studied ^a (mg/m ³)	Analytical Precision \bar{S}_i	Bias (%)	Overall Precision \bar{S}_{IT}	Accuracy (±%)
(1) 1,2,4-Trichlorobenzene	0.002 to 100	0.044	-4.3	0.093	19.3
(2) 1,2,4,5-Tetrachlorobenzene	0.003 to 31	0.042	1.4	0.097	19.5
(3) Pentachlorobenzene	0.008 to 22	0.057	-3.2	0.098	19.6

^a 10-L samples.