

FORMULA: Table 1

MW: Table 1

CAS: Table 1

RTECS: Table 1

METHOD: 1501, Issue 2

EVALUATION: PARTIAL

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OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

| | | | | |
|--|--------------|-------------------------|---------|--------------|
| COMPOUNDS: benzene | cumene | α -methylstyrene | styrene | vinyltoluene |
| (Synonyms in Table 1) <u>p-tert</u> -butyltoluene | ethylbenzene | naphthalene | toluene | xylene |

| SAMPLING | MEASUREMENT |
|--|---|
| <p>SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)</p> <p>FLOW RATE, VOLUME: Table 3</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: not determined</p> <p>BLANKS: 2 to 10 field blanks per set</p> <p>BULK SAMPLE: desirable, 1 to 10 mL; ship in separate containers from samples</p> | <p>TECHNIQUE: GAS CHROMATOGRAPHY, FID</p> <p>ANALYTE: hydrocarbons listed above</p> <p>DESORPTION: 1 mL CS₂; stand 30 min</p> <p>INJECTION VOLUME: 5 μL</p> <p>TEMPERATURE-INJECTION: 225 °C -DETECTOR: 225 °C -COLUMN: see step 11</p> <p>CARRIER GAS: N₂ or He, 25 mL/min</p> <p>COLUMN: glass, 3.0 m x 2-mm, 10% OV-275 on 100/120 mesh Chromosorb W-AW or equivalent (Table 4)</p> <p>CALIBRATION: analytes in CS₂</p> <p>RANGE AND PRECISION (\hat{S}_r): Table 4</p> <p>ESTIMATED LOD: 0.001 to 0.01 mg per sample with capillary column [1]</p> |
| ACCURACY | |
| <p>RANGE STUDIED: Table 3</p> <p>BIAS: Table 3</p> <p>OVERALL PRECISION (\hat{S}_{rT}): Table 3</p> <p>ACCURACY: Table 3</p> | |

APPLICABILITY: This method is for peak, ceiling and TWA determinations of aromatic hydrocarbons. It may be used for simultaneous measurements, though there is the possibility that interactions between analytes may reduce the breakthrough volumes and change desorption efficiencies.

INTERFERENCES: Use of the recommended column will prevent interference by alkanes ($\leq C_{10}$). Under conditions of high humidity, the breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are possible interferences. If interference is suspected, use a less polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene, styrene, toluene and xylene [2]; S311, benzene [4]; S22, p-tert-butyltoluene [3]; S23, cumene [3]; S29, ethylbenzene [3]; S26, α -methylstyrene [3]; S292, naphthalene [4]; S30, styrene [3]; S343, toluene [4]; S25, vinyltoluene [3]; S318, xylene [4].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality containing (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.
6. Naphthalene calibration stock solution, 0.40 g/mL in CS₂.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pumps, 0.01 to 1 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 1501-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, and pipet bulb.
6. Syringes, 5-, 10-, 25- and 100- μ L.
7. Volumetric flasks, 10-mL

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); benzene is a suspect carcinogen. Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the 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 (to 1 L/min for naphthalene or styrene) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range (ca. 0.01 to 10 mg analyte per sample; see Table 4).
 - a. Add known amounts of analyte (calibration stock solution for naphthalene) to eluent in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11 through 13).
 - c. Prepare calibration graph (peak area of analyte vs. mg analyte per sample).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

- a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of analyte (calibration stock solution for naphthalene) directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 through 13).
 - e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Select appropriate column temperature:

| Substance ^a | Approximate Retention Time (min), at Indicated Column Temperature | | | |
|------------------------------|---|--------|--------|-------------------------|
| | 50 °C | 100 °C | 150 °C | Programmed ^b |
| benzene | 2.5 | | | 2.5 |
| toluene | 4.3 | 1.1 | | 4.2 |
| xylene (<u>para</u>) | 7.0 | 1.4 | | 5.2 |
| ethylbenzene | 7.0 | 1.4 | | 5.5 |
| xylene (<u>meta</u>) | 7.2 | 1.5 | | 5.6 |
| cumene | 8.3 | 1.6 | | 6.0 |
| xylene (<u>ortho</u>) | 10 | 1.9 | | 6.5 |
| styrene | 16 | 2.6 | | 7.6 |
| α-methylstyrene | | 3.2 | 1.0 | 8.1 |
| vinyltoluene (<u>meta</u>) | | 3.8 | 1.2 | 8.5 |
| naphthalene | | 25 | 4.3 | 12 |

^a Data not available for p-tert-butyltoluene and p-vinyltoluene.

^b Temperature program: 50 °C for 3 min, then 15 °C/min to 200 °C.

NOTE: Alternatively, column and temperature may be taken from Table 4.

12. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Precisions and biases listed in Table 3 were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was not assessed. Measurement precisions given in Table 4 were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75%. Reference [9] provides more specific information.

REFERENCES:

- [1] User check, UBTL, NIOSH Sequence #4121-S (unpublished, December 7, 1983).
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
- [3] Ibid, V. 2, S22, S23, S25, S26, S29, S30, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [4] Ibid, V. 3, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [5] R. D. Dreisbach. "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
- [6] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington (1989); 29 CFR 1910.1000.
- [7] NIOSH Recommendations for Occupational Safety and Health. U.S. Department of Health and Human Services. DHHS (NIOSH) Publication No. 92-100 (1992).
- [8] 1992-1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, ACGIH, Cincinnati, OH (1992).
- [9] Documentation of the NIOSH Validation Tests, S22, S23, S25, S26, S29, S30, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185 (1977).

METHOD REVISED BY:

R. Alan Lunsford, Ph.D., based on results of NIOSH Contract CDC-99-74-45.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES [5].

| Name/Synonyms | Empirical Formula | Molec- ular Weight | Boiling Point (°C) | Vapor Pressure @ 25 °C (mm. Hg) | (kPa) | Density @ 20 °C (g/mL) |
|---|--|--------------------------|----------------------------------|---------------------------------------|------------------------------|----------------------------------|
| benzene CAS #71-43-2 RTECS CY1400000 | C ₆ H ₆ | 78.11 | 80.1 | 95.2 | 12.7 | 0.879 |
| p- <u>tert</u> -butyltoluene CAS #98-51-1 1- <u>tert</u> -butyl-4-methylbenzene RTECS XS8400000 | C ₁₁ H ₁₆ | 148.25 | 192.8 | 0.7 | 0.09 | 0.861 |
| cumene CAS #98-82-8 isopropylbenzene RTECS GR8575000 | C ₉ H ₁₂ | 120.20 | 152.4 | 4.7 | 0.63 | 0.862 |
| ethylbenzene CAS #100-41-4 RTECS DA0700000 | C ₈ H ₁₀ | 106.17 | 136.2 | 9.6 | 1.28 | 0.867 |
| α-methylstyrene CAS #98-83-9 isopropenylbenzene (1-methylethenyl)-benzene RTECS WL5075300 | C ₉ H ₁₀ | 118.18 | 165.4 | 2.5 | 0.33 | 0.911 |
| naphthalene CAS #91-20-3 RTECS QJ0525000 | C ₁₀ H ₈ | 128.18 | 80.2 ^a | 0.2 | 0.03 | 1.025 |
| styrene CAS #100-42-5 vinylbenzene RTECS WL3675000 | C ₈ H ₈ | 104.15 | 145.2 | 6.1 | 0.81 | 0.906 |
| toluene CAS #108-88-3 methylbenzene RTECS XS5250000 | C ₇ H ₈ | 92.14 | 110.6 | 28.4 | 3.79 | 0.867 |
| vinyltoluene ^b CAS #25013-15-4 methylstyrene (p-vinyltoluene) methylvinylbenzene RTECS WL5075000 | C ₉ H ₁₀ (<u>meta</u>) (<u>para</u>) (<u>ortho</u>) | 118.18 | 167.7 171.6 172.8 169.8 | 1.6 1.9 1.8 1.8 | 0.22 0.26 0.24 0.24 | 0.898 0.911 0.911 0.904 |
| xylene ^c CAS #1330-20-7 dimethylbenzene (p-xylene) RTECS ZE2100000 | C ₈ H ₁₀ (<u>ortho</u>) (<u>meta</u>) (<u>para</u>) | 106.17 | 144.4 139.1 138.4 | 6.7 8.4 8.8 | 0.89 1.12 1.18 | 0.880 0.864 0.861 |

^a Melting point.

^b Commercial mixture of meta and para isomers.

^c Mixture of isomers.

TABLE 2. PERMISSIBLE EXPOSURE LIMITS, PPM [6-8].

| Substance | OSHA | NIOSH | | | ACGIH | | mg/m ³ per ppm |
|---------------------|-----------|------------------|----|------|-----------------|------------|------------------------------|
| | TWA | TWA | C | STEL | TLV | STEL | |
| benzene | 1 | 0.1 ^c | 1 | | 10 ^f | | 3.19 |
| p-tert-butyltoluene | 10 | 10 | | 20 | 1 | | 6.06 |
| cumene | 50 (skin) | 50 (skin) | | | 50 (skin) | | 4.91 |
| ethylbenzene | 100 | 100 | | 125 | 100 | 125 | 4.34 |
| α-methylstyrene | 100 | | 50 | | | 100 | 50 100 |
| 4.83 | | | | | | | |
| naphthalene | 10 | 10 ^d | | 15 | 10 | 15 | 5.24 |
| styrene | 100 | 50 | | 100 | 50** | 100 (skin) | 4.26 |
| toluene | 200 | 100 | | 150 | 50 (skin) | | 3.77 |
| vinyltoluene | 100 | 100 | | | 50 | 100 | 4.83 |
| xylene | 100 | 100 ^e | | 150 | 100 | 150 | 4.34 |

- ^a Maximum duration 10 min in 8 h. ^f Suspect carcinogen
^b Maximum duration 5 min in any 3 h.
^c Potential carcinogen
^d Group III Pesticide
^e Group I Pesticide

TABLE 3. SAMPLING FLOWRATE^a, VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [3,4,9].

| Substance | Sampling | | | Breakthrough | | Range at VOL-MIN (mg/m ³) | Overall | | Accuracy (±%) |
|--------------------------|---------------------|-------------------------|-----|---------------------------|------|---|----------------------|--------------------|------------------|
| | Flowrate (L/min) | Volume ^b (L) | | Volume @ Concentration | (L) | | (mg/m ³) | Bias (%) | |
| benzene | ≤0.20 | 5 | 30 | >45 | 149 | 42- 165 | -0.4 | 0.059 | 11.4 |
| p-tert-butyltoluene | ≤0.20 | 1 | 29 | 44 | 112 | 29- 119 | -10.3 | 0.071 ^d | 20.7 |
| cumene | ≤0.20 | 1 | 30 | >45 | 480 | 120- 480 | 5.6 | 0.059 | 15.2 |
| ethylbenzene | ≤0.20 | 1 | 24 | 35 | 917 | 222- 884 | -7.6 | 0.089 ^d | 17.1 |
| α-methylstyrene | ≤0.20 | 1 | 30 | >45 | 940 | 236- 943 | -7.6 | 0.061 ^d | 16.9 |
| naphthalene ^e | ≤1.0 | 100 | 200 | >240 | 81 | 19- 83 | -2.6 | 0.055 | 11.5 |
| styrene | ≤1.0 | 1 | 14 | 21 | 1710 | 426-1710 | -7.9 | 0.058 ^d | 16.7 |
| toluene | ≤0.20 | 1 | 8 | 12 | 2294 | 548-2190 | 1.6 | 0.052 | 10.9 |
| vinyltoluene | ≤0.20 | 1 | 24 | 36 | 952 | 256- 970 | -7.0 | 0.061 ^d | 16.3 |
| xylene | ≤0.20 | 2 | 23 | 35 | 870 | 218- 870 | -1.2 | 0.060 | 12.2 |

- ^a Minimum recommended flow is 0.01 L/min.
^b V_{Min} = minimum sample volume @ OSHA TWA;
V_{Max} = maximum sample volume @ OSHA TWA
^c 10-min sample.
^d Corrected value, calculated from data in Reference 9.
^e Naphthalene shows poor desorption efficiency at low loading; 100-L minimum volume is recommended.
^f 15-min sample.
^g 5-min sample.

TABLE 4. MEASUREMENT RANGE, PRECISION AND CONDITIONS [3,4,9].

| Substance | Desorption Volume (mL) | Measurement | | Carrier Flow (mL/min) | Column Parameters ^b | | |
|----------------------------------|------------------------------|---------------|------------------------------|-----------------------------|--------------------------------|---------------|----------------------|
| | | Range (mg) | Precision (\bar{S}_r) | | t (°C) | Length (m) | Packing ^c |
| benzene | 1.0 | 0.09- 0.35 | 0.036 | 50 | 115 | 0.9 | A |
| p- tert -butyltoluene | 0.5 | 0.27- 1.09 | 0.021 ^d | 50 | 115 | 3.0 | B |
| cumene | 0.5 | 0.86- 3.46 | 0.010 | 50 | 99 | 3.0 | B |
| ethylbenzene | 0.5 | 2.17- 8.67 | 0.010 | 50 | 85 | 3.0 | B |
| α -methylstyrene | 0.5 | 0.69- 3.57 | 0.011 | 50 | 115 | 3.0 | B |
| naphthalene | 1.0 | 4.96-19.7 | 0.019 | 30 | 125 | 3.0 | C |
| styrene | 0.5 | 2.17- 8.49 | 0.013 ^d | 50 | 109 | 3.0 | B |
| toluene | 1.0 | 1.13- 4.51 | 0.011 | 50 | 155 | 0.9 | D |
| vinyltoluene | 0.5 | 2.41- 9.64 | 0.008 | 50 | 120 | 3.0 | B |
| xylene | 1.0 | 2.60-10.4 | 0.010 | 50 | 180 | 0.9 | D |

^a Injection volume, 5.0 μ L; nitrogen carrier gas.

^b All columns stainless steel, 3.2-mm outside diameter.

^c A, 50/80 mesh Porapak P; B, 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS;
C, 10% OV-101 on 100/120 mesh Supelcoport; D, 50/80 mesh Porapak Q.

^d Corrected value, calculated from data in [9].