HYDROCARBONS, AROMATIC 1501

FORMULA: Table 1 **MW:** Table 1 **CAS:** Table 1 **RTECS:** Table 1

| **METHOD:** 1501, Issue 3 | **EVALUATION:** Full | **Issue 1:** 15 August 1990 |
| | | **Issue 3:** 15 March 2003 |

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

PROPERTIES: Table 1

SYNONYMS: **Group A:** benzene toluene ethylbenzene <u>o</u>-xylene <u>m</u>-xylene <u>p</u>-xylene
(Synonyms in Table 1) **Group B:** cumene <u>p</u>-tert-butyltoluene α-methylstyrene β-methylstyrene styrene

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SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: Table 3

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Hydrocarbons listed above

DESORPTION: 1 mL CS_2, stand 30 min with agitation

INJECTION VOLUME: 1 µL (<u>Group A</u>: split 5:1;
<u>Group B</u>: split 1:1)

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: <u>Group A</u>: 40 °C (10 min) to 230°C (10 °C/min)
<u>Group B</u>: 35°C (8 min) to 225°C (10°C/min)

CARRIER GAS: He @ 2.6 mL/min

COLUMN: Capillary, fused silica
<u>Group A</u>: 30m x 0.32-mm ID; 1-µm film 100% PEG or equivalent
<u>Group B</u>: 30m x 0.53-mm ID; 3-µm film crossbonded® 35% diphenyl 65% dimethyl polysiloxane or equivalent

CALIBRATION: Solutions of analytes in CS_2

RANGE: Table 4

ESTIMATED LOD: Table 4

PRECISION ($\hat{S}_r$): Table 4

APPLICABILITY: This method is for peak, ceiling, and TWA determinations of aromatic hydrocarbons. Interactions between analytes may reduce breakthrough volumes and affect desorption efficiencies. Naphthalene, originally validated in S292 [4], failed to meet acceptable desorption efficiency recovery and storage stability criteria at the levels evaluated in this study. However, the application of this method to naphthalene levels at or near the REL/PEL continues to meet acceptable recovery criteria. Styrene failed to meet acceptable recovery criteria at the two lowest levels evaluated in this study (highest level to meet the criteria was 181 µg/sample).

INTERFERENCES: Under conditions of high humidity, the breakthrough volumes may be reduced. Other volatile organic compounds such as alcohols, ketones, ethers, and halogenated hydrocarbons are potential analytical interferences.

OTHER METHODS: This method updates NMAM 1501 issued on August 15, 1994 [1] which was based upon P&CAM 127 (benzene, styrene, toluene, and xylene) [2]; S22 (<u>p</u>-tert-butyltoluene) [3]; S23 (cumene) [3]; S29 (ethylbenzene) [3] ; S26 (α-methylstyrene) [3]; S30 (styrene); S311 (benzene) [4]; S343 (toluene) [4]; and S318 (xylenes) [4].

REAGENTS:

1. Carbon disulfide*, low benzene, chromatographic quality.
2. Analytes, reagent grade.
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

   * 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 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. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1.0 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and columns (page 1501-1).
4. Autosampler vials, glass, 1.8 mL, with PTFE-lined caps.
5. Pipets, 1-mL, and pipet bulb.
6. Syringes, 10-µL, 25-µL, and 250-µL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30°C), benzene is a suspect carcinogen. Prepare standards and samples 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 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. Include the glass wool plug in the vial along with the front sorbent section.
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 from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to carbon disulfide solvent in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 through 12).
   c. Prepare calibration graph (peak area of analyte vs. µg 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).
    a. Prepare three tubes at each of five levels plus three media blanks.
    b. Inject a known amount of DE stock solution (5 to 25 µL) directly onto front sorbent section of each charcoal tube with a microliter syringe.
    c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
    d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
    e. Prepare a graph of DE vs. µg analyte recovered.
10. Analyze a minimum of 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. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    Note: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze, and apply the appropriate dilution factor in the calculations.

Analyte	Approximate Retention Time (min)
benzene[a]	3.52
toluene[a]	6.13
ethylbenzene[a]	10.65
o-xylene[a]	12.92
m-xylene[a]	11.33
p-xylene[a]	11.04
cumene[b]	18.61
p-tert-butyltoluene[b]	21.45
α-methylstyrene[b]	19.99
β-methylstyrene[b]	20.82
styrene[b]	18.33

[a] Separation achieved using a 30-m Stabilwax fused silica capillary colum.
[b] Separation achieved using a 30-m Rtx-35 fused silica capillary column.

12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (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.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

    NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The desorption efficiency, at levels ranging from 5 times the LOQ to 0.1x the REL, was determined for each analyte by spiking known amounts (in CS_2) on coconut shell charcoal tubes. Both groups of analytes (A and B) were spiked together on the charcoal sorbent tubes. All analytes, with the exception of styrene and naphthalene, exhibited acceptable desorption efficiency recovery results at all five levels evaluated. Styrene failed to meet the 75% recovery criteria at the 18.1 µg and 90.6 µg levels. Naphthalene failed to meet the 75% criteria at all levels evaluated ranging from 48.8 µg to 976.0 µg.

Each analyte, at a level approximately 0.05x REL/PEL, was evaluated for its storage stability @ 5°C after 7, 14, and 30 days. All analytes, with the exception of naphthalene, had acceptable recoveries after 30 days storage.

REFERENCES:

[1] NIOSH [1984]. Hydrocarbons, Aromatic: Method 1501. In: Eller PM, ed. NIOSH Manual of Analytical Methods. 4th rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[2]   NIOSH [1977]. 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.
[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] NIOSH [1977]. 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.

METHOD WRITTEN BY:

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TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name/Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	(kPa)	Density @ 20 °C (g/mL)
benzene CAS #71-43-2 RTECS CY1400000	C_6H_6	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 RTECS XS8400000 1-tert-butyl-4-methylbenzene	$C_{11}H_{16}$	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 RTECS GR8575000 isopropylbenzene	C_9H_{12}	120.20	152.4	4.7	0.63	0.862
ethylbenzene CAS #100-41-4 RTECS DA0700000	C_8H_{10}	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 RTECS WL5075300 isopropenylbenzene (1-methylethenyl)-benzene	C_9H_{10}	118.18	165.4	2.5	0.33	0.909
β-methylstyrene CAS #873-66-5 RTECS DA8400500	C_9H_{10}	118.18	175.0	—	—	0.911
toluene CAS #108-88-3 RTECS XS5250000 methylbenzene	C_7H_8	92.14	110.6	28.4	3.79	0.867
xylene[c] CAS #1330-20-7 RTECS ZE2100000 dimethylbenzene (p-xylene)	C_8H_{10} (ortho) (meta) (para)	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
styrene CAS #100-42-5 RTECS WL3675000 vinylbenzene	C_8H_8	104.15	145.2	6.1	0.81	0.906

TABLE 2. PERMISSIBLE EXPOSURE LIMITS, PPM

Substance	OSHA TWA	NIOSH			ACGIH		mg/m³ per ppm
		TWA	C	STEL	TLV	STEL	
benzene	1	0.1[a]	1		10[b]		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
β-methylstyrene	100	50		100	50	100	4.83
toluene	200	100		150	50 (skin)		3.77
o-xylene	100	100[c]		150	100	150	4.34
m-xylene	100	100			100	150	4.34
p-xylene	100	100			100	150	4.34
styrene	100	50		100	50	100 (skin)	4.26

[a] Potential carcinogen
[b] Suspect carcinogen
[c] Group I Pesticide

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

Substance	Sampling			Breakthrough Volume @ Concentration		Range at VOL-MIN (mg/m³)	Overall		Accuracy (±%)
	Flowrate (L/min)	Volume[b] (L) MIN	MAX	(L)	(mg/m³)		Bias (%)	Precision ($\hat{S}_{rT}$)	
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[c]	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[c]	17.1
α-methylstyrene	≤0.20	1	30	>45	940	236 - 943	-7.6	0.061[c]	16.9
β-methylstyrene	≤0.20	1	30	>45	940	236 - 943	-7.6	0.061	16.9
toluene	≤0.20	1	8	12	2294	548 - 2190	1.6	0.052	10.9
xylene (o-,m-,p-)	≤0.20	2	23	35	870	218 - 870	-1.2	0.060	12.2
styrene	<1.00	1	14	21	1710	426 - 1710	-7.9	0.058[c]	16.7

[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] Corrected value, calculated from data in Reference 5.

TABLE 4. MEASUREMENT RANGE AND PRECISION[a]

Substance	LOD (µg/sample)	Measurement	
		Range (mg)	Precision ($\hat{S}_r$)
benzene	0.5	0.004-0.35	0.013
p-tert-butyltoluene	1.1	0.013-1.09	0.017[a]
cumene	0.6	0.039-3.46	0.017
ethylbenzene	0.5	0.045-8.67	0.015
α-methylstyrene	0.6	0.036-3.57	0.014
β-methylstyrene	0.6	0.036-0.728	0.014
toluene	0.7	0.024-4.51	0.022
o-xylene	0.8	0.044-10.4	0.014
m-xylene	0.8	0.043-0.864	0.013
p-xylene	0.7	0.043-0.861	0.015
styrene	0.4	0.181-8.49	0.014

[a] Corrected value, calculated from data in [5].