

FORMULA: Table 1

MW: Table 1

CAS: Table 1

RTECS: Table 1

METHOD: 1500, Issue 2

EVALUATION: FULL

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OSHA : Table 2

PROPERTIES: Table 1

NIOSH: Table 2

ACGIH: Table 2

COMPOUNDS:
(Synonyms
in Table 1)

benzene
cyclohexane
cyclohexene

n-heptane
n-hexane
methylcyclohexane

n-octane
n-pentane
toluene

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE, VOLUME:	Table 3	ANALYTE:	hydrocarbons listed above
SHIPMENT:	routine	DESORPTION:	1 mL CS ₂ ; stand 30 min
SAMPLE STABILITY:	at least 2 weeks	INJECTION VOLUME:	5 µL
BLANKS:	2 to 10 field blanks per set	TEMPERATURE-INJECTION:	250 °C
BULK SAMPLE:	desirable, 1 to 10 mL; ship in separate containers from samples	-DETECTOR:	250 °C
		-COLUMN:	see step 11
		CARRIER GAS:	N ₂ or He, 25 mL/min
		COLUMN:	glass, 3.0 m x 2-mm, 20% SP-2100 on 80/100 mesh Supelcoport
		CALIBRATION:	analytes in CS ₂
ACCURACY		RANGE AND PRECISION:	Table 4
RANGE STUDIED:	Table 3	ESTIMATED LOD:	0.001 to 0.01 mg per sample with capillary column [1]
BIAS:	Table 3		
OVERALL PRECISION ($\hat{S}_{r,T}$):	Table 3		
ACCURACY:	Table 3		

APPLICABILITY: This method is intended for determining the OSHA-regulated hydrocarbons included within the boiling point range of n-pentane through n-octane. It may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and change desorption efficiencies.

INTERFERENCES: At high humidity, breakthrough volumes may be reduced by as much as 50%. Other volatile organic solvents, e.g., alcohols, ketones, ethers, and halogenated hydrocarbons, are likely interferences. If interference is suspected, use a more polar column or change column temperature.

OTHER METHODS: This method is based on and supercedes Methods P&CAM 127, benzene and toluene [2]; S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S311, benzene [4]; S343, toluene [4]; S378, octane [4]; and S379, pentane [4]. For benzene or toluene in complex mixture of alkanes ($\leq C_{10}$), Method 1501 (aromatic hydrocarbons) is more selective.

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality with (optional) suitable internal standard.
2. Analytes, reagent grade.*
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, 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 (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 pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1500-1).
4. Vials, glass, 1-mL, with PTFE-lined caps.
5. Pipet, 1-mL, with 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 (0.01 to 0.05 L/min for n-pentane) 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 to eluent in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11, 12 and 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 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, 12 and 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. Check for possible contamination during shipment of field samples by comparing results from field blanks and media blanks.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1500-1. Select appropriate column temperature:

<u>Temperature</u>	<u>Approximate Retention Time (min), at Indicated Column</u>			
	<u>40 °C</u>	<u>70 °C</u>	<u>100 °C</u>	<u>Programmed^a</u>
<u>Substance</u>				
n-pentane	2.2	1.2		1.8
solvent (CS ₂)	3.0	1.6		2.4
n-hexane	5.1	2.2		3.5
benzene ^b	7.7	3.2		4.5
cyclohexane ^b	8.4	3.4		4.7
cyclohexene	9.5	3.8		4.9
n-heptane	12	4.3		5.4
methylcyclohexane	14	5.2	2.2	5.9
toluene	17	6.5	2.6	6.5
n-octane	19	8.7	3.2	7.1

^a Temperature program: 50 °C for 2 min, then 15 °C/min to 150 °C, 2-min final hold.

^b Not completely resolved.

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 (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 (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 [12] provides more specific information.

REFERENCES:

- [1] User check, UBTL, NIOSH Sequence #4213-L (unpublished, January 31, 1984).
- [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] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S28, S82, S89, S90, S94, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3., S311, S343, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [5] R. D. Driesbach, "Physical Properties of Chemical Compounds"; Advances in Chemistry Series, No. 15; American Chemical Society, Washington (1955).
- [6] R. D. Driesbach, "Physical Properties of Chemical Compounds - II"; Advances in Chemistry Series, No. 22; American Chemical Society, Washington (1959).
- [7] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1989); 29 CFR 1910.1000.
- [8] NIOSH Recommendations for Occupational Safety and Health. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 92-100 (1992).
- [9] 1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. ACGIH, Cincinnati, OH (1993).
- [10] Documentation of the NIOSH Validation Tests, S28, S82, S89, S90, S94, S311, S343, S378, S379, 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.

Name Synonyms	CAS# RTECS	Empirical Formula	Molec- ular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg) (kPa)		Density @ 20 °C (g/mL)
benzene ^a benzol; cyclohexatriene	71-43-2 CY1400000	C ₆ H ₆	78.11	80.1	95.2	12.7	0.879
cyclohexane ^a hexahydrobenzene hexamethylene	110-82-7 GU6300000	C ₆ H ₁₂	84.16	80.7	97.6	13.0	0.779
cyclohexene ^a tetrahydrobenzene benzene tetrahydride	110-83-8 GW2500000	C ₆ H ₁₀	82.15	83.0	88.8	11.8	0.811
n-heptane ^b	142-82-5 MI7700000	C ₇ H ₁₆	100.21	98.4	45.8	6.1	0.684
n-hexane ^b hexyl-hydride	110-54-3 MN9275000	C ₆ H ₁₄	86.18	68.7	151.3	20.2	0.659
methylcyclohexane ^a cyclohexylmethane	108-87-2 GV6125000	C ₇ H ₁₄	98.19	100.9	46.3	6.2	0.769
n-octane ^b	111-65-9 RG8400000	C ₈ H ₁₈	114.23	125.7	14.0	1.9	0.703
n-pentane ^b	109-66-0 RZ9450000	C ₅ H ₁₂	72.15	36.1	512.5	68.3	0.626
toluene ^a methylbenzene; toluol	108-88-3 XS5250000	C ₇ H ₈	92.14	110.6	28.4	3.8	0.867

^a Properties from [5].^b Properties from [6].

TABLE 2. EXPOSURE LIMITS, PPM [7-9].

Substance @ NTP	OSHA			NIOSH		ACGIH		mg/m ³ per ppm STEL
	TWA	C	C	Peak	TWA	C	TLV	
benzene*	10	25	50 ^b	0.1 ^d	1	10 ^d		3.19
cyclohexane	300			300		300		3.44
cyclohexene	300			300		300		3.36
n-heptane	500			85	440	400	500	4.10
n-hexane ^a	500			50		50		3.52
methylcyclohexane	500			400		400		4.01
n-octane	500			75	385	300	375	4.67
n-pentane	1000			120	610	600	750	2.95
toluene	200	300	500 ^b	100	150 ^c	100	150	3.77

^a The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.

^b Maximum duration 10 min in 8 h.

^c STEL

^d Suspect carcinogen

TABLE 3. SAMPLING FLOWRATE, VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [2-4, 10].

Substance	Flowrate (L/min)	Sampling Volume (L)		Breakthrough Volume at Concentration		Range at VOL-NOM (mg/m ³)	Overall		Accuracy (%)
		MIN	MAX ^b	(L)	(mg/m ³)		Bias (%)	Precision (\hat{S}_{IT})	
benzene	≤0.20	2 ^c	30	>45	149.1	41.5-165	0.4	0.059	±11.4
cyclohexane	≤0.20	2.5	5	7.6	1650	510-2010	1.1	0.060 ^d	±11.5
cyclohexene	≤0.20	5	7	10.4	2002	510-2030	10.6	0.073	±20.7
n-heptane	≤0.20	4	4	6.1	4060	968-4060	-6.5	0.056	±15.0
n-hexane	≤0.20	4	4	5.9	3679	877-3679	-1.8	0.062	±12.5
methylcyclohexane	≤0.20	4	4	6.1	3941	940-3941	6.1	0.052	±15.2
n-octane	≤0.20	4	4	6.5	4612	1050-4403	-2.0	0.060	±12.1
n-pentane	≤0.05	2	2	3.1	5640	1476-6190	-8.4	0.055	±16.6
toluene	≤0.20	2 ^c	8	11.9	2294	548-2190	1.6	0.052	±10.9

^a Minimum recommended flow is 0.01 L/min.

^b Approximately two-thirds the breakthrough volume.

^c 10-min sample.

^d Corrected value, calculated from data in [10].

TABLE 4. MEASUREMENT RANGE, PRECISION, AND CHROMATOGRAPHIC CONDITIONS [2-4,10].

Substance	Measurement ^a		Carrier		Column Parameters ^b			
	Range (mg)	Precision (S _r)	Gas	Flow (mL/min)	t (°C)	Length (m)	Dia-meter (mm)	Packing ^c
benzene	0.09-0.35	0.036	N ₂	50	115	0.9	3.2	A
cyclohexane	1.3 - 5.3 ^d	0.024	N ₂	50	210	1.2	6.4	B
cyclohexene	2.4 - 9.7 ^d	0.021	N ₂	50	205	1.2	6.4	B
n-heptane	4.08-16.3	0.016	He	30	80	3.0	3.2	C
n-hexane	3.56-14.5	0.014	He	30	52	6.1	3.2	D
methylcyclohexane	3.98-16.1	0.012	He	30	55	6.1	3.2	D
n-octane	4.75-18.9	0.009	He	30	52	6.1	3.2	D
n-pentane	2.98-11.8	0.014	He	30	52	6.1	3.2	D
toluene	1.13-4.51	0.011	N ₂	50	155	0.9	3.2	B

^a Injection volume, 5.0 µL; desorption volume, 1.0 mL, except cyclohexane and cyclohexene, 0.5 mL.

^b All columns stainless steel. Diameter is outside dimension.

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

^d Corrected value, calculated from data in [10].