HYDROCARBONS, BP 36°-216 °C 1500

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

METHOD: 1500, Issue 3	EVALUATION: PARTIAL	Issue 1: 15 August 1990 Issue 3: 15 March 2003

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

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1)

- cyclohexane
- cyclohexene
- n-decane
- n-dodecane
- n-heptane
- n-hexane
- methylcyclohexane
- n-nonane
- n-octane
- n-pentane
- n-undecane

SAMPLING

SAMPLER: SOLID SORBENT TUBE [1] (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 [1]

ANALYTE: Hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURES
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (8 min) - 230 °C (1 min) ramp (7.5 °C /min)

CARRIER GAS: Helium, 1 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 3.00-µm film 100% dimethyl polysiloxane

CALIBRATION: Solutions of analytes in CS_2

RANGE: Table 4

ESTIMATED LOD: Table 4

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

APPLICABILITY: This method may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and alter analyte recovery.

INTERFERENCES: At high humidity, the breakthrough volumes may be reduced. Other volatile organic solvents such as alcohols, ketones, ethers, and halogenated hydrocarbons are potential interferences.

OTHER METHODS: This method is an update for NMAM 1500 issued on August 15, 1994 [2] which was based on methods from the 2nd edition of the NIOSH Manual of Analytical Methods: S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S378, octane [4]; and S379, pentane [4].

REAGENTS:

1. Eluent: 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 pumps (0.01 to 1.0 L/min, Table 3) with flexible tubing.
3. Gas chromatograph, FID, integrator, and a Rtx-1 or equivalent capillary column (page 1500-1).
4. Glass autosampler vials (2-mL) with PTFE-lined caps.
5. Pipettes (1-mL) and pipette bulb.
6. Syringes (10, 25, 100, and 250 µL).
7. Volumetric flasks (10-mL).

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30°C). 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 the sampler to a 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. Include the glass wool plug in the vial with the front sorbent section. Discard the foam plugs.
6. Add 1.0 mL carbon disulfide 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. Additional standards may be added to extend the calibration curve if necessary.
   a. Add known amounts of analytes to carbon disulfide in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph (peak area of analyte vs. µg of analyte per sample).
9. Determine the 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. Remove and discard the back sorbent section of a media blank sampler.

c. Inject a known amount of stock solution (5 to 25 µL) directly onto the front sorbent section with a microliter syringe.
d. Allow the tubes to air equilibrate for several minutes, then cap the tubes and allow to stand overnight.
e. Desorb (steps 5 through 7) and analyze with standards and blanks (steps 11and 12).
f. Prepare a graph of DE vs. µg analyte recovered.

10. Analyze at least three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set the gas chromatograph according to the manufacturer's recommendations and to the conditions given on page 1500-1. Inject a 1-µL aliquot manually using a solvent flushing technique or with an autosampler.
NOTE: If the 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)
n-pentane	7.5
solvent (CS_2)	9.6
n-hexane	13.0
cyclohexane	16.1
cyclohexene	16.8
n-heptane	17.7
methylcyclohexane	18.9
n-octane	21.6
n-nonane	24.9
n-decane	27.8
n-undecane	30.5
n-dodecane	32.9

NOTE: Retention times may vary slightly due to column manufacturer and age of column, and be influenced by other GC instrumental parameters.

12. Measure the peak area.

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 the concentration, C, of analyte in the air volume, V(L), sampled:

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

Issues 1 and 2:

Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Table 3 does not contain data for n-decane, n-dodecane and n-heptane since they were not evaluated previously. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was assessed at 7, 14, and 30 days. 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% [2,3,4,8].

Issue 3:

The desorption efficiency, at levels ranging from 10 times the LOQ to 0.1 times the REL, was determined by spiking known amounts of analytes (in CS_2) on coconut shell charcoal tubes. All analytes exhibited acceptable desorption efficiency recovery results at six levels evaluated.

Each analyte was evaluated for its storage stability. Sorbent tubes were spiked at approximately 100 µg and stored in a drawer for 7 days, then transferred to a refrigerator at 5° C. Samples were analyzed after 7, 14, and 30 days. All analytes had acceptable recoveries (>90%), except cyclohexene, which had a 30 day recovery of 85% [1].

REFERENCES:

[1] Pendergrass SM and May L, Backup Data Report, ACS/CEMB/DART/NIOSH (1999).
[2] NIOSH[1994]. Hydrocarbons, BP 36-136°C. 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.
[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., S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1989); 29 CFR 1910.1000.
[6] NIOSH Recommendations for Occupational Safety and Health. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 92-100 (1992).
[7] 1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. ACGIH, Cincinnati, OH (1993).
[8] Documentation of the NIOSH Validation Tests, S28, S82, S89, S90, S94, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

AUTHORS:

Issues 1 and 2:

R. Alan Lunsford, Ph.D., NIOSH/DPSE

Issue 3:

Stephanie M. Pendergrass, NIOSH/DART and Leroy R. May, NIOSH/PRL

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name/ Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25°C (mm Hg)	Vapor Pressure @ 25°C (kPa)	Density @ 25°C (g/mL)
cyclohexane hexahydrobenzene CAS # 110-82-7 RTECS GU6300000	C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene tetrahydrobenzene CAS # 110-83-8 RTECS GW2500000	C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-decane CAS # 124-18-5 RTECS HD6550000	$C_{10}H_{22}$	142.28	174	NA	NA	0.730
n-dodecane CAS # 112-40-3 RTECS JR2125000	$C_{12}H_{26}$	170.34	216.2	NA	NA	0.750
n-heptane CAS # 142-82-5 RTECS MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane CAS # 110-54-3 RTECS MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane CAS # 108-87-2 RTECS GV6125000	C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-nonane CAS # 111-84-2 RTECS RA6115000	C_9H_{20}	128.26	151	NA	NA	0.718
n-octane CAS # 111-65-9 RTECS RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane CAS # 109-66-0 RTECS RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	0.626
n-undecane hendecane CAS # 1120-21-4 RTECS YQ1525000	$C_{11}H_{24}$	156.31	196	NA	NA	0.740

TABLE 2. EXPOSURE LIMITS, PPM [5-7]

	OSHA		NIOSH		ACGIH		mg/m^3
Substance	TWA	PEAK	TWA	C	TLV	STEL	per ppm
cyclohexane	300		300		300		3.44
cyclohexene	300		300		300		3.36
n-decane	none		none		none		5.82
n-dodecane	none		none		none		6.97
n-heptane	500		85	440	400	500	4.10
n-hexane [a]	500		50		50		3.52
methylcyclohexane	500		400		400		4.01
n-nonane	none		200		200		5.25
n-octane	500		75	385	300	375	4.67
n-pentane	1000		120	610	600	750	2.95
n-undecane	none		none		none		6.39

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

TABLE 3. SAMPLING FLOWRATE [a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [3, 4, 8]

	Sampling			Breakthrough Volume		Range of	Overall		
	Flowrate	Volume (L)		Vol	Concentration	Generated Samples	Bias	Precision	Accuracy
Substance	(L/min)	MIN	MAX [b]	(L)	(mg/m^3)	(mg/m^3)	(%)	($\hat{S}_{rT}$)	(%)
cyclohexane	0.01- 0.2	2.5	5	7.6	1650	510-2010	1.1	0.060[c]	±11.5
cyclohexene	0.01- 0.2	5	7	10.4	2002	510-2030	10.6	0.073	±20.7
n-hexane	0.01- 0.2	not	studied	-	-	-	-	-	-
methylcyclohexane	0.01- 0.2	4	4	6.1	4060	968-4060	-6.5	0.056	±15.0
n-nonane	0.01- 0.2	4	4	5.9	3679	877-3679	-1.8	0.062	±12.5
n-octane	0.01- 0.2	4	4	6.1	3941	940-3941	6.1	0.052	±15.2
n-pentane	0.01-0.2	4	4	6.5	4612	1050-4403	-2.0	0.060	±12.1
n-undecane	0.01-0.05	2	2	3.1	5640	1476-6190	-8.4	0.055	±16.6

[a] Minimum recommended flow is 0.01 L/min.
[b] Approximately two-thirds the breakthrough volume.
[c] Corrected value calculated from data in Ref. 3

TABLE 4. MEASUREMENT RANGE AND PRECISION [1, 3, 4, 8]

Substance	LOD (µg/sample)	Measurement Range (µg)	Measurement Precision ($\bar{S}_r$)
cyclohexane [a]	0.1	4 - 5300	0.012
cyclohexene [a]	0.08	3 - 9700	0.014
n-decane	0.06	2 - 584	0.020
n-dodecane	0.05	2 - 600	0.027
n-heptane	0.06	2 - 16300	0.014
n-hexane	0.4	10 - 14500	0.011
methylcyclohexane	0.1	4 - 16100	0.013
n-nonane	0.04	1 - 574	0.018
n-octane	0.3	11 - 18900	0.022
n-pentane	0.6	19 - 11800	0.012
n-undecane	0.05	2 - 592	0.024

[a] Corrected value, calculated from the data in [1,8].