HYDROCARBONS, HALGENATED 1003

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

METHOD:1003, Issue 2	EVALUATION: PARTIAL	Issue 1: 15 February 1984 Issue 2: 15 August 1994

OSHA : See TABLE 1
NIOSH: See TABLE 1
ACGIH: See TABLE 1

PROPERTIES: See TABLE 2

COMPOUNDS:	benzyl chloride	chlorobromomethane	1,1-dichloroethane	1,1,1-trichloroethane
(synonyms	bromoform	chlorform	1,2-dichloroethylene	tetrachloroethlene
in Table 1)	carbon tetrachloride	o-dichlorobenzene	ethylene dichloride	1,1,2-trichloroethane
	chlorobenzene	p-dichlorobenzene	hexachloroethane	1,2,3-trichloropropane

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: see EVALUATION OF METHOD [1]

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD [1]

ACCURACY: see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE: Table 4

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 4; alternates are SP-2100, Sp-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: standard solutions of analyte in CS_2

RANGE: Table 4

ESTIMATED LOD: 0.1 mg per sample [2]

PRECISION ($\bar{S}_r$): see EVALUATION OF METHOD

APPLICABILITY: See Table 3 for working ranges. This method can be used for simultaneous determination of two or more substances suspected to be present by changing gas chromatographic conditions (i.e., temperature program). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interferences.

OTHER METHODS: This method combines and replaces P&CAM 127 [3], S101 [4], S110 [5], S113 [6], S114 [7], S115 [8], S122 [9], S123 [10], S126 [11], S133 [12], S134 [13], S135 [14], S281 [15], S314 [16], S328 [17], S335 [18], S351 [19], and Method 1003 (dated 2/15/84).

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Analyte, reagent grade.
3. Calibration stock solutions:
   a. benzyl chloride, 10 mg/mL in n-heptane.
   b. bromoform, 10 mg/mL in n-heptane.
   c. o-dichlorobenzene, 300 mg/mL in acetone
   d. hexachloroethane, 25 mg/mL in toluene.
4. Decane, n-undecane, octane or other internal standards (see step 6).
5. Nitrogen or helium, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh 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 (e.g., SKC # 226-01).
2. Personal sampling pump, 0.01 to 0.2 L min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (see Table 3).
4. Vials, 2-mL, glass, PTFE-lined septum crimp caps.
5. Volumetric flasks, 10-mL.
6. Syringes, 10-µL, readable to 0.1 µL.
7. Pipet, TD, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Work with it only in a hood. Several of the analytes are suspect carcinogens (Table 1). n-Heptane, n-hexane, and acetone are fire hazards.

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 between the limits shown in Table 2.
4. Cap the samplers. 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 CS_2 to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as decane [16], n-undecane [6,19], or octane [9,13,17] at 0.1% (v/v) may be added at this step and step 8.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the appropriate range (Table 3).
   a. Add known amounts of neat analyte or calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 µL) of pure analyte, or calibration stock solution (see REAGENTS, 3.), 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 and 12).
   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 1003-1 and in Table 3. Inject sample aliquot either manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

Laboratory testing was performed with spiked samples and generated atmospheres using SKC Lot 105 coconut shell charcoal [1]. Results were:

Compound	Range mg/m³	Sample Size	Bias %	Precision Overall Measurement		Accuracy ±%	Desorption Efficiency	Ref.
Benzyl chloride	2-8	10 L	−8.4	0.096	0.031	25.6	0.90 @ 0.03-0.1 mg	[8]
Bromoform	3-10	10 L	−1.3	0.071	0.043	14.0	0.80 @ 0.025 mg	[7]
Carbon tetrachloride	65-299	15 L	−1.6	0.092	0.037	18.0	0.96 @ 1.3-4.8 mg	[16]
Chlorobenzene	183-736	10 L	0.3	0.056	0.025	11.0	0.91 @ 1.8-7.1 mg	[12]
Chlorobromomethane	640-2655	5 L	3.4	0.061	0.051	14.0	0.94 @ 3.3-13 mg	[6]
Chloroform	100-416	15 L	1.3	0.057	0.047	11.6	0.97 @ 1.8-7.4 mg	[19]
o-Dichlorobenzene	150-629	3 L	−1.9	0.068	0.013	13.7	0.86 @ 0.5-1.9 mg	[14]
p-Dichlorobenzene	183-777	3 L	−4.3	0.052	0.022	12.5	0.91 @ 0.7-2.7 mg	[15]
1,1-Dichloroethane	212-838	10 L	2.6	0.057	0.011	12.4	1.01 @ 1.9-8 mg	[10]
1,2-Dichloroethylene*	475-1915	3 L	−2.9	0.052	0.017	11.3	1.00 @ 2.4-9.5 mg	[5]
Ethylene dichloride	195-819	3 L	−2.0	0.079	0.012	15.7	0.96 @ 0.6-2.5 mg	[9]
Hexachloroethane	5-25	10 L	−6.6	0.121	0.014	25.4	0.98 @ 0.05-0.2 mg	[4]
1,1,1-Trichloroethane	904-3790	3 L	−0.6	0.054	0.018	10.6	0.99 @ 2.9-11 mg	[17]
Tetrachloroethylene	655-2749	3 L	−7.2	0.052	0.013	15.1	0.96 @ 2.1-8 mg	[18]
1,1,2-Trichloroethane	26-111	10 L	−9.0	0.057	0.010	17.5	0.97 @ 0.3-1.2 mg	[13]
1,2,3-Trichloropropane	163-629	10 L	2.1	0.068	0.027	14.2	0.95 @ 1.5-6 mg	[11]

*isomer used (i.e., cis- or trans-) in evaluation unknown.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S101, S110, S113, S114, S115, S122, S123, S126, S133, S134, S135, S281, S314, S328, S335, S351, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.

[2] User check, UBTL, NIOSH Sequences #3990-T, 3990-U and 3990-W (NIOSH, unpublished, November 3, 1983) and 4304-J (NIOSH, unpublished, April 3, 1984).

[3] 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).

[4] Ibid., V. 2., S101, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[5] Ibid., S110.

[6] Ibid., S113.

[7] Ibid., S114.

[8] Ibid., S115.

[9] Ibid., S122.

[10] Ibid., S123.

[11] Ibid., S126.

[12] Ibid., S133.

[13] Ibid., S134.

[14] Ibid., V. 3, S135, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[15] Ibid., S281.

[16] Ibid., S314.

[17] Ibid., S328.

[18] Ibid., S335.

[19] Ibid., S351.

[20] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

[21] NIOSH Current Intelligence Bulletin 27, Chloroethanes: Review of Toxicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-181 (1978).

[22] NIOSH Current Intelligence Bulletin 20, Tetrachloroethylene (Perchloroethylene), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-112 (1978).
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[24] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).
[25] Criteria for a Recommended Standard...Occupational Exposure to Chloroform, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-114 (1975).
[26] Criteria for a Recommended Standard...Occupational Exposure to Ethylene Dichloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-139 (1976).
[27] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).
[28] Criteria for a Recommended Standard...Occupational Exposure to Tetrachloroethylene (Perchloroethylene), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-185 (1976).

METHOD WRITTEN (REVISED) BY:

G. David Foley and Yvonne T. Gagnon, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

TABLE 1. GENERAL INFORMATION.

Compound RTECS	Synonyms	OSHA/NIOSH/ACGIH (ppm)
Benzyl chloride[a] ($C_6H_5CH_2Cl$); XS8925000	(chloromethyl) benzene; α-chlorotoluene; CAS #100-44-7	1/C 1.0/1
Bromoform ($CHBr_3$); PB5600000	tribromomethane; CAS #75-25-2	0.5 (skin)/0.5 (skin)/0.5 (skin)
Carbon tetrachloride[ab] (CCl_4); FG4900000	tetrachloromethane; CAS #56-23-5	10, C 25/STEL 2 (1 h)/5 (skin)
Chlorobenzene (C_6H_5Cl); CZ0175000	monochlorobenzene; phenyl chloride; CAS #108-90-7	75/--/10
Chlorobromomethane (CH_2BrCl); PA5250000	bromochloromethane; Halon 1011; CAS #74-97-5	200/200/200
Chloroform[ab] ($CHCl_3$); FS9100000	trichloromethane; CAS #67-66-3	C 50/STEL 2/10
o-Dichlorobenzene[c] (1,2-$C_6H_4Cl_2$); CZ4500000	1,2-dichlorobenzene; CAS #95-50-1	50/C 50/25 (skin); STEL 50
p-Dichlorobenzene[ac] (1,4-$C_6H_4Cl_2$); CZ45500000	1,4-dichlorobenzene; CAS #106-46-7	75/1.7 (LOQ)/75, STEL 110
1,1-Dichloroethane (CH_3CHCl_2); KI0175000	ethylidene chloride; CAS #75-34-3	100/100/100
1,2-Dichloroethylene (ClCH=CHCl); KV9360000	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200/200/200
Ethylene dichloride[ab] ($ClCH_2CH_2Cl$); KI0525000	1,2-dichloroethane; CAS #107-06-2	50, C 100/1, STEL 2/10
Hexachloroethane[ac] (CCl_3CCl_3); KI4025000	perchloroethane; CAS #67-72-1	1 (skin)/1/1 (skin)
1,1,1-trichloroethane (CH_3CCl_3); KJ2975000	methyl chloroform; CAS #71-55-6	350/C 350/350, STEL 450
Tetrachloroethylene[ab] ($Cl_2C=CCl_2$); KX3850000	perchloroethylene; CAS #127-18-4	100, C 200, P 300/0.4 (LOQ)/ 25, STEL 100
1,1,2-Trichloroethane[ad] (Cl_2CHCH_2Cl); KJ3150000	vinyl trichloride; CAS #79-00-5	10 (skin)/10 (skin)/10 (skin)
1,2,3-Trichloropropane[a] ($CH_2ClCHClCH_2Cl$); TZ9275000	allyl trichloride; glycerol trichlorohydrin; CAS #96-18-4	50/10 (skin)/10 (skin)

[a]Suspect carcinogen [20,21,22]; [b]Group I Pesticide; [c]Group II Pesticide; [d]Group III Pesticide

TABLE 2. PHYSICAL PROPERTIES

Compound RTECS	M.W.	mg/m^3 = 1 ppm @ NTP	Synonyms	Properties
Benzyl chloride ($C_6H_5CH_2Cl$)	126.58	5.17	(chloromethyl) benzene; -chlorotoluene	liquid; BP 179 °C; MP −48 to −43 °C; d 1.100 @ 20 °C; flash pt. 67 °C
Bromoform ($CHBr_3$)	252.75	10.33	tribromomethane	liquid, d 2.887; BP 148 °C; nonflammable
Carbon tetrachloride (CCl_4)	153.84	6.29	tetrachloromethane	liquid; d 1.585; BP 76.7 °C; FP −23.0 °C; VP 91.3 mm @ 20 °C; vapor density (air = 1) 5.3
Chlorobenzene (C_6H_5Cl)	112.56	4.60	monochlorobenzene; phenyl chloride	liquid; d 1.105 @ 25 °C; BP 131.6 °C; MP −45 °C; flash pt. 29.4 °C (CC)
Chlorobromomethane (CH_2BrCl)	129.39	5.29	bromochloromethane; Halon 1011	liquid; d 1.93 @ 20 °C; BP 68 °C; MP −88 °C; nonflammable
Chloroform ($CHCl_3$)	119.39	4.88	trichloromethane	liquid, d 1.485 @ 20 °C; BP 61.2 °C; FP -63.5 °C
o-Dichlorobenzene (1,2-$C_6H_4Cl_2$)	147.00	6.01	1,2-dichlorobenzene	liquid; d 1.284; BP 172 to 179 °C; FP −17 °C; flash pt. 65.5 °C
p-Dichlorobenzene (1,4-$C_6H_4Cl_2$)	147.00	6.01	1,4-dichlorobenzene	solid crystals; d 1.458; BP 173.7 °C; MP 53 °C; sublimes; flash pt. 65.5 °C
1,1-Dichloroethane (CH_3CHCl_2)	98.95	4.05	ethylidene chloride	liquid, d 1.174 @ 20 °C; BP 57 to 59 °C; FP −98 °C
1,2-Dichloroethylene (ClCH=CHCl)	96.94	3.96	acetylene dichloride; 1,2-dichloroethene	liquid; transisomer; d 1.257; BP 47 to 49 °C; MP −57°C; cis-isomer; d 1.282; BP 58 to 60 °C; flash pt. 3.9 °C; FP −80 °C
Ethylene dichloride ($ClCH_2CH_2Cl$)	98.96	4.05	1,2-dichloroethane	liquid; d 1.2554 @ 20 °C; BP 83.5 °C; FP −35.5 °C; flash pt. 13 °C; explosive limits in air 6 to 16%
Hexachloroethane (CCl_3CCl_3)	236.74	9.66	perchloroethane	solid; d 2.091; MP 185 °C; BP sublimes at 187 °C
1,1,1-trichloroethane (CH_3CCl_3)	133.42	5.45	methyl chloroform	liquid; d 1.325; BP 75 °C; FP −30.4 °C; nonflammable
Tetrachloroethylene ($Cl_2C=CCl_2$)	165.83	6.78	perchloroethylene	liquid; d 1.625 @ 20 °C; BP 121 °C; FP −22.4 °C
1,1,2-Trichloroethane (Cl_2CHCH_2Cl)	133.41	5.45	vinyl trichloride	liquid; d 1.4432 @ 20 °C; BP 113.7 °C; FP −36.4 °C; VP 19 mm Hg @ 20 °C
1,2,3-Trichloropropane ($CH_2ClCHClCH_2Cl$)	147.43	6.03	allyl trichloride; glycerol trichlorohydrin	liquid; d 1.3888 @ 20 °C; BP 156.2 °C; FP −15 °C; flash pt. 82.2 °C (OC)

TABLE 3. SAMPLING LIMITS.

Compound	Air Sample Volume (L)			Working Range, ppm, at Max Sample Volume
	Min	Max	Target	
Benzyl chloride	6 @ 1 ppm	50	10	0.6 to 5.8
Bromoform	4 @ 0.5 ppm	70	10	0.2 to 4
Carbon tetrachloride	3 @ 10 ppm	150	15	2 to 105
Chlorobenzene	1.5 @ 75 ppm	40	10	10 to 430
Chlorobromomethane	0.5 @ 200 ppm	8	5	18 to 450
Chloroform	1 @ 50 ppm	50	15	2 to 190
o-Dichlorobenzene	1 @ 50 ppm	60	3	16 to 1100
p-Dichlorobenzene	1 @ 75 ppm	10	3	27 to 330
1,1-Dichloroethane	0.5 @ 100 ppm	15	10	4 to 250
1,2-Dichloroethylene	0.2 @ 200 ppm	5	3	16 to 560
Ethylene dichloride	1 @ 50 ppm	50	3	16 to 1320
Hexachloroethane	3 @ 1 ppm	70	10	0.3 to 8.3
1,1,1-Trichloroethane	0.1 @ 350 ppm	8	3	18 to 1450
Tetrachloroethylene	0.2 @ 100 ppm	40	3	9 to 1900
1,1,2-Trichloroethane	2 @ 10 ppm	60	10	1.8 to 64
1,2,3-Trichloropropane	0.6 @ 50 ppm	60	10	3 to 310

TABLE 4. MEASUREMENT PARAMETERS.

Compound	Column*	Temp. (°C) Column/Injector/Detector	Range (mg per sample)
Benzyl chloride	A	160/170/210	0.02 to 0.15
Bromoform	A	130/170/210	0.02 to 0.15
Carbon tetrachloride	B	60/155/200	0.2 to 7
Chlorobenzene	A	105/190/250	0.4 to 10
Chlorobromomethane	A	80/170/210	0.5 to 15
Chloroform	B	75/155/200	0.4 to 11
o-Dichlorobenzene	C	140/225/250	0.1 to 3
p-Dichlorobenzene	A	140/225/275	0.2 to 4
1,1-Dichloroethane	A	50/100/175	0.4 to 12
1,2-Dichloroethylene	A	60/170/210	0.2 to 7
Ethylene dichloride	C	70/225/250	0.1 to 4
Hexachloroethane	D	110/170/210	0.02 to 0.3
1,1,1-Trichloroethane	C	70/225/250	0.6 to 17
Tetrachloroethylene	C	90/225/250	0.4 to 12
1,1,2-Trichloroethane	C	70/250/225	0.05 to 2
1,2,3-Trichloropropane	E	160/180/230	0.3 to 9

*A = 3 m x 3-mm OD stainless steel, 10% SP-1000 on 80/100 mesh Chromosorb WHP.
B = 6 m x 3-mm OD, otherwise same as A.
C = 3 m x 3-mm OD stainless steel, 10% OV-101 on 100/120 mesh Chromosorb WHP.
D = 3 m x 6-mm OD glass, 3% SP-2250 on 80/100 mesh Chromosorb WHP.
E = 3 m x 3-mm OD stainless steel, 10% FFAP on 80/100 mesh Chromosorb WHP.