

Table 1

MW: Table 2

CAS: Table 1

RTECS: Table 1

METHOD: 1003, Issue 3	EVALUATION: PARTIAL	Issue 1: 15 February 1984 Issue 3: 15 March 2003
OSHA: See TABLE 1 NIOSH: See TABLE 1 ACGIH: See TABLE 1	PROPERTIES: See TABLE 2	

COMPOUNDS: See TABLE 1 (synonyms)

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg) (Lot # 2000)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	compounds listed above
VOL-MIN:	Table 3	DESORPTION:	1 mL CS ₂ , stand 30 min
-MAX:	Table 3	INJECTION VOLUME:	1 µL
SHIPMENT:	Routine	TEMPERATURE:	<u>Group A:</u> Inj = 200°C, Det = 250°C ; 35°C (3 min) to 150°C (8°C/min). <u>Group B:</u> Inj = 225°C, Det = 250°C ; 35°C (3 min) to 190°C (8°C/min).
SAMPLE STABILITY:	30 days for all analytes	CARRIER GAS:	He, (<u>Group A:</u> 2.6 mL/min) (<u>Group B:</u> 4.7 mL/min)
BLANKS:	2 to 10 field blanks per set	COLUMN:	<u>Group A:</u> capillary, fused silica, 30 m x 0.32-mm ID; 1.80-µm film diphenyl/ dimethyl polysiloxane, Rtx [®] -502.2 or equivalent. <u>Group B:</u> capillary, fused silica, 30 m x 0.53 - mm ID; 3-µm film 35% diphenyl- 65% dimethyl polysiloxane, Rtx [®] -35 or equivalent.
ACCURACY		CALIBRATION:	standard solutions of analytes in CS ₂
RANGE STUDIED:	see EVALUATION OF METHOD [1]	RANGE:	see Evaluation of Method
BIAS:	see EVALUATION OF METHOD [1]	ESTIMATED LOD:	Table 4
OVERALL PRECISION ($\hat{S}_{r,T}$):	see EVALUATION OF METHOD [1]	PRECISION ($\hat{S}_{s,T}$):	Table 4
ACCURACY:	see EVALUATION OF METHOD [1]		

APPLICABILITY: See Table 3 for working ranges. This method can be used for simultaneous determination of two or more of the analytes of interest either by use of both of the capillary columns listed above or by modifying the analytical parameters (i.e., temperature program) of the method. High humidity during sampling will decrease total breakthrough volume.

INTERFERENCES: None identified but as the number of different analytes sampled increases so does the chance for interferences. The choice of capillary column or analytical parameters may be modified to circumvent such interferences.

OTHER METHODS: This method is an update for NMAM Method 1003 (Issue 1, 2/15/84) [2]. Trichloroethylene, NIOSH Method 1022, was included in this method update [3]. Method improvements include higher recoveries at lower sample recovery levels, lower LOD and LOQ values, incorporation of capillary column chromatography, and acceptable recoveries in a 30 day storage stability study.

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Analytes, reagent grade quality.
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 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, Lot# 2000 or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and columns (see page 1003-1).
4. Vials, 2-mL, glass, PTFE-lined septum crimp caps.
5. Volumetric flasks, 10-mL.
6. Syringes, 10- μ L to 1-mL, readable to 0.1 μ L.
7. Pipet, 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). Wear appropriate protection clothing and work with these compounds 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 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. The glass wool plug should be included in the vial containing the front sorbent section. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS₂ to each vial. Cap each vial.
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 from below the LOD to 10x the LOQ or greater if required (see Table 3).
 - a. Add known amounts of neat analyte or calibration stock solution to CS₂ 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. μ g 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 blank sampler.
 - b. Inject a known amount (2 to 20 μL) of pure analyte, or calibration stock solution, 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. μg 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. 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, 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):

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

EVALUATION OF METHOD:

The current laboratory evaluation of the analytes listed in this method included the incorporation of capillary column chromatography, the improvement of LOD/LOQ values, a desorption efficiency study ranging from approximately 3-5X LOQ to 0.1x the REL/PEL, and the inclusion of a 30 day storage stability study. Most of the analytes evaluated over this range exhibited acceptable recoveries [4]. However four analytes had unacceptable recoveries at the lowest level evaluated [4]. These analytes included benzyl chloride, chloroform, carbon tetrachloride and chlorobenzene. For these compounds the LOQ was adjusted accordingly. All of the analytes evaluated during the storage stability study were determined to be stable after 7, 14, and 30 days storage [4]. Bromoform was marginally stable at 30 days [4].

The initial laboratory evaluation was conducted using spiked samples and generated atmospheres and using SKC Lot 105 coconut shell charcoal as the collection media [1]. Results were:

Compound	Range mg/m ³	Sample Size	Bias %	Precision		Accuracy ±%	Desorption Efficiency	Ref.
				Overall	Measurement			
Benzyl chloride	2-8	10 L	-8.4	0.096	0.031	25.6	94% @ 96-303 µg	4
Bromoform	3-10	10 L	-1.3	0.071	0.043	14.0	94% @ 35-111 µg	4
Carbon tetrachloride	65-299	15 L	-1.6	0.092	0.037	18.0	93% @ 32-4800 µg	4,5
Chlorobenzene	183-736	10 L	0.3	0.056	0.025	11.0	92% @ 111-7100µg	4,6
Chlorobromomethane	640-2655	5 L	3.4	0.061	0.051	14.0	98% @39-13,000µg	4,7
Chloroform	100-416	15 L	1.3	0.057	0.047	11.6	97% @ 24-7400 µg	4,8
<i>o</i> -Dichlorobenzene	150-629	3 L	-1.9	0.068	0.013	13.7	94% @ 19-1900 µg	4,9
<i>p</i> -Dichlorobenzene	183-777	3 L	-4.3	0.052	0.022	12.5	98% @ 25-2700 µg	4,10
1,1-Dichloroethane	212-838	10 L	2.6	0.057	0.011	12.4	101% @20-8000 µg	4,11
1,2-Dichloroethylene*	475-1915	3 L	-2.9	0.052	0.017	11.3	101% @19-9500 µg	4,12
Ethylene dichloride	195-819	3 L	-2.0	0.079	0.012	15.7	94% @ 2.5-2500 µg	4,13
Hexachloroethane	5-25	10 L	-6.6	0.121	0.014	25.4	98% @ 34-756.8 µg	4
1,1,1-Trichloroethane	904-3790	3 L	-0.6	0.054	0.018	10.6	100%@23-11000µg	4,14
Tetrachloroethylene	655-2749	3 L	-7.2	0.052	0.013	15.1	95% @ 8-8000 µg	4,15
1,1,2-Trichloroethane	26-111	10 L	-9.0	0.057	0.010	17.5	100% @18-1200 µg	4,16
1,2,3-Trichloropropane	163-629	10 L	2.1	0.068	0.027	14.2	99% @ 21-6000 µg	4,17

*mixed isomers used (i.e., cis- and trans-).

REFERENCES:

- [1] NIOSH [1977]. 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, available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
- [2] NIOSH [1994]. Hydrocarbons, Halogenated: Method 1003. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods. 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
- [3] NIOSH [1994]. Trichloroethylene: Method 1022. In: Eller, PM, Cassinelli, ME, eds. 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 and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
- [4] Pendergrass SM [1998]. Backup Data Report for NMAM 1003, Issue 3 Method Development. Cincinnati, OH: National Institute for Occupational Safety and Health, (unpublished, December).
- [5] NIOSH [1977]. Carbon tetrachloride: Method S314, NIOSH manual of analytical methods, 2nd ed., Vol. 1, Cincinnati, OH: U.S. Department of Health, Education, and Welfare, (NIOSH) Publication 77-157-A.
- [6] *Ibid.*, S133.
- [7] *Ibid.*, S113.
- [8] *Ibid.*, Vol 3., S351, (NIOSH) Publication 77-157-C.
- [9] *Ibid.*, S135.
- [10] *Ibid.*, S281.
- [11] *Ibid.*, Vol. 2, S123, (NIOSH) Publication 77-157-A.
- [12] *Ibid.*, S110.
- [13] *Ibid.*, S122.
- [14] *Ibid.*, Vol 3, S328, (NIOSH) Publication 77-157-C.
- [15] *Ibid.*, S335.
- [16] *Ibid.*, Vol. 2, S134, (NIOSH) Publication 77-157-A.
- [17] *Ibid.*, S126.

METHOD REVISED BY:

Stephanie M. Pendergrass, NIOSH/ DART.

TABLE 1. GENERAL INFORMATION.

Compound RTECS	Synonyms	OSHA/NIOSH/ACGIH (ppm)
Group A		
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 ₆ H ₅ Cl); CZ0175000	monochlorobenzene; phenyl chloride; CAS #108-90-7	75/--/10
Chloroform ^{ab} (CHCl ₃); FS9100000	trichloromethane; CAS #67-66-3	C 50/STEL 2/10
1,1-Dichloroethane (CH ₃ CHCl ₂); KI0175000	ethylidene chloride; CAS #75-34-3	100/100/100
Ethylene dichloride ^{ab} (ClCH ₂ CH ₂ Cl); KI0525000	1,2-dichloroethane; CAS #107-06-2	50, C 100/1, STEL 2/10
Tetrachloroethylene ^{ab} (Cl ₂ C=CCl ₂); KX3850000	perchloroethylene; CAS #127-18-4	100, C 200, P 300/0.4 (LOQ)/ 25, STEL 100
Trichloroethylene ^a (ClCH = CCl ₂); KX4550000	ethylene trichloride; trichloroethene; CAS # 79-01-6	100 ppm (Ca 200 ppm)/Ca 50 ppm
1,1,1-trichloroethane (CH ₃ CCl ₃); KJ297500	methyl chloroform; CAS #71-55-6	350/C 350/350, STEL 450
Group B		
Benzyl chloride ^a (C ₆ H ₅ CH ₂ Cl); XS8925000	(chloromethyl) benzene; α-chlorotoluene; CAS #100-44-7	1/C 1.0/1
Chlorobromomethane (CH ₂ BrCl); PA5250000	bromochloromethane; Halon 1011; CAS #74-97-5	200/200/200
o-Dichlorobenzene ^c (1,2-C ₆ H ₄ Cl ₂); CZ4500000	1,2-dichlorobenzene; CAS #95-50-1	50/C 50/25 (skin); STEL 50
p-Dichlorobenzene ^{ac} (1,4-C ₆ H ₄ Cl ₂); CZ45500000	1,4-dichlorobenzene; CAS #106-46-7	75/1.7 (LOQ)/75, STEL 110
1,2-Dichloroethylene (ClCH=CHCl); KV9360000	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200/200/200
Hexachloroethane ^{ac} (CCl ₃ CCl ₃); KI4025000	perchloroethane; CAS #67-72-1	1 (skin)/1/1 (skin)
1,1,2-Trichloroethane ^{ad} (Cl ₂ CHCH ₂ Cl); KJ3150000	vinyl trichloride; CAS #79-00-5	10 (skin)/10 (skin)/10 (skin)
1,2,3-Trichloropropane ^a (CH ₂ ClCHClCH ₂ Cl); 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
Group A				
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 ₆ H ₅ Cl)	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)
Chloroform (CHCl ₃)	119.39	4.88	trichloromethane	liquid, d 1.485 @ 20 °C; BP 61.2 °C; FP -63.5 °C
1,1-Dichloroethane (CH ₃ CHCl ₂)	98.95	4.05	ethylidene chloride	liquid, d 1.174 @ 20 °C; BP 57 to 59 °C; FP -98 °C
Ethylene dichloride (ClCH ₂ CH ₂ Cl)	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%
Tetrachloroethylene (Cl ₂ C=CCl ₂)	165.83	6.78	perchloroethylene	liquid; d 1.625 @ 20 °C; BP 121 °C; FP -22.4 °C
1,1,1-trichloroethane (CH ₃ CCl ₃)	133.42	5.45	methyl chloroform	liquid; d 1.325; BP 75 °C; FP -30.4 °C; nonflammable
Trichloroethylene (ClCH=CCl ₂)	131.40	5.37	ethylene trichloride; trichloroethene	liquid; d 1.459 @ 20 °C; BP 87.2 °C; FP -72.8 °C; VP 58 mm Hg @ 20 °C (9.9 kPa); explosive range 11 to 41% v/v in air
Group B				
Benzyl chloride (C ₆ H ₅ CH ₂ Cl)	126.58	5.17	(chloromethyl) benzene; α-chlorotoluene	liquid; BP 179 °C; MP -48 to -43 °C; d 1.100 @ 20 °C; flash pt. 67 °C
Chlorobromomethane (CH ₂ BrCl)	129.39	5.29	bromochloromethane; Halon 1011	liquid; d 1.93 @ 20 °C; BP 68 °C; MP -88 °C; nonflammable
o-Dichlorobenzene (1,2-C ₆ H ₄ Cl 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 ₆ H ₄ Cl 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
1,2-Dichloroethylene (ClCH=CHCl)	96.94	3.96	acetylene dichloride; 1,2-dichloroethene	liquid; trans isomer; 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
Hexachloroethane (CCl ₃ CCl ₃)	236.74	9.66	perchloroethane	solid; d 2.091; MP 185 °C; BP sublimes at 187 °C
1,1,2-Trichloroethane (Cl ₂ CHCH ₂ Cl)	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 ₂ ClCHClCH ₂ Cl)	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	
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
Chloroform	1 @ 50 ppm	50	15	2 to 190
1,1-Dichloroethane	0.5 @ 100 ppm	15	10	4 to 250
Ethylene dichloride	1 @ 50 ppm	50	3	16 to 1320
1,1,1-Trichloroethane	0.1 @ 350 ppm	8	3	18 to 1450
Tetrachloroethylene	1.0 @ 100 ppm	40	3	9 to 1900
Trichloroethylene	0.2 @ 100 ppm	30	10	0.3 to 62.1
Benzyl chloride	6 @ 1 ppm	50	10	0.6 to 5.8
Chlorobromomethane	0.5 @ 200 ppm	60	5	18 to 450
<i>o</i> -Dichlorobenzene	1 @ 50 ppm	10	3	16 to 1100
<i>p</i> -Dichlorobenzene	1 @ 75 ppm	8	3	27 to 330
1,2-Dichloroethylene	0.2 @ 200 ppm	5	3	16 to 560
Hexachloroethane	3 @ 1 ppm	70	10	0.3 to 8.3
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	Limit of Detection (LOD)	Limit of Quantitation (LOQ)	Precision (S _r)
Bromoform	6.0	19.3	0.051
Carbon tetrachloride	4.0	20.0	0.046
Chlorobenzene	0.6	110.0	0.025
Chloroform	0.8	15.0	0.035
1,1-Dichloroethane	2.0	5.1	0.030
Ethylene dichloride	0.7	2.3	0.026
Tetrachloroethylene	2.0	7.1	0.032
1,1,1-Trichloroethane	1.0	3.0	0.009
Trichloroethylene	0.6	1.9	0.018
Benzyl chloride	1.0	4.5	0.076
Chlorobromomethane	1.5	41.0	0.053
<i>o</i> -Dichlorobenzene	0.8	2.7	0.022
<i>p</i> -Dichlorobenzene	2.0	7.5	0.041
1,2-Dichloroethylene	2.0	5.1	0.041
Hexachloroethane	2.0	6.6	0.021
1,1,2-Trichloroethane	1.0	3.0	0.036
1,2,3-Trichloropropane	1.0	2.7	0.020

Units = µg analyte per sample

Note: For a few of the compounds in this method the LOQ values, when compared to the preceding method development results, may appear higher. This can be explained by the fact that in the initial method development no recovery study was conducted at a level near or above the instrumentally determined LOQ recoveries for each analyte.