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MANUAL OF ANALYTICAL METHODS

THIRD EDITION

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16. Abstract (Limit: 200 words)

This supplement contains air and biological analytical methods which have been evaluated by NIOSH for use in determining concentrations of the following substances: acetaldehyde (75070), alkaline dusts, aminoethanol compounds, arsenic (7440382), asbestos (1332214) fibers, soluble barium (7440393), benzene (71432), beryllium (7440417), biphenyl (92524), bromotrifluoromethane (75638), 1,3-butadiene (106990), cadmium (7440439), chlorinated-diphenyl-ether, chloroacetic-acid (79118), diborane (19287457), dichlorodifluoromethane (75718), 1,2-dichlorotetrafluoroethane (1320372), ethylene-dibromide (106934), ethylene-oxide (75218), fibers, furfural (98011), halogenated hydrocarbons, iodine (7553562), methyl-chloride (74873), methyl-ethyl-ketone-peroxide (1338234), methylene-chloride (75092), mineral-oil mist, naphthylamines, nickel-carbonyl (13463393), nitroethane (79243), nitromethane (75525), 2-nitropropane (79469), organotin compounds, phosphorus (7723140), polychlorobenzenes, polychlorobiphenyls (1336363), pyridine (110861), stibine (7803523), sulfur-dioxide (7446095), tetrachlorodifluoroethanes, 1,1,2,2-tetrachloroethylene (127184), tetraethyl-lead (78002), toluene (108883), toluene-2,4-diisocyanate (584849), trichloroethylene (79016), trichlorofluoromethane (75694), 1,1,2-trichloro-1,2,2-trifluoroethane (76131), vanadium-oxide (1314347), and vinylidene-chloride (75354).

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

NIOSH-Publication, Analytical-chemistry, Chemical-analysis, Air-quality-sampling, Trace-analysis, Environmental-contamination, Vapors, Organic-solvents, Hazardous-materials

c. COSATI Field/Group

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(See ANSI-Z39.18) *See Instructions on Reverse*

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N0819

TRANSMITTAL NOTICE

This is the second supplement to the NIOSH Manual of Analytical Methods, 3rd edition (printed February 15, 1984, first supplement dated May 15, 1985). The contents of this supplement are dated August 15, 1987 and include the 51 methods on the reverse side of this page.

ACTION: To bring your Manual up to date, please do the following:

- REMOVE the following pages: v through xiii (Table of Contents), 1 and 2 (Introduction), ALKALINE DUSTS (Method 7401), AMINOETHANOL COMPOUNDS (Method 2007), ARSENIC (Method 7900), BERYLLIUM (Method 7102), CADMIUM (Method 7048), ETHYLENE DIBROMIDE (Method 1008), ETHYLENE OXIDE (Method 1607)(1), HYDROCARBONS, HALOGENATED (Method 1003), ISOCYANATE GROUP (Method 5505)(2), METHYLENE CHLORIDE (Method 1005), POLYCHLOROBIPHENYLS (Method 5503), and pp. A-11 through A-49 (Indexes).

- ADD the enclosed methods alphabetically(3) to your Manual. Add the enclosed Table of Contents(4) and Indexes(5).

- CHECK your methods against the enclosed Table of Contents to make sure you have all current methods. If methods are missing, contact GPO or NIOSH for replacements.

- NOTE new precautions which should be observed when analyzing blood and tissue samples(6) (e.g., Methods 8000, 8001, 8004 and 8005).

NOTES: (1) This method has been replaced by Methods 1614 and 3702 (enclosed)
(2) This method is no longer recommended for use (see Teass, A. W. and M. J. Seymour, APPL. IND. HYG. 2: 182 (1987).
(3) The alphabetical arrangement is most useful; however, the methods may be arranged numerically. As detailed on pp. 2-3 of the Introduction, Methods are numbered as follows: Organic Gases, 1000-4999; Organic Aerosols, 5000-5999; Inorganic Gases, 6000-6999; Inorganic Aerosols, 7000-7999; Biologicals, 8000-8999; Bulks, 9000-9999.
(4) Current Issue dates have been added for each method. Previous versions should be discarded.
(5) The Index of Second Edition Method Numbers has been made more useful by a cross-reference to 3rd ed. method names.
(6) "Recommendations for Prevention of HIV Transmission in Health-Care Settings," Morbidity & Mortality Weekly Report 36: 25, U.S. Department of Health and Human Services, Centers for Disease Control (Aug 21, 1987).

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Methods included with the August 15, 1987, Supplement to the NIOSH Manual of Analytical Methods, 3rd ed.:

Method No.		Method
3507		ACETALDEHYDE
7401	*	ALKALINE DUSTS
2007	*	AMINOETHANOL COMPOUNDS
7900	*	ARSENIC
7402		ASBESTOS FIBERS
7056		BARIUM, SOLUBLE
3700		BENZENE - portable GC
7102	*	BERYLLIUM
2530		BIPHENYL
1017		BROMOTRIFLUOROMETHANE
1024		1,3-BUTADIENE
7048	*	CADMIUM
5025		CHLORINATED DIPHENYL ETHER
2008		CHLOROACETIC ACID
6006		DIBORANE
1018		DICHLORODIFLUOROMETHANE and 1,2-DICHLOROTETRAFLUOROETHANE
1008	*	ETHYLENE DIBROMIDE
1614		ETHYLENE OXIDE
3702		ETHYLENE OXIDE
7400	*	FIBERS
2529		FURFURAL
1003	*	HYDROCARBONS, HALOGENATED
6005		IODINE
1001		METHYL CHLORIDE
3508		METHYL ETHYL KETONE PEROXIDE
1005	*	METHYLENE CHLORIDE
5026		MINERAL OIL MIST
5518		NAPHTHYLAMINES
6007		NICKEL CARBONYL
2526		NITROETHANE
2527		NITROMETHANE
2528		2-NITROPROPANE
5504		ORGANOTIN COMPOUNDS
7905		PHOSPHORUS
5517		POLYCHLOROBENZENES
5503	*	POLYCHLOROBIPHENYLS
1613		PYRIDINE
6008		STIBINE
6004		SULFUR DIOXIDE
1016		1,1,1,2-TETRACHLORO-2,2-DIFLUORO-ETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE
1019		1,1,2,2-TETRACHLOROETHANE
2533		TETRAETHYL LEAD
2534		TETRAMETHYL LEAD
4000		TOLUENE
2535		TOLUENE-2,4-DIISOCYANATE
1022		TRICHLOROETHYLENE
3701		TRICHLOROETHYLENE (portable GC)
1006		TRICHLOROFLUOROMETHANE
1020		1,1,2,-TRICHLORO-1,2,2-TRIFLUORO-ETHANE
7504		VANADIUM OXIDE
1015		VINYLIDENE CHLORIDE

*Revision of a previously-issued 3rd ed. method.

CONTENTS

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Each revised method and chapter is identified as to author. More than 50 NIOSH chemists and industrial hygienists contributed. Special recognition is also due the following:

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I. INTRODUCTION

A. PURPOSE AND SCOPE

This Manual is a collection of air and biological analytical methods which NIOSH has evaluated. The scientific literature contains equally accurate methods. We plan to augment this Manual in the future with methods developed, evaluated or revised by NIOSH. There will be situations where users of these methods will need to modify them to accommodate interfering compounds from the workplace under investigation, to take advantage of special capabilities of the laboratory or to make possible the analysis of a single sample for several contaminants. For example, in elemental analysis by atomic absorption or emission, filter samples containing relatively high levels of organic particulate matter may require digestion in a larger quantity of acid for a longer period of time. As another example, chromatographic procedures are commonly modified to eliminate interferences by changing the column and conditions and by using a more specific detector. The automation of sample work-up and measurement procedures usually requires some modification of the nonautomated procedure. When solid sorbent samplers are used, the volume of air sampled should be reduced if air contamination from vaporous compounds is relatively high and, in some cases, may be increased if such contamination is relatively low. In any case, data showing the reliability of the method used should be obtained.

These methods are intended to promote accuracy, sensitivity and specificity in the analyses [1] while preserving practicability [2]. Some older methods have been retained or refined with the recognition that many laboratories do not have the newer instruments.

Direct-reading instruments and passive monitors are being used with increasing frequency for evaluating workplace air. Direct-reading methods give the chemist and industrial hygienist the opportunity to perform selected analyses at the work site and take action as necessary. Passive monitors eliminate the need for bulky and expensive air sampling pumps, and are being applied to the sampling of many gases. The laboratory chemist is being presented with requests for more complicated measurements; witness the increasing requests for multiple elemental analyses and the deconvolution of complex mixtures by gas chromatography-mass spectrometry, high pressure liquid chromatography and Fourier transform infrared spectrometry. The demand for increased selectivity, resolving power and reduced analysis turnaround time will no doubt continue. This Manual will reflect those changes in future Supplements.

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[1] Keith, L. H., N. I. McClelland, et al. "Principles of Environmental Analysis," Anal. Chem., 55, 2210-2218 (1983).

[2] Horwitz, W. "Practicability in Regulatory Analytical Chemistry," Anal. Chem., 51, 741A (1979).

B. HOW TO USE THIS MANUAL

1. LOCATING A METHOD:

	Use one of the following:
a. By Method Title (methods are arranged alphabetically in Air, Biological, and Bulk sections of the Manual; some methods are combinations of several compounds)	1. Methods section; or 2. Contents (page v); or 3. Index of Names and Synonyms (page A-31; "yellow pages")
b. By Third Edition Method Number (see the system description below)	Index of Third Edition Method Numbers (page A-11)
c. By Second Edition Method Number (P&CAM or S-numbers from Second Edition of the NIOSH Manual of Analytical Methods)	Index of Second Edition Method Numbers (page A-17)
d. By Chemical Abstracts Service Registry Number (CAS #)	Index of Names and Synonyms (page A-31; "yellow pages")

2. THIRD EDITION METHOD NUMBERING SYSTEM

Substances having the same sampler, sample preparation and measurement technique may be grouped together in one method. Substances are assigned method numbers based on the following system:

AIR SAMPLES:

General:	Method Number:
Gas	0001-0499
Aerosol	
Total	0500-0599
Respirable	0600-0699
Open	0700-0999

Organic Compounds:

Gas	
Active Sampling	
Solid Sorbent	
Charcoal, coconut shell	
Halogenated	1000-1299
Ketones	1300-1399
Alcohols	1400-1449
Esters	1450-1499
Hydrocarbons	1500-1549
Mixtures	1550-1599
Other	1600-1999
Silica gel	2000-2499
Other solid sorbents (porous polymer, etc.	2500-3499

FORMULA: CH_3CHO

M.W.: 44.05

ACETALDEHYDE

METHOD: 3507
ISSUED: 8/15/87

OSHA: 200 ppm
NIOSH: no recommended standard [1]
ACGIH: 100 ppm; STEL 150 ppm
(1 ppm = 1.801 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.78 g/mL @ 20 °C;
BP 20.4 °C; MP -123 °C;
VP 100 kPa (750 mm Hg; 99% v/v) @ 20 °C;
explosive range 4 to 60% v/v in air

SYNONYMS: ethanal; CAS #75-07-0.

SAMPLING

SAMPLER: LIQUID IN BUBBLER
(midget bubbler containing 15 mL
Girard T solution @ pH 4.5)

FLOW RATE: 0.1 to 0.5 L/min

VOL-MIN: 6 L @ 200 ppm
-MAX: 60 L

SHIPMENT: seal bubblers to prevent leakage
before shipping; protect from light

SAMPLE STABILITY: 100% recovered after 1 week
@ 25 °C in dark [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 170 to 670 mg/m³ [2]
(60-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.053 [2]

MEASUREMENT

TECHNIQUE: HPLC, UV

ANALYTE: Girard T derivative

SAMPLE PREPARATION: dilute 5 mL sample to 100 mL with HPLC mobile phase

INJECTION VOLUME: 50 µL

COLUMN: 50 cm x 2 mm ID SS, Zipax SCX

DETECTOR: UV @ 245 nm for acetaldehyde

MOBILE PHASE: $HPO_4^{2-}/H_2PO_4^-$ buffer;
0.75 mL/min

CALIBRATION: standard solutions of acetaldehyde in Girard T reagent

RANGE: 2 to 60 mg per sample [2]

ESTIMATED LOD: 0.1 mg per sample [2]

PRECISION (s_r): 0.024 @ 11 to 43 mg per sample [2]

APPLICABILITY: The working range is 18 to 372 ppm (33 to 670 mg/m³) for a 60-L air sample. The method is sensitive enough for short-term exposure sampling and can be used to measure lower concentrations by diluting samples to less than the recommended 100 mL.

INTERFERENCES: Other volatile aldehydes and ketones (e.g., acetone, acrolein, benzaldehyde, formaldehyde, furfural, methyl ethyl ketone, and propionaldehyde) compete for the Girard T reagent which should be kept at a two-fold molar excess over aldehyde concentration. Chromatographic conditions may be adjusted to resolve acetaldehyde from other aldehydes [2].

OTHER METHODS: This revises S345 [3]. Other reported methods for acetaldehyde use collection in 2,4-dinitrophenylhydrazine solution [4,5].

REAGENTS:

1. Acetaldehyde.*
2. Citric acid.
3. Disodium hydrogen phosphate (Na_2HPO_4).
4. Girard T reagent [(carboxymethyl)-trimethylammonium chloride hydrazide] recrystallized from 95% ethanol.
5. Water, distilled, deionized (DD).
6. Ethanol, 95%.
7. Sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$).
8. Girard T solution: 5.39 g citric acid, 6.63 g Na_2HPO_4, and 16.77 g Girard T reagent diluted to 500 mL with DD water. Store in annealed flask in the dark. Use within two weeks.
9. HPLC mobile phase: 0.22 M Na_2HPO_4, 0.019 M $NaH_2PO_4 \cdot H_2O$ in 20% ethanol. Dissolve and dilute 31.2 g Na_2HPO_4 and 26.2 g $NaH_2PO_4 \cdot H_2O$ to 1 L with DD water. Mix 100 mL of this solution with 200 mL 95% ethanol; dilute to 1 L with DD water. Filter through 5-µm PTFE filter and degas prior to use. Bubble helium through the solution to prevent bacterial growth.
10. Calibration stock solution, 4.32 mg/mL acetaldehyde in 0.2 M Girard T solution. Weigh 216 mg freshly-distilled acetaldehyde into 50-mL volumetric flask containing 49 mL Girard T solution. Make to volume with Girard T solution. Use within one day.
11. Helium.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: bubbler, glass, midget, with fritted glass stems, annealed,* with PTFE stoppers for shipping.
2. Personal sampling pump, 0.1 to 0.5 L/min, with trap made from midget bubbler with stem broken off and inert, flexible connecting tubing.
3. High pressure liquid chromatograph, with 245-nm UV detector, integrator, and column (page 3507-1) with 50-µL injection loop or autosampler.
4. Syringe, 2-mL, Luer-lock.
5. Distillation apparatus for preparation of high purity acetaldehyde.
6. Flasks, volumetric, 1-L; 10-, 50-, and 100-mL; and 500-mL, annealed.*
7. Pipets, 0.02- to 1-mL; 5-, 10-, and 15-mL.
8. Marker, glass.
9. Cylinder, graduated, 250-mL.
10. Filter, 5-µm, PTFE, 37-mm, with holder for liquid filtration.
11. Balance, readable to 0.1 mg.

*Heat in an oxidizing atmosphere at 580 °C.

SPECIAL PRECAUTIONS: Acetaldehyde is extremely volatile and a fire hazard. Cool containers of acetaldehyde to ice bath temperature to reduce pressure buildup and open in an exhaust hood only.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler and trap in line.
2. Add exactly 15 mL Girard T solution to each bubbler using a 15-mL pipet. Mark the initial liquid level in the bubbler with a glass marker. Make impinger-to-trap and trap-to-sampling pump connections with flexible inert tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.5 L/min for a total sample size of 6 to 60 L.

   NOTE: Higher flow rates will cause frothing of the collection medium. If amount of liquid condensed in the trap is greater than 1 mL, collection efficiency of bubbler may be reduced and sample may be invalid.

SAMPLE PREPARATION:

4. Tap bubbler stem lightly against bubbler body to drain contents into the body. If necessary, bring samples up to the 15-mL mark with distilled water. Swirl bubbler to mix contents well. Do not add solution collected in the trap to the sample.
5. Transfer a 5-mL aliquot to a 100-mL flask and bring to volume with HPLC mobile phase.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least five working standards over the range 0.007 to 4 mg acetaldehyde per mL (0.1 to 60 mg acetaldehyde per sample).
   a. Add known amounts of calibration stock solution to Girard T solution in 10-mL volumetric flasks and dilute to the mark. Dilute 5 mL of each of these solutions to 100 mL with HPLC mobile phase. Prepare at least two blanks in the same manner.
   b. Analyze together with samples and blanks (steps 8 and 9).
   c. Prepare calibration graph (peak area vs. mg acetaldehyde per sample).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

8. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 3507-1. Inject 50-µL sample aliquot with injection loop or autosampler.

   NOTE: If peak area is above the linear range of the working standards, dilute with HPLC mobile phase, reanalyze, and apply the appropriate dilution factor in calculations.
9. Measure peak area.

CALCULATIONS:

10. Determine the mass, mg of acetaldehyde found in the sample (W), and in the average media blank (B).
11. Calculate concentration, C, of acetaldehyde in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S345 was issued on March 16, 1979 [3], and validated over the range 170 to 670 mg/m³ at 21 °C and 756 mm Hg using a 60-L sample [2,6]. Overall precision, s_r, was 0.053 with an average recovery of 101.2% representing a non-significant bias. The concentration of acetaldehyde was independently verified by calibrated gas chromatograph. Collection efficiency of a single bubbler was determined to be >0.998 when 61-L air samples were taken at 0.5 L/min in atmospheres containing 670 mg/m³ acetaldehyde.

REFERENCES:
[1] 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.
[2] Backup Data Report S345, Acetaldehyde, prepared under NIOSH Contract 210-76-0123 (unpublished).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, S345, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Kuwata, K., M. Uebori and Y. Yamasaki. J. Chromatog. Sci., 17, 264-268 (1979).
[5] Lipari, F. and S. J. Swarin. J. Chromatog., 247, 297-306 (1982).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Eugene R. Kennedy, Ph.D., NIOSH/DPSE; Method S345 was validated under NIOSH Contract 210-76-0123.

FORMULA: NaOH, KOH, LiOH, and basic salts

M.W.: 40.00 (NaOH); 56.11 (KOH)

ALKALINE DUSTS

METHOD: 7401
ISSUED: 2/15/84
REVISION #1: 8/15/87

OSHA: 2 mg/m³ (NaOH)
NIOSH: 2 mg/m³/15 min (NaOH) [1]
ACGIH: C 2 mg/m³ (NaOH)

PROPERTIES: basic, hygroscopic, caustic solids and aerosols; VP not significant

SYNONYMS: alkali; caustic soda; lye; sodium hydroxide (CAS #1310-73-2); potassium hydroxide (CAS #1310-58-3)

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 70 L @ 2 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [2]

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.76 to 3.9 mg/m³ [2]
(360-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.062 [2]

MEASUREMENT

TECHNIQUE: ACID-BASE TITRATION

ANALYTE: OH^- (alkalinity)

EXTRACTION: 5.00 mL 0.01 N HCl, 15 min under nitrogen with stirring

TITRATION: 0.01 N NaOH under nitrogen, endpoint by pH electrode

CALIBRATION: 0.01 N NaOH standardized with 0.01 N HCl

RANGE: 0.14 to 1.9 mg per sample [2]

ESTIMATED LOD: 0.03 mg per sample (as NaOH) [2]
(7×10^{-4} mmoles of alkalinity)

PRECISION (s_r): 0.033 @ 0.38 to 1.5 mg NaOH per sample [2]

APPLICABILITY: The working range is 0.4 to 5.4 mg/m³ for a 360-L air sample. The method measures total alkalinity due to alkali hydroxides, carbonates, borates, silicates, phosphates, and other basic salts, expressed as equivalents of NaOH.

INTERFERENCES: None identified. Carbon dioxide in the air may react with alkali on the filter to produce carbonates but does not interfere when titrated. The carbonates will produce the equivalent amount of strong alkali that was consumed on the filter [2].

OTHER METHODS: This revises Methods S381 [3],7401 (dated 2/15/84), and P&CAM 241 [4].

REAGENTS:

1. Sodium carbonate, primary standard grade.
2. Hydrochloric acid stock solution, 0.1 N. Standardize with sodium carbonate primary standard.
3. Dilute hydrochloric acid, 0.01 N. Dilute 10.0 mL 0.1 N stock HCl to 100 mL in a volumetric flask with distilled water.
4. Water, distilled, CO_2-free. Boil and cool under N_2 or bubble nitrogen through distilled water for 30 min. Store with an Ascarite trap.
5. Nitrogen, compressed.
6. Sodium hydroxide, 50% w/v.* Dissolve 50 g NaOH in CO_2-free distilled water and dilute to 100 mL.
7. Stock sodium hydroxide, 0.1 N. Dilute 4 mL 50% NaOH to 1.0 L with CO_2-free distilled water. Store under Ascarite trap.
8. Working sodium hydroxide solution, 0.01 N. Dilute 10 mL stock (0.1 N NaOH) to 100 mL with CO_2-free distilled water.
9. Standard buffer solutions, pH 4 and 7.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter (Millipore Fluoropore or equivalent), 1.0-µm pore size, supported by a cellulose backup pad in a cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. pH meter with pH electrode and recorder.
4. Titration vessel, 150 to 200 mL beaker, flask or jar with cover containing openings for the pH electrode and N_2 inlet and outlet.
5. Stirrer, magnetic, and stir bar.
6. Glass rod, ca. 5-mm diameter and 10 cm long to hold filter under liquid surface in titration vessel.
7. Pipets, 5- and 10-mL.
8. Volumetric flasks, 100- and 1000-mL.
9. Burets, 50-mL, readable to 0.1 mL.

SPECIAL PRECAUTIONS: NaOH solutions are very caustic [1]; handle them with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 70 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer the sample filter to a titration vessel with tweezers. Place the filter face down in the titration vessel.
4. Place the end of a glass rod in the center of the filter to maintain the filter below the liquid surface during the analysis.
5. Cover the titration vessel, add 5.00 mL 0.01 N HCl, start the magnetic stirrer and N_2 purge (ca. 100 cm^3/min).
6. Allow to stand 15 min (with stirring).

CALIBRATION AND QUALITY CONTROL:

7. Calibrate the pH meter with pH 4 and pH 7 buffer solutions.

8. Standardize the 0.1 N HCl stock solution with sodium carbonate in triplicate [4].
   a. Dry 3 to 5 g primary standard grade Na_2CO_3 at 250 °C for 4 hrs. Cool in a dessicator.
   b. Weigh ca. 2.5 g Na_2CO_3 to the nearest mg. Dissolve and make up to exactly 1 L with CO_2-free distilled water. The concentration is ca. 0.05 N Na_2CO_3.
   c. Place 5.00 mL 0.05 N Na_2CO_3 solution into a titration vessel and titrate potentiometrically to a pH of 5.
   d. Remove electrodes, rinse them into the titration vessel, and bubble N_2 gas through contents of the titration vessel for 3 to 5 min to remove dissolved CO_2.
   e. Proceed with the titration to the inflection point.
   f. Calculate the normality of the stock HCl solution:

$$N_{HCl} = \frac{(\text{g } Na_2CO_3 \text{ weighed})(\text{mL } Na_2CO_3 \text{ solution used in titration})}{(52.99)\ (\text{mL HCl used})}$$

9. Standardize the working (ca. 0.01 N) NaOH solution against the standardized HCl solution by following steps 8.c. and 8.e, substituting the standardized HCl stock solution for the Na_2CO_3 solution and the 0.01 N NaOH solution for the 0.1 N HCl solution. Calculate the normality of the NaOH titrating solution.

$$N_{NaOH} = \frac{(N_{HCl})(\text{mL HCl used})}{(\text{mL NaOH used})}.$$

10. Prepare at least two spiked media blank samples to check analytical recoveries at levels expected on the field samples.

MEASUREMENT:

11. Back-titrate the excess HCl in the samples, blanks and spiked blank solutions with the standardized NaOH solution while maintaining the N_2 purge.
12. Observe the pH meter. Calculate the endpoint (mL of 0.01 N NaOH used).

CALCULATIONS:

13. Using the volume (mL) of HCl added to the sample (V_{HCl-s}) and average blank (V_{HCl-b}), and the volume of NaOH used for the titration of the sample (V_{NaOH-s}) and average blank (V_{NaOH-b}), the normality of these reagents (N_{HCl} and N_{NaOH}) and the volume of air sampled, V (L), calculate the concentration, C (mg/m^3), of alkalinity (as NaOH with equivalent weight, EW, equal to 40.0):

$$C = \frac{(V_{HCl-s} - V_{HCl-b})(N_{HCl}) - (V_{NaOH-s} - V_{NaOH-b})(N_{NaOH})}{V} \cdot EW \cdot 10^3, \ mg/m^3$$

EVALUATION OF METHOD:

Method S381 [2] was issued on July 8, 1977, and was validated using generated atmospheres of NaOH over the range 0.76 to 3.9 mg/m^3 using a 360-L sample [2,6]. Overall precision, s_r, was 0.062 with an average recovery of 105%, representing an insignificant bias. The NaOH concentration was independently verified by analyzing additional samples for sodium by atomic absorption spectrophotometry. An overall average collection efficiency of greater than 99% was found by sampling 1 to 360 L in an atmosphere of 7.50 mg/m^3 (NaOH) using backup Fluoropore filters and also by sampling (two samples) 615 L using backup impingers filled with water.

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Sodium Hydroxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-105 (1975).
[2] Backup Data Report No. S381, Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, available as Order No. PB 275-838 from NTIS, Springfield, VA 22161 (July 8, 1977).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S381, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Ibid, V. 1, P&CAM 241, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, American Water Works Association and Water Pollution Control Federation (1981).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: R. DeLon Hull, NIOSH/DBBS and M. E. Cassinelli, NIOSH/DPSE; S381 originally validated under NIOSH Contract No. 210-76-0123.

FORMULA: Table 1

M.W.: Table 1

AMINOETHANOL COMPOUNDS
METHOD: 2007
ISSUED: 5/15/85
REVISION #1: 8/15/87

COMPOUNDS and SYNONYMS: 2-aminoethanol: ethanolamine; 2-hydroxyethylamine; CAS #141-43-5.
2-dibutylaminoethanol: CAS #102-81-8.
2-diethylaminoethanol: 2-hydroxytriethylamine; CAS #100-37-8.

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(silica gel, 300 mg/150 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 4 L
-MAX: 24 L

FIELD TREATMENT: add 20 µL conc. HCl to silica gel immediately after sampling

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeks @ 25 °C [1]

FIELD BLANKS: 10% (≥2) of samples

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1,2]

BIAS: not significant [1,2]

OVERALL PRECISION (s_r): 0.056 [2]

MEASUREMENT

!TECHNIQUE: GAS CHROMATOGRAPHY, FID

!ANALYTE: compounds above

!DESORPTION: 2 mL 4:1 (v/v) methanol:water; stand 2 hrs with occasional shaking

!INJECTION VOLUME: 3 µL

!TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 250 °C
-COLUMN: 90 °C, 3 min; 90 to 225 °C @ 16°/min, hold 6 min

!CARRIER GAS: N_2 or He, 30 mL/min

!COLUMN: 1.8 m x 2 mm ID silanized glass, 10% Carbowax 20 M + 2% KOH on 80/100 mesh Chromosorb WAW

!CALIBRATION: solutions of analyte in 4:1 methanol:water containing 0.12 N HCl

!RANGE: 0.1 to 6 mg per sample [2]

!ESTIMATED LOD: 0.005 mg per sample [2]

!PRECISION (s_r): 0.026 @ 0.6 to 2.7 mg per sample [2]

APPLICABILITY: The working range is 5 to 300 mg/m³ for each compound in a 20-L air sample. Water vapor does not significantly affect collection efficiency [3]. Sensitivity may be improved at least ten-fold by using a photoionization or nitrogen-selective detector.

INTERFERENCES: None identified [3]. The chromatographic column or separation conditions may be changed to circumvent interference problems. A DB-5 fused silica capillary column may be used.

OTHER METHODS: This revises P&CAM 270 [3], S140 [4], and Method 2007 (dated 5/15/85).

REAGENTS:

1. Eluent: Four parts methanol to one part distilled water (v/v).
   NOTE: Do not use deionized water which may contain formaldehyde.
2. Analyte, reagent grade.*
3. Alkalinizing solution: 0.20 N NaOH (8.0 g NaOH/L) in eluent.
4. HCl, conc. (38%, 12 N) (needed for field use).*
5. HCl, 0.12 N, in eluent. Dissolve 10.0 mL conc. HCl in eluent to make 1 L solution.
6. Benzaldehyde.
7. Calibration stock solutions, 10 mg/mL, in 0.12 N HCl in eluent for each analyte.
8. Nitrogen or helium, purified.
9. Hydrogen, prepurified.
10. Air, filtered.
11. pH paper.
12. KOH, saturated solution.
13. Glass wool.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7-cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 45/60 mesh chromatographic grade silica gel (front = 300 mg; back = 150 mg) separated by a plug of silylated glass wool. A silylated plug of glass wool is at each end of the tube. Pressure drop across the tube at 0.2 L/min airflow must be less than 3.2 kPa. Tubes are commercially available. Do not use sampling tubes constructed with metal parts or urethane foam plugs. Conc. HCl will react with these materials.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Syringe for dispensing HCl, 50-µL with glass barrel, PTFE-tipped plunger and inert (platinum or PTFE) needle (for field use).
4. Gas chromatograph, FID, integrator and column (page 2007-1).
5. Coated capillary injection port liner: Soak liner and small quantity of glass wool in saturated KOH. Air-dry liner and glass wool. Loosely pack glass wool in liner.
6. Vials, 2-mL, glass, PTFE-lined crimp caps.
7. Volumetric flasks, 10-mL.
8. Syringe, 10-µL, readable to 0.1 µL.
9. Micropipets, 10- to 100-µL.
10. Pipets, 0.5- and 2-mL, with pipet bulb.

SPECIAL PRECAUTIONS: The analytes are eye irritants [5]. Avoid skin contact or inhalation of conc. HCl.

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 of 4 to 24 L.
   NOTE: If samples are to be eluted immediately or will be stored in a freezer for less than 14 days, the following step may be eliminated.
4. Immediately after sampling, stabilize the samples by adding exactly 20 µL conc. HCl to each section of silica gel in each sampler using a syringe.
   NOTE 1: The amount of HCl added must be measured carefully because the sample will be neutralized and made alkaline (step 9) for proper chromatography.
   NOTE 2: Iron impurities in silica gel will turn yellow upon addition of acid.
5. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

6. Place the first glass wool plug and the front section of the sampler in a vial. Place the second plug and backup section in a separate vial.

7. Add 2.0 mL eluent to each vial. Attach cap to each vial.
   NOTE: If conc. HCl was not added to the silica gel after sampling, desorb the samples in 2.0 mL 0.12 N HCl in eluent. The acid increases desorption efficiency.
8. Allow to stand 2 hrs with occasional agitation.
9. Transfer a 0.5-mL aliquot of each sample to another vial. Add 0.5 mL alkalinizing solution and attach cap. Mix thoroughly. Check the solution pH with pH paper. If the solution pH is <9 add alkalinizing solution until solution pH is >9.
10. If 2-aminoethanol is present, repeat step 9 with another 0.5-mL aliquot. Add 10 µL benzaldehyde to the basic solution, mix thoroughly and let stand 20 min.
    NOTE: Benzaldehyde derivatizes 2-aminoethanol to 2-benzylideneaminoethanol which has a higher molecular weight, thereby decreasing the GC detection limit. Underivatized 2-aminoethanol can be determined by this method if the sample size is large.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least five working standards over the range 0.05 to 6 mg of each analyte.
    a. Add known amounts of analyte or calibration stock solution to 0.12 N HCl in eluent in 10-mL volumetric flasks and dilute to the mark.
    b. Treat the working standards with base and benzaldehyde as needed (steps 9 and 10).
    c. Analyze together with samples and blanks (steps 14 and 15).
    d. Prepare calibration graph (peak area vs. mg analyte).
12. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling. 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 or calibration stock solution directly onto front sorbent section with a microliter syringe.
    c. Add 20.0 µL conc. HCl.
    d. Cap the tube. Allow to stand overnight.
    e. Desorb (steps 6 through 10) and analyze with working standards (steps 14 and 15).
    f. Prepare a graph of DE vs. mg analyte recovered.
13. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

14. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2007-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: The temperature program separates all three compounds. Isothermal column conditions are 225, 150, and 90 °C for 2-aminoethanol, 2-dibutylaminoethanol and 2-diethylaminoethanol, respectively. The column packing degrades rapidly at 225 °C; keep operating time at a minimum near this temperature.
    NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
    NOTE 3: When using a capillary column system, use the split injection port liner coated with KOH to improve amine peak shape.
15. Measure peak area.

CALCULATIONS:

16. 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.

17. 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:
All three compounds were evaluated under Method P&CAM 270 using a smaller bed of silica gel (front = 150 mg; back = 150 mg) than given above [3]. Desorption efficiencies for 0.1 mg analyte were found to be 0.97 for 2-aminoethanol, 0.85 for 2-diethylaminoethanol, and 0.93 for 2-dibutylaminoethanol [3]. Only 2-diethylaminoethanol was evaluated under Method S140 using the suggested sorbent tube. In all cases, laboratory testing was performed with spiked samples and generated atmosphere [1,2,6]. All analytes were stable on silica gel up to four weeks when stabilized with acid. Results were:

Compound	Method	Range Studied (mg/m^3)	Sample size (L)	Precision (s_r)	
				Measurement	Overall
2-aminoethanol	P&CAM 270 [3]	30.4 to 63.6	30	<0.070	0.057
2-dibutylaminoethanol	P&CAM 270 [3]	unknown	unknown	unknown	unknown
2-diethylaminoethanol	S140 [4]	25 to 113	24	0.026	0.056

Method S140 [4] was issued on January 19, 1979, and validated over the range 25 to 113 mg/m^3 at 23 °C and 762 mm Hg using 24-L samples [2,7]. Coast Engineering Laboratory 40/60 mesh silica gel was the collecting medium. Average recovery was 97.1%, representing a non-significant bias. The concentration of 2-diethylaminoethanol was independently verified using midget bubblers containing 15 mL 2% HCl. Desorption efficiency was 0.964 in the range 0.6 to 2.3 mg per sample. Breakthrough (5% on back section) was not achieved after 5.3 hrs when sampling an atmosphere containing 88 mg/m^3 2-diethylaminoethanol at 0.2 L/min at 82% relative humidity.

REFERENCES:
[1] Wood, G. O. and J. W. Nickols. Development of Air-Monitoring Techniques Using Solid Sorbents, October 1, 1976 - December 31, 1977, Progress Report LA-7295-PR, Los Alamos Scientific Laboratory, Los Alamos, NM, NIOSH IA-77-12 (1978).
[2] Backup Data Report No. S140, prepared under NIOSH Contract 210-76-0123 (NIOSH, unpublished, 1979); Report on NIOSH Sequence #5162 (unpublished, April 2, 1986).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 270, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Ibid., Vol. 5, S140, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Diethylaminoethanol and Ethanolamine, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[6] Wood, G. O., R. G. Anderson and J. W. Nickols. Sampling and Analysis of Aminoethanols in Air, Report LA-UR-77-1398, Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, NM (1977) (presented at the 1977 American Industrial Hygiene Conference, May 1977, New Orleans, LA).

[7] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Karen J. Williams, NIOSH/DPSE.

Table 1. Structural formulas, molecular weights, permissible exposure limits and properties.

Compound	Formula	MW	mg/m³ = 1 ppm @ NTP	OSHA NIOSH* ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
2-aminoethanol	$HOCH_2CH_2NH_2$; C_2H_7NO	61.08	2.50	3 ppm * 3 ppm (STEL 6 ppm)	171	48 Pa (470 ppm)	1.0180
2-dibutylamino-ethanol	$(C_4H_9)_2N(CH_2)_2OH$; $C_{10}H_{23}NO$	173.30	7.09	2 ppm * 2 ppm (skin) (STEL 4 ppm)	228	not available	0.859
2-diethylamino-ethanol	$(C_2H_5)_2N(CH_2)_2OH$; $C_6H_{15}NO$	117.19	4.79	10 ppm * 10 ppm (skin)	163	130 Pa (1300 ppm)	0.8921

*No recommended criteria for a standard have been established by NIOSH.

FORMULA: As

M.W.: 74.92 (As)

ARSENIC and compounds, as As
METHOD: 7900
ISSUED: 2/15/84
REVISION #1: 8/15/87

OSHA: 0.01 mg/m³
NIOSH: 0.002 mg/m³/15 min [1]
ACGIH: 0.2 mg/m³; suspect carcinogen (As_2O_3)

PROPERTIES: soft, reactive metalloid; MP 848 °C; VP (As_2O_3) 0.0075 Pa (5.6×10^{-8} mm Hg: 0.45 µg As/m³) @ 25 °C; valence ± 3, 5 in salts

SYNONYMS: vary depending upon the compound; CAS #7440-38-2 (As).

SAMPLING

SAMPLER: FILTER (0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 30 L @ 0.002 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable if refrigerated

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: see APPLICABILITY

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME ARSINE GENERATION

ANALYTE: arsenic

ASHING: conc. HNO_3, 3 mL; conc. H_2SO_4, 1 mL; conc. $HClO_4$, 1 mL; 140 °C

FINAL SOLUTION: 4% H_2SO_4, 25 mL

FLAME: hydrogen-argon

WAVELENGTH: 193.7 nm

BACKGROUND CORRECTION: D_2 or H_2 continuum

CALIBRATION: As in 4% H_2SO_4

RANGE: 0.05 to 2.0 µg per sample [2]

ESTIMATED LOD: 0.02 µg per sample [2]

PRECISION (s_r): 0.11 [2]

APPLICABILITY: The working range is 0.00025 to 0.01 mg/m³ for a 200-L air sample and 0.002 to 0.07 mg/m³ for a 30-L air sample. This method collects particulate arsenic only; if arsenic trioxide vapor is present, use the sampler in Method 7901. This is an elemental analysis, not compound specific. Volatile organic arsenic compounds, As_2O_3 vapor, and arsine are not collected efficiently by this sampling method.

INTERFERENCES: Background absorption is overcome by the use of D_2 or H_2 continuum.

OTHER METHODS: This revises P&CAM 139 [2] and Method 7900 (dated 2/15/84); a similar method appears in the criteria document [1]. Method 7901 uses a sampler designed to collect As_2O_3 vapor and an alternate measurement technique (graphite furnace-AAS). Method 7300 (ICP-AES) also gives an alternate measurement technique.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Sulfuric acid, conc.
4. Perchloric acid, conc.*
5. Calibration stock solution, 1000 µg/mL.* Commercially available or dissolve 1.320 g primary standard As_2O_3 in 25 mL 20% (w/v) KOH. Neutralize with 20% (v/v) HNO_3 to a phenolphthalein endpoint. Add 10 mL conc. HNO_3 and dilute to 1 L with distilled or deionized water.
6. Ashing acid, 3 volumes HNO_3, 1 volume H_2SO_4, and 1 volume $HClO_4$.
7. Hydrogen.
8. Argon.
9. Distilled or deionized water.
10. Sodium borohydride, pellets.
11. Air, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with appropriate hydrogen burner head or quartz tube furnace, and arsenic hollow cathode lamp or EDL and arsine generation system.
4. Regulators, two-stage, for air, hydrogen and argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Pipets, volumetric, as needed.*
8. Hotplate, surface temperature 140 °C.

*Clean all glassware with conc. nitric acid before use and rinse thoroughly with distilled or deionized water.

SPECIAL PRECAUTIONS: Arsenic is a recognized carcinogen; handle appropriately [1]. Perform all perchloric acid digestions in a perchloric acid fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 30 to 1000 L. Do not exceed ca. 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
   NOTE: Analyze the backup pad separately if qualitative indication of As_2O_3 vapor is desired. Use Method 7901 if quantitative collection of As_2O_3 vapor is desired.
4. Add 5 mL ashing acid and cover with a watchglass.
5. Heat on hotplate (140 °C) until the solution is colorless.
6. Add 1 mL conc. HNO_3 and/or 70% $HClO_4$ drop by drop as needed to complete the ashing.
7. Remove the watchglass.
8. Heat on 140 °C hotplate until dense SO_3 fumes appear.
9. Allow the mixture to cool.
10. Transfer the solution quantitatively to a 25-mL volumetric flask.
11. Dilute to volume with distilled or deionized water.

CALIBRATION AND QUALITY CONTROL:

12. Prepare working standards. Add known amounts, covering the range 0.2 to 8 µg As/100 mL (0.05 to 2 µg As per sample), of 1000 µg/mL As calibration stock solution to 100-mL volumetric flasks containing 4 mL conc. H_2SO_4 and dilute to volume with distilled or deionized water.
13. Analyze working standards together with the blanks and samples (steps 18 through 25).
14. Prepare calibration graph (absorbance vs. solution concentration, µg/mL).
15. Analyze a standard for every 10 samples.
16. Check analytical recoveries with at least one spiked media blank per 10 samples.
17. Use method of additions occasionally to check for interferences.

ANALYTICAL PROCEDURE:

18. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7900-1.
19. Set up arsine generator per manufacturer's instructions.
20. Pipet 5 mL aliquot of the 25-mL sample into the arsine generation flask.
21. Add 25 mL distilled or deionized water, 3 mL conc. HCl, and mix well.
22. Connect the flask to the generation system.
23. Introduce a single sodium borohydride pellet or sodium borohydride solution to the sample solution.
24. Allow the gases to flush into the flame of the atomic absorption instrument.
25. Record the absorbance readings.

    NOTE: If the absorbance values of the samples are above the linear range of the standards, dilute the solutions, or use a smaller aliquot, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

26. Using the measured absorbances, calculate the corresponding solution concentrations (µg/mL) of As in the sample, C_s, and average media blank, C_b, from the calibration graph.
27. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of As in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

This method was evaluated in July, 1976, over the range 0.02 to 3 µg per sample by laboratory testing with spiked filters. Precision and accuracy data are given on page 7900-1 [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-149 (175).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 139, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

METHOD REVISED BY: Mark Millson, NIOSH/DPSE.

FORMULA: various

M.W.: various

ASBESTOS FIBERS
METHOD: 7402
ISSUED: 8/15/87

OSHA: 0.2 asbestos fibers (>5 μm long/mL)
NIOSH: 0.1 asbestos f/mL [1]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, f/mL

PROPERTIES: solid, fibrous

SYNONYMS: actinolite asbestos [CAS #13768-00-8], grunerite asbestos (amosite) [CAS #12172-73-5], anthophyllite asbestos [CAS #17068-78-9], chrysotile asbestos [CAS #12001-29-5], crocidolite asbestos [CAS #12001-28-4], tremolite asbestos [CAS #14567-73-8].

SAMPLING

SAMPLER: FILTER
(0.8-to 1.2-μm cellulose ester membrane, 25-mm diameter; conductive cassette)

FLOW RATE*: 0.5 to 16 L/min (step 4)

VOL-MIN*: 400 L @ 0.1 fiber/mL (step 4)
-MAX*: (step 4)
*Adjust for 100 to 1300 fibers/mm² (step 4)

SHIPMENT: routine (securely packed to reduce shock)

SAMPLE STABILITY: stable

FIELD BLANKS: 10% (≥2) of samples

ACCURACY

RANGE STUDIED: 80 to 100 fibers counted

BIAS: not determined

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: MICROSCOPY, TRANSMISSION ELECTRON (TEM)

ANALYTE: asbestos fibers

SAMPLE PREPARATION: modified Jaffe wick

EQUIPMENT: transmission electron microscope; energy dispersive X-ray system (EDS) analyzer

CALIBRATION: qualitative electron diffraction; calibration of TEM magnification and EDS system

RANGE: 100 to 1300 fibers/mm² filter area [2]

ESTIMATED LOD: 1 confirmed asbestos fiber above 95% of expected mean blank value

PRECISION: 0.28 when 65% of fibers are asbestos; 0.20 when adjusted fiber count is applied to PCM count [3].

APPLICABILITY: The working range is 0.04 to 0.5 fiber/mL for a 1-m³ air sample. The method measures asbestos fibers of the smallest diameter (<0.05 μm) but allows comparison of fiber counts to be made with phase contrast light microscopic (PCM) data when fiber diameters are rigidly defined.

INTERFERENCES: Non-asbestiform amphiboles may interfere in the TEM analysis if the individual particles have aspect ratios greater than 3:1. These interferences can only be eliminated by quantitative zone axis electron diffraction analysis. High concentrations of background dust interfere with fiber identification.

OTHER METHODS: NIOSH Method 7400 (dated 8/15/87) (phase-contrast microscopy) designed for use with this method.

REAGENTS:

1. Acetone. See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl, cellulose ester membrane filter, 0.8- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean count is >5 fibers/100 fields. These are defined as laboratory blanks.
   NOTE 2: Use an electrically-conductive extension cowl to reduce electrostatic effects on fiber sampling and during sample shipment. Ground the cowl when possible during sampling.
2. Personal sampling pump, ≥0.5 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, transmission electron, operated at 100 kV, with electron diffraction and energy-dispersive X-ray capabilities, and having a fluorescent screen with inscribed or overlaid calibrated scale (Step 15).
   NOTE: The scale is most efficient if it consists of a series of lines inscribed on the screen or partial circles every 2 cm distant from the center.
4. Diffraction grating replica with known number of lines/mm.
5. Slides, glass, pre-cleaned, 25- x 75-mm.
6. Knife, #10 surgical steel, curved-blade.
7. Tweezers.
8. Grids, 200-mesh TEM copper, carbon-coated.
9. Petri dishes, 15-mm depth. The top and bottom of the petri dish must fit snugly together. To assure a tight fit, grind the top and bottom pieces together with an abrasive such as carborundum to produce a ground-glass contact surface.
10. Foam, clean polyurethane, spongy, 12-mm thick.
11. Low-temperature oxygen plasma asher.
12. Filters, Whatman No. 1 qualitative paper or equivalent, or lens paper.
13. Vacuum evaporator.
14. Cork borer, No. 5 (8-mm).
15. Pen, waterproof, marking.
16. Reinforcement, page, gummed.
17. Asbestos standard bulk materials for reference.
18. Carbon rods, sharpened to 1 mm x 8 mm.
19. Microscope, light, phase contrast (PCM), with Walton-Beckett graticule (see method 7400).
20. Grounding wire, 22-gauge, multi-strand.

SPECIAL PRECAUTIONS: Acetone is extremely flammable (flash point = 0 °F). Take precautions not to ignite it. Heating of >1 mL acetone must be done in a fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line [4].
2. For personal sampling, fasten sampler to worker's lapel near worker's mouth. Remove the top cover from end of the cowl extension (open face) and orient sampler face down. Wrap joint between extender and monitor body with shrink tape to prevent air leaks. Where possible, especially at low %RH, attach sampler to electrical ground to reduce electrostatic effects during sampling.

3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove top covers from the field blank cassettes and store top covers and cassettes in a clean area (e.g., closed bag or box) during sampling. Replace top covers when sampling is completed.
4. Sample at 0.5 L/min or greater [5]. Adjust sampling rate, Q (L/min), and time, t (min), to produce fiber density, E, of 100 to 1300 fibers/mm^2 [3.85•10^4 to 5•10^5 fibers per 25-mm filter with effective collection area (A_c= 385 mm^2)] for optimum accuracy. Do not exceed ca. 0.5 mg total dust loading on the filter. These variables are related to the action level (one-half the current standard), L (fibers/mL), of the fibrous aerosol being sampled by:

$$t = \frac{A_c \cdot E}{Q \cdot L \cdot 10^3}, \text{ min.}$$

NOTE: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 hrs (700 to 2800 L) is appropriate in non-dusty atmospheres containing ca. 0.1 fiber/mL. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/mL, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust [5].

5. At the end of sampling, replace top cover and small end caps.
6. Ship samples upright with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in the shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

7. Remove a circular section from any quadrant of each sample and blank filter using a cork borer [6].
8. Affix the circular filter section to a clean glass slide with a gummed page reinforcement. Label the slide with a waterproof marking pen.
   NOTE: Up to eight filter sections may be attached to the same slide.
9. Place the slide in a petri dish which contains several paper filters soaked with 2 to 3 mL acetone. Cover the dish. Wait 2 to 4 min for the sample filter(s) to fuse and clear.
   NOTE: The "hot block" clearing technique may be used instead of steps 8 and 9 [7,8].
10. Place the slide containing the collapsed filters into a low-temperature plasma asher. Etch at 100 °C for ca. 2 min at an O_2 pressure of 130 Pa (1 mm Hg) [9].
    NOTE: Plasma ashers may vary. Determine optimum etching time (ca. 1/2 the time needed to completely ash a filter) on blank filters before etching samples.
11. Transfer the slide to a rotating stage inside the bell jar of a vacuum evaporator. Evaporate a 1- by 5-mm section of a graphite rod onto the cleared filter(s). Remove the slide to a clean, dry, covered petri dish [6].
12. Prepare a second petri dish as a Jaffe wick washer with the wicking substrate prepared from filter or lens paper placed on top of a 12-mm thick disk of clean, spongy polyurethane foam [10]. Cut a V-notch on the edge of the foam and filter paper. Use the V-notch as a reservoir for adding solvent.
    NOTE: The wicking substrate should be thin enough to fit into the petri dish without touching the lid.

13. Place the carbon-coated TEM grids face up on the filter or lens paper. Label the grids by marking with a pencil on the filter paper or by putting registration marks on the petri dish halves and marking with a waterproof marker on the dish lid. In a fume hood, fill the dish with acetone until the wicking substrate is saturated.
    NOTE: The level of acetone should be just high enough to saturate the filter paper without creating puddles.
14. Remove about a quarter section of the carbon-coated filter from the glass slide using a surgical knife and tweezers. Carefully place the excised filter, carbon side down, on the appropriately-labeled grid in the acetone-saturated petri dish. When all filter sections have been transferred, slowly add more solvent to the wedge-shaped trough to bring the acetone level up to the highest possible level without disturbing the sample preparations. Cover the petri dish. Elevate one side of the petri dish by placing a slide under it (allowing drops of condensed acetone to form near the edge rather than in the center where they would drip onto the grid preparation).

CALIBRATION AND QUALITY CONTROL:

15. Determine the TEM magnification on the fluorescent screen:
    a. Define a field of view on the fluorescent screen either by markings or physical boundaries.
       NOTE: The field of view must be measurable or previously inscribed with a scale or concentric circles (all scales should be metric) [10].
    b. Insert a diffraction grating replica into the specimen holder and place into the microscope. Orient the replica so that the grating lines fall perpendicular to the scale on the TEM fluorescent screen. Ensure that goniometer stage tilt is zero.
    c. Adjust microscope magnification to 10,000X. Measure the distance (mm) between the same relative positions (e.g., between left edges) of two widely-separated lines on the grating replica. Count the number of spaces between the lines.
       NOTE: On most microscopes the magnification is substantially constant only within the central 8 to 10 cm diameter region of the fluorescent screen.
    d. Calculate the true magnification (M) on the fluorescent screen:

$$M = \frac{X \cdot G}{Y}$$

       where: X = total distance (mm) between the two grating lines;
              G = calibration constant of the grating replica (lines/mm);
              Y = number of grating replica spaces counted
    e. After calibration, note the apparent sizes of 0.25 and 3.0 µm on the fluorescent screen. (These dimensions are essentially the diameter boundary limits for counting asbestos fibers by phase contrast microscopy.)
16. Measure 20 grid openings at random on a 200-mesh copper grid by placing a grid on a glass slide and examining it under the PCM. Use the Walton-Beckett graticule to measure the grid opening diameters. Calculate an average graticule field diameter from the data and use this number to calculate the graticule field area for an average grid opening.
    NOTE: A grid opening is considered as one graticule field.
17. Obtain reference selected area electron diffraction (SAED) or microdiffraction patterns from standard asbestos materials prepared for TEM analysis.
    NOTE: This is a visual reference technique. No quantitative SAED analysis is required [10]. Microdiffraction may produce clearer patterns on very small fibers or fibers partially obscurred by other material.
    a. Set the specimen holder at zero tilt.

b. Center a fiber, focus, and center the smallest field-limiting aperture on the fiber. Use a 20-cm camera length and 10X binocular head. Obtain a diffraction pattern. Photograph each distinctive pattern and keep the photo for comparison to unknowns.

NOTE: Not all fibers will present diffraction patterns. The objective lens current may need adjustment to give optimum pattern visibility. There are many more amphiboles which give diffraction patterns similar to the analytes named on p.7402-1. Some, but not all, of these can be eliminated by chemical separations. Also, some non-amphiboles (e.g., pyroxenes, some talc fibers) may interfere.

18. Acquire energy-dispersive X-ray (EDX) spectra on approximately 5 fibers having diameters between 0.25 and 0.5 µm of each asbestos variety obtained from standard reference materials [10].

NOTE: The sample may require tilting to obtain adequate signal. Use same tilt angle for all spectra.

a. Prepare TEM grids of all asbestos varieties.

b. Use acquisition times (at least 100 sec) sufficient to show a silicon peak at least 75% of the monitor screen height at a vertical scale of $\geq$500 counts per channel.

c. Estimate the elemental peak heights visually as follows:

(1) Normalize all peaks to silicon (assigned an arbitrary value of 10).

(2) Visually interpret all other peaks present and assign values relative to the silicon peak.

(3) Determine an elemental profile for the fiber using the elements Na, Mg, Si, Ca, and Fe. Example: 0-4-10-3-<1 [10].

NOTE: In fibers other than asbestos, determination of Al, K, Ti, S, P, and F may also be required for fiber characterization.

(4) Determine a typical range of profiles for each asbestos variety and record the profiles for comparison to unknowns.

MEASUREMENT:

19. Perform a diffraction pattern inspection on all sample fibers counted under the TEM, using the procedures given in step 17. Assign the diffraction pattern to one of the following structures:

a. chrysotile;

b. amphibole;

c. ambiguous;

d. none.

NOTE: There are some crystalline substances which exhibit diffraction patterns similar to those of asbestos fibers. Many of these, (brucite, halloysite, etc.) can be eliminated from consideration by chemistry. There are, however, several minerals (e.g., pyroxenes, massive amphiboles, and talc fibers) which are chemically similar to asbestos and can be considered interferences. The presence of these substances may warrant the use of more powerful diffraction pattern analysis before positive identification can be made. If interferences are suspected, morphology can play an important role in making positive identification.

20. Obtain EDX spectra in either the TEM or STEM modes from fibers on field samples using the procedure of step 18. Using the diffraction pattern and EDX spectrum, classify the fiber:

a. For a chrysotile structure, obtain EDX spectra on the first five fibers; one out of ten thereafter. Label the range profiles from 0-5-10-0-0 to 0-10-10-0-0 as "chrysotile."

b. For an amphibole structure, obtain EDX spectra on the first 10 fibers; one out of ten thereafter. Label profiles ca. 0-2-10-0-7 as "possible amosite"; profiles ca. 1-1-10-0-6 as "possible crocidolite"; profiles ca. 0-4-10-3-<1 as "possible tremolite"; and profiles ca. 0-3-10-0-1 as "possible anthophyllite."

NOTE: The range of profiles for the amphiboles will vary up to ±1 unit for each of the elements present according to the relative detector efficiency of the spectrometer.

c. For an ambiguous structure, obtain EDX spectra on all fibers. Label profiles similar to the chrysotile profile as "possible chrysotile." Label profiles similar to the various amphiboles as "possible amphiboles." Label all others as "unknown" or "non-asbestos."
NOTE: Fibers smaller than 0.2 µm in diameter may not produce sufficient peak heights to allow an elemental profile to be determined. Identify these fibers as "unknown".

21. Counting and Sizing:
a. Insert the sample into the specimen grid holder and scan the grid at zero tilt at low magnification (ca. 300 to 500X). Ensure that the carbon film is intact and unbroken over ca. 75% of the grid openings.
b. In order to determine how the grid should be sampled, estimate the number of fibers per grid opening during a low-magnification scan (ca. 1000X). This will allow the analyst to cover most of the area of the grid during the fiber count and analysis. Use the following rules when picking grid openings to count [10]:
(1) Light (<5 fibers per grid opening): count every grid opening in which the carbon film is intact.
(2) Moderate (5 to 25 fibers per grid opening): count every fifth grid opening. If the carbon film is damaged, proceed to the next available grid opening in which the film is intact.
(3) Heavy (>25 fibers per opening): count every tenth grid opening. If the carbon film is damaged, proceed to the next available opening in which the carbon film is intact.
c. Increase magnification to 10,000X. Begin counting at one end of the grid and systematically traverse the grid by rows, reversing direction at row ends. Count at least 2 field blanks per sample set to document possible contamination of the samples. Use the mean fiber count for the field blanks, B, in step 22. Count fibers and asbestos structures using the following rules:
NOTE: Microscopes which traverse nonlinearly or erratically, causing incomplete coverage of the grid opening are not suitable for asbestos analysis [11]. Before using a specific microscope for counting, it should be examined for accuracy and reproducibility of traverses.
(1) Count all particles less than 3 µm diameter which meet the definition of a fiber (aspect ratio ≥3:1, with parallel sides).
NOTE: Particles which are of questionable morphology should be analyzed by SAED and EDX to aid in identification.
(2) Size each fiber as it is counted and record the diameter and length (mm):
(a) Move the fiber to the center of the screen. Read the length of the fiber directly from the scale on the screen.
NOTE: For fibers which extend beyond the field of view, the fiber must be moved and superimposed upon the scale until its entire length has been measured.
(b) When a fiber has been sized, return to the starting point and continue the traverse to the next fiber.
(3) Record other asbestos structures according to the following morphological definitions. Label combinations of these structures according to the dominant quality.
(a) Bundle - compact arrangement of parallel fibers in which separate fibers or fibrils may only be visible at the ends or edges of the bundle.
NOTE: Asbestos bundles having aspect ratios of 3:1 or greater and less then 3 µm in diameter are counted as fibers.

(b) Cluster - network of randomly-oriented interlocking fibers arranged so that no fiber is isolated from the group. Dimensions of clusters can only be roughly estimated and clusters are defined arbitrarily to consist of more than four individual fibers [10].

(c) Matrix - one or more fibers attached to or embedded in a non-asbestos particle.

(4) Count fibers which are partially obscured by the grid.

NOTE: If a fiber is partially obscured by the grid bar at the edge of the field of view, count it as a fiber greater than 5 µm only if more than 2.5 µm of fiber is visible. Otherwise, log the fiber as a "short" fiber, measuring only that portion which is visible.

(5) When counting is complete, calculate the asbestos fiber fraction shorter than 5 µm and thinner than ca. 0.25 µm (the number of asbestos fibers which would be undetected by phase contrast microscopy).

d. Size all fibers using the scale on the fluorescent screen.

NOTE: Data can be recorded directly off the screen in mm and later converted to µm by computer. Count and record identified asbestos fibers and structures >1 µm long of all diameters [11]. However, when comparing TEM data to the PCM counts, all fibers, regardless of identification, greater than 5 µm long and between 0.25 and 3.0 µm diameter which have aspect ratios of 3:1 or greater should be included. This size adjustment is necessary to test comparability of counts between the two methods. If the size-adjusted counts show reasonable equivalency, then further analysis using the small-fiber data will show what fraction of airborne asbestos fibers is being missed by the PCM method.

CALCULATIONS:

22. Calculate and report fiber density on the filter, E, by dividing the total fiber count F, minus the mean field blank count, B, by the number of fields counted, n, (for each sample), and the field area, A_f.

$$E = \frac{\left(\frac{F}{n_f} - \frac{B}{n_b}\right)}{A_f}, \text{ fibers/mm}^2$$

NOTE: The field area, A_f, is considered to be one grid opening, and the size may vary depending upon the type of grids used. This value is known from step 16.

23. Calculate and report the average concentration, C, (fibers/mL) of fibers in the air sample, V (L), using the effective collection area of the filter, A_c (385 mm² for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}$$

24. As an integral part of the report, give the model and manufacturer of the TEM as well as the model and manufacturer of the EDS system.

EVALUATION OF METHOD:

The TEM method has been shown to have a precision of 0.275 (s_r) in an evaluation of mixed amosite and wollastonite fibers. The estimate of the asbestos fraction, however, had a precision of 0.11 (s_r). When this fraction was applied to the PCM count, the overall precision of the combined analysis was 0.20 [3].

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METHOD WRITTEN BY: James W. Carter; Paul A. Baron, Ph.D.; and David G. Taylor, Ph.D.; NIOSH/DPSE.

FORMULA: Ba

M.W.: 137.34

BARIUM, soluble compounds

METHOD: 7056

ISSUED: 8/15/87

OSHA: 0.5 mg/m³
NIOSH: no recommended standard [1]
ACGIH: 0.5 mg/m³

PROPERTIES: solubility @ 100 °C [2]:
$BaCO_3$: 0.006 g/100 g H_2O;
$BaCl_2$: 59 g/100 g H_2O;
$Ba(NO_3)_2$: 34 g/100 g H_2O;
BaO: 91 g/100 g H_2O

SYNONYMS: vary depending upon compound; CAS #7440-39-3.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 50 L
-MAX: 2000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.28 to 1.08 mg/m³ [3]
(168-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.054 [3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: barium ion (Ba^{2+})

EXTRACTION: hot water leach, 10 mL, 10 min, twice; conc. HCl, 3 drops; evaporate to dryness

FINAL SOLUTION: 5% HCl/1.1 mg/mL Na^+, 5 mL

FLAME: nitrous oxide-acetylene reducing

WAVELENGTH: 553.6 nm

CALIBRATION: standard solutions of Ba^{2+} in 5% HCl/1.1 mg/mL Na^+

RANGE: 0.025 to 0.2 mg per sample [3]

ESTIMATED LOD: 0.002 mg per sample [3]

PRECISION (s_r): 0.025 @ 0.043 to 0.18 mg per sample [3]

APPLICABILITY: The working range is 0.13 to 10 mg/m³ for a 200-L air sample. This method determines Ba^{2+} in water-soluble barium compounds. Insoluble barium compounds (e.g., $BaSO_4$) require an ashing procedure.

INTERFERENCES: Ionization of barium in the flame is controlled by addition of sodium chloride to samples and standards. Calcium, at >0.1%, gives a positive interference unless background correction is used.

OTHER METHODS: This revises Method S198 [4].

REAGENTS:

1. Water, distilled or deionized.
2. Nitric acid (HNO_3), conc.
3. Hydrochloric acid (HCl), conc.
4. Sodium chloride (NaCl).
5. 5% HCl (v/v)/1.1 mg/mL Na^+: Dilute 5 mL conc. HCl and 0.28 g NaCl to 100 mL with deionized water.
6. Calibration stock solution, 1000 µg Ba/mL. Commercially available or dissolve 1.437 g $BaCO_3$ in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl.
7. Nitrous oxide, 98%.
8. Acetylene, 99.6%.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with nitrous oxide-acetylene burner head and barium hollow cathode lamp.
   NOTE: Background correction (e.g., D_2 or H_2 lamp) needed for samples with >0.1% (w/v) Ca^{2+}.
4. Regulators, two-stage, for nitrous oxide and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 10- and 100-mL.*
7. Pipets, 4- to 400-µL, and 5-mL.
8. Hotplate, surface temperature 140 °C.
9. Forceps or tweezers, plastic-tipped.
10. Centrifuge, and centrifuge tubes, 50-mL.

*Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 50 to 2000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Open cassette filter holders and transfer samples and blanks to clean beakers.
4. Add 10 mL boiling distilled water. Let sit 10 min with occasional swirling. Decant extract to a centrifuge tube.
5. Wash filter and beaker twice with ca. 2 mL hot distilled water and add to centrifuge tube.
6. Repeat extraction and washing (steps 4 and 5), adding the solutions to the centrifuge tube.
7. Remove filter with forceps and rinse with stream of hot distilled water into centrifuge tube.
8. Rinse original beaker three times with ca. 2 mL hot distilled water and add to centrifuge tube. Centrifuge and decant the solution to a second beaker.
9. Add three drops conc. HCl to sample and evaporate to dryness.
10. Cool each beaker. Pipet 5.0 mL 5% HCl/1.1 mg/mL Na^+ solution into each beaker. Swirl to dissolve residue.

CALIBRATION AND QUALITY CONTROL:

11. Add known amounts of calibration stock solution to 10-mL volumetric flasks and dilute to volume with 5% HCl/1.1 mg/mL Na^+ solution to produce Ba^{2+} concentrations in the range 0.4 to 40 µg/mL (0.002 to 0.2 mg per sample). Prepare fresh daily.

12. Analyze working standards with the blanks and samples (steps 19 and 20).
13. Prepare calibration graph (absorbance vs. solution concentration, µg/mL).
14. Aspirate a standard for every ten samples to check instrument drift.
15. Check recoveries with at least one spiked media blank per ten samples.
16. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7056-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If absorbance values for samples are above the linear range of the standards, dilute with 5% HCl/1.1 mg/mL Na^+ solution, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of barium in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of barium, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S198 was validated using atomized aqueous solutions of barium chloride to generate atmospheres at approximately 0.3 to 1.1 mg/m^3 [3]. Samples taken at 1.4 L/min showed 100% collection efficiency. Recovery of barium chloride standards spiked on filters was 102% with s_r = 1.4% in the range 0.043 to 0.18 mg barium per sample.

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METHOD REVISED BY: Mary Ellen Cassinelli, NIOSH/DPSE.

FORMULA:  ; C_6H_6

M.W.: 78.11

BENZENE by portable GC

METHOD: 3700

ISSUED: 8/15/87

OSHA: 1 ppm; STEL 5 ppm
NIOSH: C 1 ppm (suspect carcinogen) [1]
ACGIH: 10 ppm; 25 ppm STEL (suspect carcinogen)
(1 ppm = 3.19 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.879 g/mL @ 20 °C;
BP 80.1 °C; MP 5.5 °C;
VP 12.7 kPa (95.2 mm Hg; 12.5% v/v) @ 25 °C;
explosive range 1.3 to 7.1% v/v in air

SYNONYMS: CAS #71-43-2.

SAMPLING

SAMPLER: AIR BAG (Tedlar)

FLOW RATE: 0.02 to 0.05 L/min or higher; fill bag to ≤80% of capacity; spot samples possible (step 2.a.)

SAMPLE STABILITY: bags should be analyzed as soon after collection as possible (≤4 hrs)

FIELD BLANKS: clean air, either in bag or from a non-work area

ACCURACY

RANGE STUDIED: 1 to 100 ppm

BIAS: not significant

OVERALL PRECISION (s_r): 0.136

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: benzene

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 0.1 to 500 ppm

ESTIMATED LOD: 0.15 ng per injection (0.05 ppm for a 1-mL injection)

PRECISION (s_r): 0.127

APPLICABILITY: The working range is 0.1 to 500 ppm (0.3 to 1600 mg/m³) in relatively non-complex atmospheres where benzene is known to be present (see EVALUATION OF METHOD).

INTERFERENCES: Any compound having the same or nearly the same retention time as benzene on the column in use.

OTHER METHODS: Methods 1500 (Hydrocarbons, BP 36 - 126 °C) and 1501 (Hydrocarbons, aromatic) use activated charcoal sampler tubes.

REAGENTS:

1. Benzene* in air, working standards prepared in the field by filling Tedlar bags with commercially prepared and certified standards (preferred) or prepared in the field by injecting known amounts of pure benzene into Tedlar bags containing a metered volume of pure air or nitrogen.
2. Cylinder of air, nitrogen or helium for use as carrier gas and field blanks.*

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop and (if appropriate) strip chart recorder.
2. Personal sampling pump, 0.02 to 0.05 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
   NOTE: Pumps lubricated with petroleum products should not be used.
3. Sample bags, Tedlar, 2- to 20-L or other appropriate sizes.
4. Syringes, gas-tight, of various sizes appropriate to the GC.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labeling bags.

SPECIAL PRECAUTIONS: Benzene is a suspect carcinogen [1]. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING:

1. Start GC instrument and recorder and allow to warm up according to manufacturer's instructions.
   NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. Spot sample. Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration; and
   b. Integrated air sample for TWA determination.
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
      NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
      (2) Attach the sample bag to the outlet port of a personal sampling pump with a minimum length of flexible tubing.
      (3) Pump the air sample into the bag at a rate calculated to fill $\leq$80% of the sample bag capacity over the sampling period.
      NOTE: The flow rate must be known within $\pm$5% throughout the sampling period.

(4) Within 4 hrs after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2.a).

3. Obtain the benzene peak height of the injected sample.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph by at least three replicate determinations of at least five working standards. Plot peak height vs. mass of benzene.
   b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
   c. Determine the ability of the GC column to separate the benzene peak from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph (peak height vs. mass of benzene) by triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate mass, W (ng), of benzene in sample by comparison of sample peak height with daily calibration graph (step 5). Determine concentration, C, of benzene in the injected sample, V (mL):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

NOTE: Some GCs will perform this calculation electronically.

EVALUATION OF METHOD:

This method was evaluated over the range 1 to 100 ppm (3.2 to 320 ppm) benzene using a Photovac 10A10 portable GC. Certified standard gas mixtures of benzene in air were obtained from Scott Specialty Gases Inc., and these were used to establish the calibration graph. Once this graph was established, bias was assessed by analyzing a bag sample containing an unknown concentration and comparing the concentration obtained with that obtained from analysis of replicate charcoal tube sample taken from the same bag.

A limitation in the use of this type of portable GC (e.g., packed column, room temperature isothermal) is the limited ability to separate the analyte from any interferences present. In the evaluation of this method, a six-foot SE-30 column was used. Its ability to separate the benzene peak from other contaminants was not evaluated. However, the use of this or any other packed column operated at room temperature to separate complex mixtures is severely limited. Therefore, the application of this method should be confined to relatively uncomplicated atmospheres.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Benzene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 74-137 (1974); as revised in August, 1976, and by E. J. Baier, NIOSH Testimony to U.S. Department of Labor, July, 1977.

METHOD WRITTEN BY: J.C. Posner, Ph.D., NIOSH/DPSE

FORMULA: Be

M.W.: 9.01

BERYLLIUM and compounds, as Be

METHOD: 7102
ISSUED: 2/15/84
REVISION #1: 8/15/87

OSHA: 2 µg/m³; C 5 µg/m³
NIOSH: not to exceed 0.5 µg/m³ [1]
ACGIH: 2 µg/m³ (suspect carcinogen)

PROPERTIES: hard, light metal; valence +2;
MP 1284 to 1300 °C;
d 1.85 g/mL (20 °C)

SYNONYMS: CAS #7440-41-7; other synonyms vary as to compound.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 25 L @ 2 µg/m³
-MAX: 1000 L @ 2 µg/m³

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 2.7 to 11.8 µg/m³ [2]
(40-L samples)

BIAS: not significant

OVERALL PRECISION (s_r): 0.064 [2]

MEASUREMENT

!
!TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE
!
!ANALYTE: beryllium
!
!ASHING REAGENTS: HNO_3, 10 mL; H_2SO_4, 1 mL
!
!CONDITIONS: 150 °C until brown fumes disappear;
! 400 °C to dense fumes of H_2SO_4
!
!FINAL SOLUTION: 2% Na_2SO_4, 3% H_2SO_4;
! 10 mL
!
!GRAPHITE FURNACE: 110 °C dry 20 sec;
! 900 °C char 10 sec;
! 2800 °C atomize 18 sec
!
!WAVELENGTH: 234.9 nm
!
!BACKGROUND CORRECTION: D_2 or H_2 continuum
!
!INJECTION VOLUME: 10 µL
!
!CALIBRATION: Be^{++} in 2% Na_2SO_4,
! 3% H_2SO_4
!
!RANGE: 0.05 to 1 µg per sample [3]
!
!ESTIMATED LOD: 0.005 µg per sample [3]
!
!PRECISION (s_r): 0.008 [3]
!

APPLICABILITY: The working range is 0.5 to 10 µg/m³ for a 90-L air sample. The method is applicable to ceiling measurements using a 25-L air sample.

INTERFERENCES: Calcium interference is masked by 3% (v/v) sulfuric acid. Sodium, potassium, and aluminum enhance beryllium absorbance; this effect is overcome by addition of 2% (w/v) sodium sulfate to both standards and samples. Perchloric, phosphoric, and hydrofluoric acids produce interfering non-atomic peaks. These must be removed by digesting to dryness.

OTHER METHODS: This revises Method P&CAM 288 [3], which replaced Method S339 [4]. Flame atomic absorption and plasma emission (ICP-AES) are not sensitive enough for beryllium at these levels.

REAGENTS:

1. Nitric acid, conc.
2. Sulfuric acid, conc.
3. Sodium sulfate, reagent grade.
4. Sodium sulfate, 2% (w/v)/3% sulfuric acid (v/v). Add 10 g sodium sulfate and 15 mL H_2SO_4 to deionized water. Dilute to 500 mL.
5. Calibration stock solution, 1000 µg Be/mL,* commercially available, or dissolve 1.000 g Be metal in a minimum volume of 1+1 HCl, dilute to 1 L with 1% (v/v) HCl
6. Argon, prepurified.
7. Water, distilled or deionized.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter in three-piece cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace and background corrector.
4. Beryllium hollow cathode lamp.
5. Pressure regulator, two-stage, for Argon.
6. Beakers, Phillips, 125-mL.*
7. Watchglasses.*
8. Volumetric flasks, 10-mL.*
9. Pipets, 10-mL delivery, with pipet bulb.*
10. Automatic pipettor with tips, 10-µL and assorted sizes for standards.
11. Hotplate, 150 to 400 °C.
12. Waterbath, 60 to 70 °C.
13. Bottles, polyethylene, 25-mL.

*Clean all glassware with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Beryllium is very toxic and a suspected human carcinogen [1]. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 25 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open cassettes and transfer filters to clean Phillips beakers.
4. Add 10 mL conc. HNO_3 and 1 mL conc. H_2SO_4. Cover with watchglass.
5. Heat in fume hood on hotplate (150 °C) until brown fumes of HNO_3 disappear, then at 400 °C until dense fumes of H_2SO_4 appear.
   NOTE: Verify that the compounds in the samples are soluble with this ashing procedure, e.g., ore or mining samples will require HF in the digestion. If additional ashing acids are used (e.g., HF, $HClO_4$, or H_3PO_4), evaporate to complete dryness at this point.
6. Cool and rinse watchglass and sides of beaker with distilled water and evaporate just to dryness. Remove beaker immediately and air-cool.
7. Pipet 10.0 mL 2% Na_2SO_4/3% H_2SO_4 solution into beaker and cover. Start sulfate reagent blanks at this step.
8. Heat in 60 to 70 °C waterbath for 10 min. Allow to stand overnight before analysis to ensure complete dissolution of $BeSO_4$.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 0.005 to 1 µg Be per sample.

a. Use serial dilutions of known amounts of calibration stock solution in 2% Na_2SO_4/ 3% H_2SO_4 to prepare working standards. Store in polyethylene bottles. Stable at least four weeks.
b. Analyze together with samples and blanks (steps 11 and 12).
NOTE: Analyze working standards alternately with the samples to compensate for the increasing Be signal as the graphite tube ages.

10. Analyze three quality control blind spikes and three analyst spikes.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations and to conditions on page 7102-1.
12. Inject 10-µL aliquots of samples into graphite tube. Record absorbance (peak height mode).

CALCULATIONS:

13. Read absorbance of samples, A; average media blanks, A_b; average sulfate reagent blanks, A_r; and working standards, A_s.
14. Using the working standard, C_s (µg/mL), analyzed adjacent to the sample of interest, calculate concentration, C (µg/m³), of Be in the air volume sampled, V (L):

$$C = \frac{(A - A_b) \cdot C_s \cdot 10^4}{(A_s - A_r)V}, \mu g/m^3$$

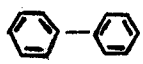
EVALUATION OF METHOD:

This method was evaluated using NBS Standard Reference Material No. 2675 for Be over the range of 0.1 to 0.4 µg Be/filter (equivalent to one-half to two times the OSHA PEL). Beryllium recovery was 98.2% with a measurement precision, s_r, of 0.008 [3]. This method is an improvement of S339 [4], which was validated over the range of 2.68 to 11.84 µg/m³ using a 40-L sample. Mean recovery was 106.9% with overall precision of 0.064 [2].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Beryllium, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 72-10268 (1972); and as revised in August, 1977 in NIOSH testimony at OSHA hearing.
[2] Documentation of the NIOSH Validation Tests, S339, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 288, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 79-141 (1979).
[4] Ibid., V. 3, S339, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY: Mary Ellen Cassinelli, NIOSH/DPSE; S339 validated under NIOSH Contract CDC-99-74-45.

FORMULA:  ; $C_{12}H_{10}$

M.W.: 154.21

BIPHENYL

METHOD: 2530

ISSUED: 8/15/87

OSHA: 0.2 ppm
NIOSH: no recommended standard [1]
ACGIH: 0.2 ppm
(1 ppm = 6.30 mg/m³ @ NTP)

PROPERTIES: solid; d 1.041 g/mL @ 20 °C;
MP 69 °C; BP 255 °C;
VP 1.3 Pa (0.01 mm Hg; 13 ppm) @ 25 °C;
flash point 113 °C

SYNONYMS: diphenyl; CAS #92-52-4.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Tenax GC, 20 mg/10 mg)

FLOW RATE: 0.01 to 0.5 L/min

VOL-MIN: 3 L @ 0.2 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: 95% recovery after 7 days @ room temperature

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.64 to 2.4 mg/m³ [2]
(30-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.068 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: biphenyl
!
!DESORPTION: 1 mL CCl_4, stand 15 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 225 °C
! -DETECTOR: 250 °C
! -COLUMN: 135 °C
!
!CARRIER GAS: nitrogen, 50 mL/min
!
!COLUMN: 1.8 m x 4 mm ID glass packed with 5%
! OV-17 on 80/100 mesh Chromosorb WHP
!
!CALIBRATION: standard solutions of biphenyl in
! CCl_4
!
!RANGE: 4 to 120 µg per sample
!
!ESTIMATED LOD: 0.09 µg per sample [2]
!
!PRECISION (s_r): 0.019 [2] @ 19 to 76 µg per
! sample
!

APPLICABILITY: The working range is 0.02 to 0.63 ppm (0.13 to 4 mg/m³) for a 30-L air sample. Measurement of concentrations down to 0.004 mg/m³ may be possible if the desorption efficiency remains adequate.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S24 [3].

REAGENTS:

1. Acetone, reagent grade.*
2. Hexane, reagent grade.*
3. Carbon tetrachloride (CCl_4), reagent grade.*
4. Biphenyl, reagent grade.
5. Calibration stock solution, 1.2 mg/mL. Dilute an accurately weighed 120-mg portion of biphenyl to 100 mL with carbon tetrachloride.
6. Desorption efficiency (DE) stock solution, 12 mg/mL. Dilute an accurately weighed 120-mg portion of biphenyl to 10 mL with hexane.
7. Nitrogen, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 6 cm long, 6 mm OD, 4 mm ID, containing two sections of cleansed 35/60 mesh Tenax GC (front = 20 mg; back = 10 mg), separated by 2-mm urethane foam plug. A silylated glass wool plug is placed at both ends. Pressure drop across the tube at 0.5 L/min must be less than 3.4 kPa. Tubes are commercially available.
   NOTE: Cleanse bulk Tenax GC by placing it in sintered glass filter fitted to large vacuum flask. Add volume of acetone equal to twice that of sorbent and mix, then remove acetone by filtration. Repeat washing six times. Dry sorbent at 120 °C under vacuum for 4 h.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (see page 2530-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10- and 100-mL.
7. Pipets, 1-mL, and other convenient sizes.
8. Balance, readable to 0.1 mg.

SPECIAL PRECAUTIONS: Hexane (flash point = -22 °C) and acetone (flash point = -18 °C) are highly flammable and carbon tetrachloride is highly toxic. Prepare sorbent, samples, and standards in 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 0.5 L/min for a total sample size of 3 to 30 L.
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 CCl_4 to each vial. Cap each vial.
7. Allow to stand 15 min with occasional agitation.
   NOTE: Fine particles of Tenax tend to plug an autosampler syringe. For use with autosampler, transfer supernatant solutions to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.1 to 120 µg biphenyl per sample. Use serial dilutions for the smallest concentrations.
   a. Add known amount of calibration stock solution to CCl_4 in 10-mL volumetric flask and dilute to the mark.

b. Analyze with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (peak height or area vs. µg biphenyl per sample).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 2 to 10 µL of DE stock solution (or of a serially diluted solution in hexane) 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 with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg biphenyl recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2530-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CCl_4, reanalyze and apply the appropriate dilution factor in calculations.
    NOTE 2: Under these conditions, t_r for biphenyl is approximately 6 min.
12. Measure peak height or area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of biphenyl 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 biphenyl in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S24 was issued on November 25, 1977 [3], and validated over the range 0.64 to 2.4 mg/m³ using 32-L samples collected on Tenax GC, Lot 04901 (Applied Science Laboratories) [2]. The biphenyl concentration was independently determined by UV analysis of samples collected in methanol. Overall precision, s_r, was 0.068 with an average recovery of 92.7%, representing a non-significant bias. Desorption efficiency averaged 0.987 in the range 19 to 76 µg per sample. For samples collected at 2.5 mg/m³, 25 °C, and >85% RH, breakthrough to the backup section averaged 3.9% between 31.5 and 48.6 L, and 9.4% between 48.6 and 64.2 L. Recovery from a set of samples stored one week under ambient conditions was 95.0% relative to a set analyzed immediately. Previous work showed desorption efficiency to be poor (<0.7) for biphenyl on SKC Lots 104 and 105 charcoals [2,4].

REFERENCES:
[1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[2] Backup Data Report No. S24, Diphenyl, prepared under NIOSH Contract No. 210-76-0123 (November, 1977), available as "Ten NIOSH Analytical Methods, Set 4," Order No. PB281-038 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S24, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Failure Report S24, NIOSH Contract CDC-99-74-45 (unpublished, 1977).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., NIOSH/DPSE; S24 originally validated under NIOSH Contract No. 210-76-0123.

FORMULA: $CBrF_3$

M.W.: 148.92

BROMOTRIFLUOROMETHANE

METHOD: 1017
ISSUED: 8/15/87

OSHA: 1000 ppm
NIOSH: no recommended standard [1]
ACGIH: 1000 ppm
(1 ppm = 6.09 mg/m³ @ NTP)

PROPERTIES: gas; vapor density 5 (air = 1);
BP -57.8 °C; MP -168 °C;
nonflammable

SYNONYMS: Refrigerant 13B1; trifluorobromomethane; CAS #75-63-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(two coconut shell charcoal tubes in series, 400 mg/200 mg and 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.3 L @ 1000 ppm
-MAX: 1 L

SHIPMENT: separate front and back tubes; in dry ice

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 2890 to 11,500 mg/m³ [2]
(1-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.065 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: bromotrifluoromethane

DESORPTION: 5 mL methylene chloride; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 225 °C
-COLUMN: 160 °C
-DETECTOR: 260 °C

CARRIER GAS: N_2, 25 mL/min

COLUMN: stainless steel, 1.2 x 6 mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of analyte in methylene chloride

RANGE: 2 to 18 mg per sample [2]

ESTIMATED LOD: 0.05 mg per sample

PRECISION (s_r): 0.038 @ 3 to 12 mg per sample [2]

APPLICABILITY: The working range is 330 to 3000 ppm (2000 to 18,000 mg/m³) for a 1-L air sample.

INTERFERENCES: None reported.

OTHER METHODS: This revises Method S125 [3].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality.*
2. Bromotrifluoromethane, 99%.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8 mm OD, 6 mm ID, followed by 7 cm long, 6 mm OD, 4 mm ID) connected in series with a short piece of tubing, flame-sealed ends and plastic end caps. Each tube contains two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg + 200 mg; back tube = 100 mg + 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes each front section and a 3-mm urethane foam plug follows each back section. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1017-1).
4. Vials, 10-mL, PTFE-lined caps.
5. Syringes, gas tight, 10-µL to 3-mL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 5-mL.
8. DE apparatus. Glass tubing, through which nitrogen flows at ca. 200 mL/min, with T-connection and septum. Wrap outlet of tubing with heating tape and connect tubing to inlet of test sampler.

SPECIAL PRECAUTIONS: Methylene chloride is a suspect carcinogen and is metabolized to carbon monoxide, a toxic gas [4].

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 with the smaller tube nearer the sampling pump.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 0.3 to 1 L.
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with dry ice.

SAMPLE PREPARATION:

5. Pipet 5.0 mL chilled CH_2Cl_2 into a series of vials.
6. Place the front and back sorbent sections of the front sampler tube in a vial. Discard the glass wool and foam plugs. Immediately cap the vial. Similarly place the front and back sorbent sections of the back sampler tube in a separate vial.
7. Allow to stand 30 min with occasional agitation. Analyze within 6 hrs.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known volumes of bromotrifluoromethane gas with a gas-tight syringe to 5.0 mL CH_2Cl_2 in 10-mL volumetric flasks by slowly bubbling the gas through the liquid with the tip of the syringe needle near the bottom of the volumetric flask. Dilute to the mark. Use serial dilutions as needed to obtain bromotrifluoromethane concentrations in the range 0.01 to 3.6 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg bromotrifluoromethane).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Connect a large charcoal tube (400 mg/200 mg) to the outlet of the DE apparatus. Start nitrogen flow (ca. 200 mL/min) through the DE apparatus and into the charcoal tube. Inject a known amount (0.01 to 3 mL; 0.05 to 18 mg @ NTP) for bromotrifluoromethane gas into the septum. Allow the N_2 flow to continue for 20 sec.
   b. Cap the tube. Allow to stand overnight at -10 °C.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. mg bromotrifluoromethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1017-1. 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 an aliquot of the desorbed liquid with CH_2Cl_2 reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE of bromotrifluoromethane found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of bromotrifluoromethane in the air volume sample, V (L):

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

EVALUATION OF METHOD:

Method S125 was issued on May 9, 1975 [3], and validated over the range 2890 to 11,500 mg/m³ at 25 °C and 760 mm Hg using 1-L samples [2]. Generated concentrations were produced by calibrated gas flows and verified by a total hydrocarbon analyzer, standardized with gas standards. Overall precision, s_r, was 0.065, with average recovery of 100%. Desorption efficiency was 0.81 in the range 3 to 12 mg per sample. Breakthrough (effluent = 5% of test concentration) occurred in 90 min when a concentration of 12,370 mg/m³ was sampled at a rate of 0.046 L/min.

REFERENCES:
[1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154069 from NTIS, Springfield, VA 22161.
[2] Documentation of the NIOSH Validation Tests, S125, 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.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S125, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

METHOD REVISED BY: Y. T. Gagnon, K. J. Williams, and G. David Foley, NIOSH/DPSE.

FORMULA: C_4H_6, CH_2=CHCH=CH_2

M.W.: 54.09

1,3-BUTADIENE
METHOD: 1024
ISSUED: 8/15/87

OSHA: 1000 ppm
NIOSH: potential carcinogen [1]
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 2.21 mg/m³ @ NTP)

PROPERTIES: gas; vapor density 1.9 (air = 1);
BP -4.4 °C; VP 280 kPa (26 psig) @ 25 °C;
explosive range 2.0 to 11.5% v/v in air

SYNONYMS: CAS #106-99-0

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut charcoal, 400- and 200-mg in separate tubes)

FLOW RATE: 0.01 to 0.5 L/min

VOL-MIN: 3 L
-MAX: 25 L @ 100 ppm

SHIPMENT: separate front and back tubes, chill below -4 °C

SAMPLE STABILITY: at least two months for quality assurance blind spikes stored in a freezer

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.19 to 19 mg/m³
(25-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION (s_r): 0.060

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,3-butadiene

DESORPTION: 4 mL methylene chloride; 30 min

INJECTION: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 °C
-COLUMN: see APPENDIX A

CARRIER GAS: helium

MAKEUP GAS: nitrogen, 30 mL/min

COLUMNS: fused silica, 10-m x 0.50-mm ID
1.8-µm CP WAX 57 CB (backflushable pre-column), and 50-m x 0.32-mm ID
Al_2O_3/KCl PLOT (see APPENDIX A)

CALIBRATION: vapor-spiked sampling media

RANGE: 1 to 480 µg per sample

ESTIMATED LOD: 0.2 µg per sample

PRECISION (s_r): 0.025

APPLICABILITY: Assuming 25-L sampling volumes: the upper limit of the sampler is 220 mg/m³ (100 ppm); the measurement range covers 0.044 to 19 mg/m³ (0.02 to 8.7 ppm). At higher levels, desorbed samples may require dilution. Below 0.9 mg/m³ (0.4 ppm), the desorption efficiency falls below 75% and allowance should be made for decreased accuracy.

INTERFERENCES: Pentane, methyl acetylene, or vinylidene chloride may chromatographically interfere at high levels. High humidity (>80% RH) or other hydrocarbons present at permissible levels may significantly decrease the sampler's capacity for 1,3-butadiene.

OTHER METHODS: This revises Method S91 [2].

REAGENTS:

1. Methylene chloride,* chromatographic quality with hydrocarbon (cyclohexene) preservative.
2. 1,3-Butadiene,* 99.5%, in cylinder equipped for gas withdrawal, with needle valve.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, purified.
6. Nitrogen, purified.
7. Water, distilled.

*See Special Precautions.

EQUIPMENT:

1. Sampler: Tandem charcoal tubes. Each tube is flame-sealed glass (8.5 cm long, 8-mm OD, 6-mm ID), has plastic caps for resealing, and contains activated coconut shell charcoal (such as SKC Lot 120) preceded by silylated glass wool and followed by a 3-mm urethane foam plug. The front tube holds 400 mg charcoal. The back tube holds 200 mg.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., Blue Ice or dry ice), and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see APPENDIX A).
5. Ice, wet.
6. Vials, 5-mL, 2-mL, 1-mL, and other convenient sizes, with PTFE-lined septum caps.
7. Pipettes, TD, 4-, 2-, and 1-mL.
8. Syringes, gas-tight, 250-, 100-, 25-, and 10-µL.
9. Beaker, 150-mL.
10. Gas drying tube with serum cap to fit stem and 2-cm piece of plastic tubing to fit over serum cap.

SPECIAL PRECAUTIONS: 1,3-Butadiene is a potential carcinogen, teratogen, and reproductive hazard [1]. Methylene chloride is toxic, very volatile, and a suspect carcinogen [3]. Work should be performed in a well-ventilated fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.01 to 0.5 L/min for a sample size of 3 to 25 L.
4. Separate the tubes, cap, and pack securely for shipment. Chill below -4 °C during shipment and storage.

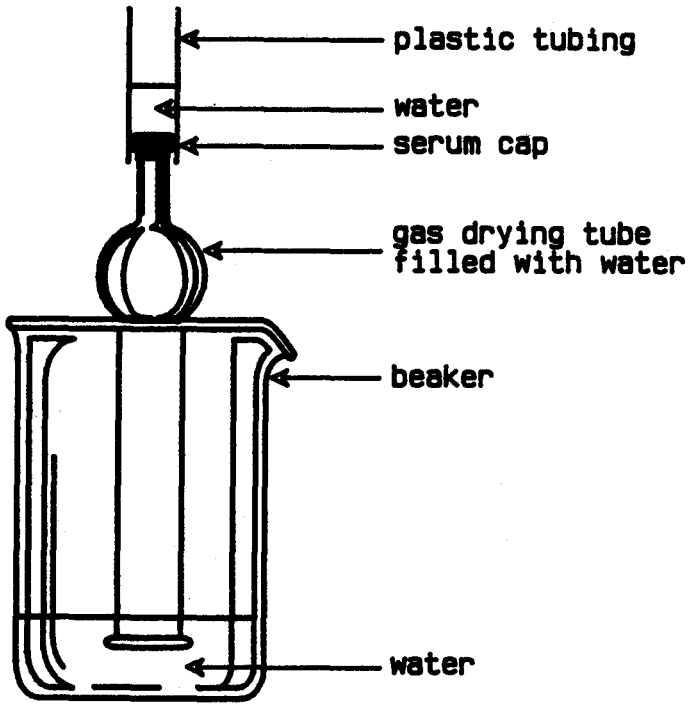
SAMPLE PREPARATION:

5. Add 4.0 mL methylene chloride to 5-mL vials and 2.0 mL to 2-mL vials. Loosely cap vials and thoroughly chill in ice.
6. Place front sorbent sections in 5-mL vials and back sections in 2-mL vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Remove from ice and allow to stand 30 min with occasional agitation.
8. Transfer sample solution to appropriate vial and cap if using an autosampler. Thoroughly chill solution and vial before making transfer.

CALIBRATION AND QUALITY CONTROL:

NOTE: The accurate measurement of pure 1,3-butadiene gas by gas-tight syringe is a critical step in the calibration. Even a slight obstruction (e.g., flakes of PTFE from the plunger tip which obstruct the needle) can cause 1,3-butadiene to be liquified as the plunger is depressed, making delivery incomplete. Bracketing gas samples with water, as described below, allows the volume taken to be approximately verified, and assures complete delivery. The precision of the analysis of multiple independent standards is another indicator of the accuracy of the volumes taken.

9. Make up stock solutions in triplicate at three concentration levels, e.g., 200 µL of 1,3-butadiene gas in 1 mL solution, and both 200 and 50 µL of gas in 4 mL solution:
   a. Prepare a beaker and drying tube assembly as shown below. Bubble 1,3-butadiene under the lower edge of the drying tube so that water is displaced and the gas is trapped in the tube.



   b. Pipet 1 or 4 mL of methylene chloride into a 1- or 5-mL vial, cap, and thoroughly chill.
   c. Take a known amount (50 or 200 µL) of 1,3-butadiene from the drying tube with a 100- or 250-µL gas-tight syringe. Bracket the gas in the syringe with small amounts of water (5 to 10% of syringe volume) taken from the area above the serum cap before and after withdrawing the gas. Do not take water from inside the drying tube, since it may contain a significant amount of dissolved 1,3-butadiene.
   d. Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
   e. Agitate and continue to chill the vial to complete dissolution.
10. Calibrate daily with media blanks and triplicate independent media standards of at least five levels ranging from, e.g., 0.5 to 200 µL 1,3-butadiene gas per sample:
   a. Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
   b. Take pure gas (50 or 200 µL, as in step 9.c) for the higher levels, or 40 µL of stock solution for lower levels.
   c. Inject the gas and surrounding water plugs or the stock solution at a point inside the sampler near the glass wool plug while drawing clean air through tube at 0.05 L/min. Continue to draw air through the tube for 5 min or just until the stock solution evaporates.
   d. Seal tube with plastic caps.
   e. Store at temperature below -4 °C overnight, then desorb (steps 5 through 8).
   f. Analyze media standards and blanks together with samples (steps 13 and 14).
   g. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in µg/mL).

11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in calibration range (step 10).
    a. Dilute the stock solutions (step 9) with methylene chloride to extend the range of standards down to 0.1 µg/mL. Avoid including water in the portions diluted.
    b. Transfer solutions as in step 8 if using an autosampler, and analyze together with media standards (steps 13 and 14).
    c. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare DE calibration graph of peak area or height vs. µg/mL 1,3-butadiene.
    d. Read the concentrations, µg/mL, in media standards and blanks from DE calibration graph and multiply by the desorption volume to calculate the masses recovered.
    e. Prepare a graph of DE vs. µg taken. DE = (mass found - blank mass)/(mass taken).
12. Analyze three quality control blind spikes to insure that calibration graph (step 10) is in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1024-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If detector response is above range of working standards, dilute with methylene chloride, reanalyze, and apply appropriate dilution factor in calculations.
14. Measure peak area or height.
    NOTE: Vinylidene chloride, an impurity in methylene chloride, elutes just after 1,3-butadiene and may be used as an internal standard.

CALCULATIONS:

15. Determine the concentration, µg/mL, of 1,3-butadiene found in each sample front (W_f) and back (W_b) sorbent section from calibration graph (step 10), and multiply by desorption volume and dilution factor, if any, to calculate the mass, µg, found.
    NOTE 1: This calibration method corrects for media blank and DE. Do not duplicate corrections.
    NOTE 2: For any sampler with $W_b > W_f/10$, report breakthrough and possible sample loss.

16. Calculate concentration of 1,3-butadiene in the volume of air sampled, V (L):

$$C = \frac{(W_f + W_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The detector responses determined for triplicate standard solutions at each of five levels were linear over the range 0.3 to 440 µg per sample. The pooled s_r was 0.038. The estimated limit of detection was 0.02 µg/mL.

The capacity of a 400-mg charcoal sorbent section was 31 L for a sample at 80% RH and approximately 56 ppm 1,3-butadiene. When exposed to 0.7 and 2.5 mL of pure 1,3-butadiene gas followed by 80% RH air, breakthrough occurred after 35 L and 28.5 L, respectively. The corresponding respective time-weighted average concentrations were 20 and 88 ppm.

For the analysis of media standards at levels of 1.1, 4.4, 18, 125, and 480 µg per sample, the pooled s_r was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%,

respectively. Adding water to media standards just after spiking or during desorption had no significant effect on desorption efficiencies.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26 µg 1,3-butadiene and stored either at ambient temperature or in a freezer below -4 °C. Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the frozen samples, and 95% (1), 76% (7), 61% (14), and 65% (21) for the ambient samples.

In a preliminary evaluation of precision and accuracy, charcoal tubes were spiked with 125 µg 1,3-butadiene via calibrated sampling valve. The recovery was 102.2% versus media standards (corrected for desorption efficiency) and 96.8% versus standard solutions (uncorrected for desorption efficiency); the s_r of the response was 0.016. Subsequently, simulated samples were exposed to known amounts of approximately 10% 1,3-butadiene in helium, followed by 25 L of air at 80% RH. The 1,3-butadiene concentration was independently determined by packed column gas chromatography with thermal conductivity detection. Media standards were prepared via calibrated sampling valves. The recovery from six simulated samples at 463 µg per sample was 101.6% versus media standards and 91.3% versus standard solutions; the s_r of the response was 0.047. At 45.3 µg per sample, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the s_r of the response was 0.048. At 4.64 µg per sample, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the s_r of the response was 0.011. In the latter experiment, the two lowest levels of media standards appeared to be high, possibly due to absorption and release of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71 µg, with the three lowest levels of media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the s_r of the response was 0.023. The s_r of the response pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision of the total sampling and analytical method was 0.060. For levels at and above 45 µg (0.8 ppm in 25 L), apparent biases may be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, based on the linear response and near-zero intercept observed for the standard solution calibrations and the higher than expected desorption efficiencies for the samples, there appeared to be a positive bias in the preparation of the simulated samples.

The method has been used in six industrial hygiene surveys, for a total of 621 samples, most of which were collected under conditions of high ambient temperature and humidity. Only two samples showed severe breakthrough ($W_b > W_f/10$). Results for field samples at levels as high as 7.3 mg per sample were not significantly changed by dilution and reanalysis. In all, over 2000 analyses were made over a period of six months without any deterioration of the chromatographic columns. During the course of the analyses, twenty sets of standard solutions and media standards were prepared and analyzed, each set consisting of triplicates at each of five levels corresponding to 1.08 to 1.10, 4.32 to 4.40, 17.3 to 17.6, 108 to 110, and 432 to 441 µg per sample. For the five levels of standard solutions, the respective pooled relative standard deviations of the observed responses were 0.093, 0.074, 0.059, 0.055, and 0.071. For each set of standard solutions, the deviations of the responses were determined relative to the line resulting from a weighted linear regression of response on concentration. The 95% confidence intervals for the mean relative deviations from linearity for the five levels were -0.002 ± 0.003, 0.000 ± 0.003, -0.020 ± 0.002, 0.002 ± 0.002, and -0.019 ± 0.002, respectively. For the media standards, the respective pooled relative standard deviations for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were 60.4 ± 0.4, 66.4 ± 0.3, 70.5 ± 0.2, 86.2 ± 0.3, and 91.2 ± 0.2.

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below -4 °C, and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663 µg per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092, 0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were 0.986 ± 0.032, 0.961 ± 0.014, 0.994 ± 0.008, 1.029 ± 0.015, 1.064 ± 0.021, and 1.074 ± 0.021. Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the 2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of 0.060 ± 0.080, 0.005 ± 0.128, -0.003 ± 0.092, 0.060 ± 0.179, 0.249 ± 0.188, and 0.018 ± 0.247 percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were 0.017 ± 0.009 percent per µg and 0.045 ± 0.051 percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable — the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

REFERENCES:

[1] NIOSH Current Intelligence Bulletin 41, "1,3-Butadiene," U.S. Department of Health and Human Services, Publ. (NIOSH) 84-105 (1984).

[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S91, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[3] NIOSH Current Intelligence Bulletin 46, "Methylene Chloride," U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

[4] Grubbs, F. E. "Procedures for Detecting Outlying Observations in Samples," Technometrics, V. 11, No. 1, 1-21 (February 1969).

[5] MacCallum, R. N., and J. J. McKetta. "Low Pressure Z_S of C_4 Hydrocarbons," Hydrocarbon Process. Petrol. Refiner, V. 42, No. 5, 191-4 (May 1963).

METHOD WRITTEN BY: R. Alan Lunsford, Ph.D., Yvonne T. Gagnon, and John Palassis, NIOSH/DPSE.

APPENDIX A. GAS CHROMATOGRAPH COLUMN SELECTION, INSTALLATION, AND OPERATION:

Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. The column specified in NIOSH Method S91 [2] is 6-m x 3-mm OD stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS. It provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other C_4 to C_6 hydrocarbons are present, interferences are likely. For the development of this method, a 50-m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with Al_2O_3/KCl (Cat. # 7515, Chrompack, Bridgewater, NJ) was chosen as the analytical column because it provides a very efficient separation at temperatures above ambient. However, water from the samples deactivates the aluminum oxide, reducing retention times, and high-boiling or polar substances may accumulate on the column and irreversibly degrade the separation. The degradation was eliminated by using a backflushable pre-column, i.e., 10-m x 0.5-mm ID fused-silica CP Wax 57 CB (Cat. # 7648, Chrompack, Bridgewater, NJ). The pre-column allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed. Eliminating the solvent peak significantly reduces the time required to complete the analysis.

Figures 1 and 2 schematically illustrate the installation and operation of the recommended columns in a Hewlett-Packard 5880A gas chromatograph with split-splitless capillary inlet systems installed in the "B" and "C" injector positions. The only change to the "B" system involves the normally closed (NC) port of the "B" solenoid valve. Originally, it was connected to the capped port of the tee in the "B" septum purge line. (If desired, switching between normal operation of the "B" system and backflushable pre-column operation could be easily achieved by adding a manually operated three-way valve.) Replumb the components of the "C" system as shown, and extend lines from the normally open (NO) port of the "C" solenoid and the "C" backpressure regulator into the oven. Connect the lines and columns with a zero-dead-volume cross (e.g., Part # ZX1, Valco, Houston, TX) and graphite ferrules.

Set the initial oven temperature to 50 °C and the "C" backpressure regulator to 185 kPa. With the solenoid valves activated (inject mode), set the "C" flow control to 20 mL/min and the "B" controls so that the effluent from the analytical column and the "C" split vent total 10 mL/min. Then, with the solenoid valves deactivated (backflush or normal mode), adjust the "B" backpressure regulator until the flow from the "C" split vent returns to the value previously measured. This establishes a reverse flow of 10 mL/min through the pre-column. Program the oven to hold the initial temperature (50 °C) for 2 min, then rise to 120 °C at 20 °C/min, and hold for 8 min. Adjust the time from injection to backflush by injecting standards and progressively decreasing the time from 2 min until the methylene chloride peak is removed without attenuating the butadiene response. It may be necessary to clear higher hydrocarbons from the analytical column by programming the oven to 200 °C at 30 °C/min and holding 4 min. Program the solenoid valves to be activated at the end of each run to prepare for the next injection.

Using the backflushable pre-column, there remains a slight problem with retention drift. While in inject mode, the pre-column strips residual water from the carrier gas. This activates the aluminum oxide surface of the analytical column and causes retention to increase. The effect is most noticeable when starting up after the system has been idle. When beginning a sequence of samples, it is advisable to analyze solvent blanks until the retention drift (e.g., of vinylidene chloride) becomes tolerable.

APPENDIX B. CONVERSION OF 1,3-BUTADIENE VOLUME TO MASS:

MacCallum and McKetta [5] determined the compressibility factor, Z, which corrects for non-ideal behavior, for 1,3-butadiene at temperatures, T, ranging from 10 to 75 °C, and pressures, P, from approximately 420 to 1050 mm Hg. Multiple regression of the observed values against P, PT, and PT^2, yields the following equation (standard error of the estimated Z is 0.000635 for 13 degrees of freedom):

$$Z = a + bP + cPT + dPT^2.$$

where: a = 1.00095
b = -4.84089×10^{-5}
c = 4.44816×10^{-7}
d = -1.15744×10^{-9}

The mass, M, of 1,3-butadiene, corrected for compressibility and the presence of water vapor (when the gas is stored above water), may be calculated by the following equation:

$$M = \frac{(P - P_V) \cdot V \cdot 54.09}{Z \cdot 62.36 \cdot (T + 273.2)}, \ \mu g.$$

where: P_V = vapor pressure of water @ T °C (mm Hg)
V = volume of 1,3-butadiene (µL)
54.09 = molecular weight of 1,3-butadiene ($g \cdot mol^{-1}$)
62.36 = gas constant ($mm\ Hg \cdot L \cdot mol^{-1} \cdot K^{-1}$)
273.2 = absolute temperature of 0 °C (K)

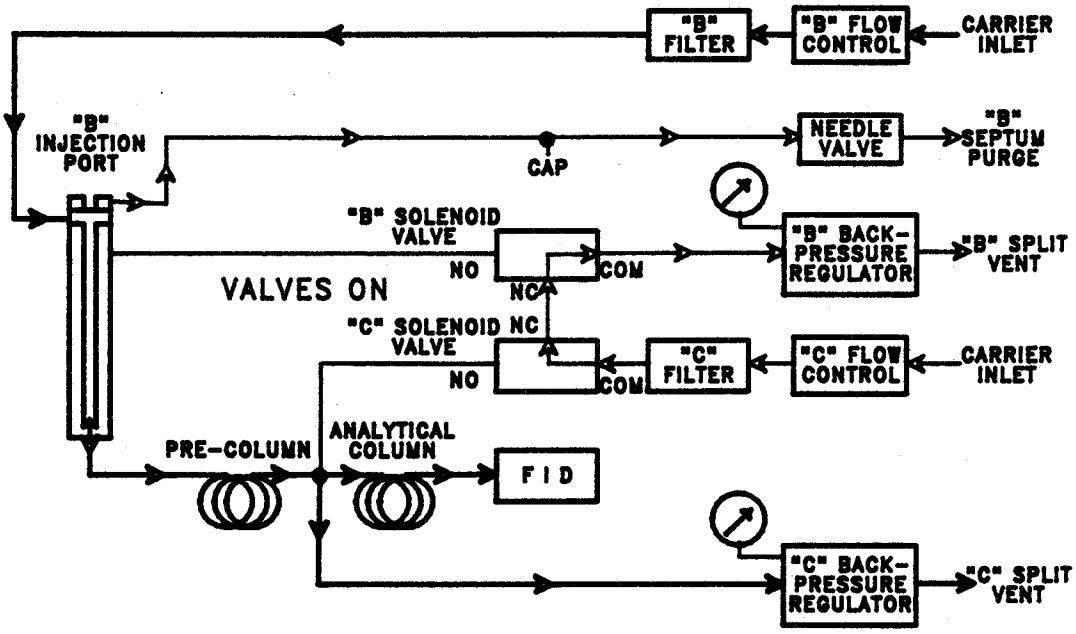


Figure 1. Flow diagram for pre-column system in inject mode.

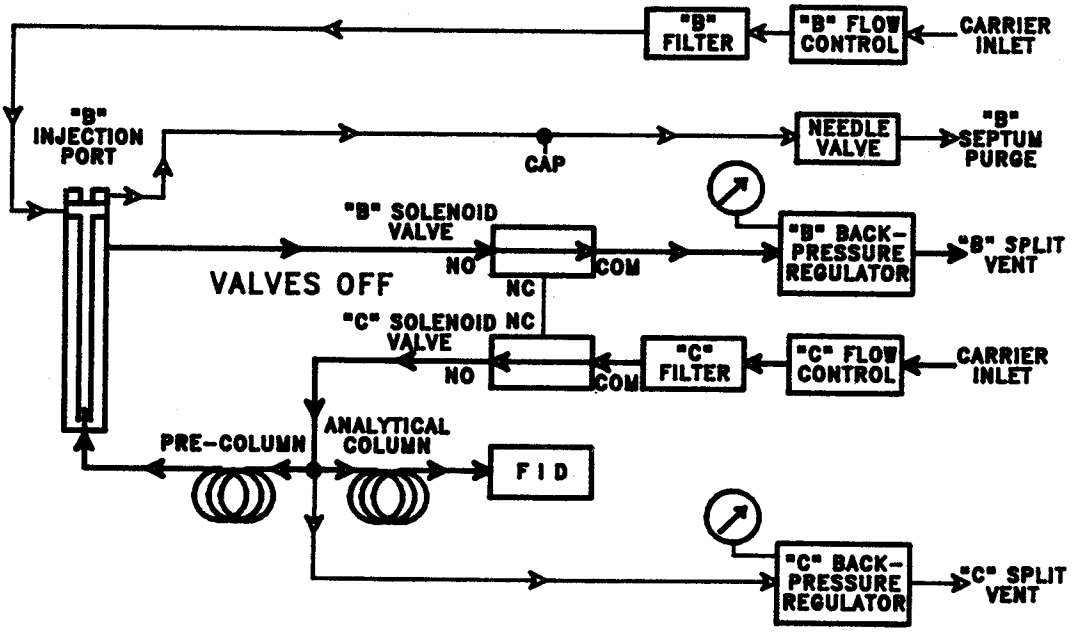


Figure 2. Flow diagram for pre-column system in backflush (normal) mode.

FORMULA: Cd

M.W.: 112.40 (Cd); 128.40 (CdO)

CADMIUM and compounds, as Cd

METHOD: 7048

ISSUED: 2/15/84

REVISION #1: 8/15/87

OSHA: 0.1 mg/m³, C 0.3 (fume); 0.2, C 0.6 (dust)
NIOSH: 0.04 mg/m³; 0.2/15 min [1]; carcinogen [2]
ACGIH: 0.05 mg/m³ (dust, salts); C 0.05 (fume)

PROPERTIES: soft metal; valence 2; BP 765 °C; MP 320.9 °C

SYNONYMS: vary depending upon the compound; CAS #7440-43-9 (Cd); CAS #1306-19-0 (CdO).

SAMPLING

SAMPLER: FILTER (0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 25 L @ 0.1 mg/m³
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.12 to 0.98 mg/m³ [3] (25-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.06 [3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, FLAME

ANALYTE: cadmium

ASHING: conc. HNO_3, 6 mL; 140 °C
conc. HCl, 6 mL; 400 °C

FINAL SOLUTION: 0.5 N HCl; 25 mL

FLAME: air-acetylene, oxidizing

WAVELENGTH: 228.8 nm

BACKGROUND CORRECTION: D_2 or H_2 continuum

CALIBRATION: Standard solutions of Cd in 0.5 N HCl

RANGE: 2.5 to 30 µg per sample [3]

ESTIMATED LOD: 0.05 µg per sample [4]

PRECISION (s_r): 0.05 @ 3 to 23 µg per sample [2,3,6]

APPLICABILITY: The working range is 0.1 to 2 mg/m³ for a 25-L air sample, and 0.01 to 0.2 mg/m³ for a 250-L air sample. This is an elemental analysis and it will not distinguish Cd fume from Cd dust. Aliquots of the ashed samples can be analyzed separately for many additional metals.

INTERFERENCES: Background correction is required to control molecular or flame absorption. Iron does not interfere at 20 parts Fe to 1 part Cd [3].

OTHER METHODS: This method combines and replaces P&CAM 173 [5], S312 [6], and S313 [7]. A similar method appears in the criteria document [1]. Method 7300 (ICP-AES) is an alternate, multielement measurement method.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 0.5 N. Add 41.5 mL conc. HCl to water; dilute to 1 L.
4. Calibration stock solution, 100 µg Cd/mL.* Commercially available or dissolve 0.100 g Cd metal in minimum volume of (1+1) HCl. Dilute to 1 L with 0.5 N HCl.
5. Distilled-deionized water.
6. Air, filtered.
7. Acetylene.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and cadmium hollow cathode lamp and background correction.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Micropipets, 5 to 300 µL.*
8. Hotplate, surface temperature 400 °C.

*Clean with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

Cadmium compounds are very toxic and should be considered carcinogens [1,2]; handle with extra care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 2 and 3 L/min for 15 min (30 to 45 L) for ceiling measurements, or at 1 to 3 L/min for a total sample size of 25 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [3,5,7]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 2 mL conc. HNO_3, cover with a watchglass, and heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Start reagent blanks at this point.
5. Repeat 2 more times using 2 mL conc. HNO_3 each time.
6. Add 2 mL conc. HCl, cover with a watchglass, and heat on hotplate (400 °C) until the volume is reduced to ca. 0.5 mL.
7. Repeat 2 more times using 2 mL conc. HCl. Do not allow the solution to go to dryness at any point.
8. Cool solution and add 10 mL distilled water.
9. Transfer the solution quantitatively to a 25-mL volumetric flask.
10. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

11. Add known amounts, covering the range 0 to 30 µg Cd per sample, of calibration stock solution to 100-mL volumetric flasks and dilute to volume with 0.5 N HCl.

12. Analyze the working standards together with the blanks and samples (steps 17 and 18).
13. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
14. Aspirate a standard after every 10 samples to check for instrument drift.
15. Check recoveries with at least 2 spiked media blanks per 10 samples.
16. Use method of additions occasionally to check for interferences.

MEASUREMENT:

17. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7048-1.
18. Aspirate standards and samples. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 0.5 N HCl, reanalyze, and use the appropriate dilution factor in calculations.

CALCULATIONS:

19. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of cadmium in the sample, C_s, and average media blank, C_b, from the calibration graph.
20. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of cadmium in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

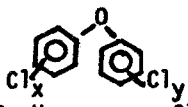
EVALUATION OF METHOD:

Method S312 was issued on June 12, 1976 [6], and validated over the range 0.12 to 0.98 mg/m^3 for a 25-L sample of CdO dust [3]. Method S313 was issued on November 26, 1976 [7], and validated over the range 0.12 to 0.57 mg/m^3 for a 25-L sample of Cd fume, and over the range 0.04 to 0.18 mg/m^3 for a 140-L sample of Cd fume [3].

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Cadmium, Appendix II, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-192 (1976).
[2] Current Intelligence Bulletin 42: Cadmium. U.S. Department of Health and Human Services, Publ. (NIOSH) 84-116 (Sept. 27, 1984).
[3] Documentation of the NIOSH Validation Tests, S312 and S313, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[4] User check, UBTL, NIOSH Seq. #3990-M (unpublished, November 29, 1983).
[5] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[6] Ibid, V. 3, Method S312, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[7] Ibid, Method S313.

METHOD REVISED BY: Mark Millson and R. DeLon Hull, NIOSH/DPSE; S312 and S313 originally validated under NIOSH Contract CDC-94-74-45.

FORMULA:  ;
$C_{12}H_{[10-(x+y)]}Cl_{(x+y)}O$ where (x+y) = 1 to 6

M.W.: 204.66 (x+y = 1); 239.10 (x+y = 2); 376.88 (x+y = 6)

CHLORINATED DIPHENYL ETHER
METHOD: 5025
ISSUED: 8/15/87

OSHA: 0.5 mg/m³
NIOSH: no recommendation [1]
ACGIH: 0.5 mg/m³; STEL 2 mg/m³

PROPERTIES: Table 1 [1,2]

SYNONYMS: chlorinated diphenyl oxide; CAS #55720-99-5.

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 8 L @ 0.5 mg/m³
-MAX: 200 L

SHIPMENT: within 1 hr of sampling, transfer filter and backup pad to screw-cap bottle; otherwise, routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

BULK SAMPLE: may be required for proper identification of analytes

ACCURACY

RANGE STUDIED: 0.1 to 1 mg/m³ [3]
(90-L samples)

BIAS: not determined

OVERALL PRECISION (s_r): 0.070 [3]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ELECTROLYTIC CONDUCTIVITY DETECTION

ANALYTE: chlorinated diphenyl ether

DESORPTION: 10 mL isooctane, stand 2 hrs

INJECTION VOLUME: 15 µL

TEMPERATURE-FURNACE: 760 °C
-TRANSFER LINE: 225 °C
-VENT: 250 °C
-COLUMN: 210 °C

GASES-FURNACE: H_2, 150 mL/min
-CARRIER: N_2, 150 mL/min

COLUMN: 1.5 m x 2 mm ID glass; 5% SE-30 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of chlorinated diphenyl ether in isooctane

RANGE: 0.004 to 0.15 mg per sample [4]

ESTIMATED LOD: 0.0002 mg per sample [3]

PRECISION (s_r): 0.019 @ 0.02 to 0.09 mg per sample [3]

APPLICABILITY: The working range is 0.05 to 1.5 mg/m³ for a 90-L air sample. The method has been evaluated only for the hexachloro derivative. The sampler may not be adequate for the monochloro or dichloro derivatives, which have higher vapor pressures.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S119 [4].

REAGENTS:

1. Isooctane, chromatographic quality.
2. Calibration stock solution, 2 µg/µL chlorinated diphenyl ether* in isooctane. Prepare in duplicate.
3. Nitrogen, purified.
4. Hydrogen, prepurified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter, supported by cellulose backup pad in two-piece polystyrene filter holder.
2. Personal sampling pump, 0.5 to 1.5 L/min, with flexible connecting tubing.
3. Gas chromatograph, electrolytic conductivity detector, effluent vent, integrator and column (page 5025-1).
4. Vials, 20-mL, PTFE-lined caps, for shipping filters.
5. Syringes, 25-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, 10-mL.
8. Tweezers.

SPECIAL PRECAUTIONS: Prolonged skin contact with chlorinated diphenyl ether can cause chloracne; acute and chronic exposure can cause liver damage [1,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.5 and 1.5 L/min for a total sample size of 8 to 200 L.
3. Within 1 hr of sampling, using tweezers, carefully transfer the filter and backup pad to a vial.

SAMPLE PREPARATION:

4. Pipet 10.0 mL isooctane into each vial containing a sample or blank filter and backup pad. Seal and gently swirl the vial to wet the filter and backup pad. Allow to stand 2 hrs.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to isooctane in 10-mL volumetric flasks and dilute to the mark to obtain concentrations in the range 0.0004 to 0.015 mg chlorinated diphenyl ether/mL.
   b. Analyze with samples and blanks (steps 8 and 9).
   c. Prepare calibration graph (sum of areas of selected peaks vs. mg chlorinated diphenyl ether).
6. Determine recovery (R) at least once for each batch of filters used for sampling in the calibration range. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of calibration stock solution onto the filter. Allow filters to air dry.
   b. Store samples overnight in vials.
   c. Prepare (step 4) and analyze with working standards (steps 8 and 9).
   d. Graph R vs. mg chlorinated diphenyl ether.
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

8. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5025-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Open the effluent vent to keep the solvent from passing into the detector. Close the effluent vent after the solvent peak has eluted.
   NOTE: Under conditions given, the solvent elutes in about 20 sec. The large quantity of solvent injected may cause malfunction of the conductivity cell, unless it is vented.
9. Sum the areas of selected peaks.
   NOTE: Use a bulk sample if necessary to identify the appropriate chromatographic peaks.

CALCULATIONS:

10. Determine the mass, mg (corrected for R) of chlorinated diphenyl ether found in the sample (W) and in the average media blank (B) from the calibration graph.
11. Calculate concentration, C, of chlorinated diphenyl ether in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, mg/m^3$$

EVALUATION OF METHOD:

Method S119 was evaluated over the range 0.1 to 1 mg/m³ hexachlorodiphenyl ether at 22 °C and 767 mm Hg using 90-L samples [3]. Overall precision, s_r, was 0.070; no reference method was used. The test atmospheres were generated from solutions (0.25 to 0.5% w/v) of chlorinated diphenyl ether (Chem Samples) in toluene, using a fluid aspirator, cyclone and an impactor. Sampling with two filters in series was conducted in an atmosphere containing 1 mg/m³ chlorinated diphenyl ether. Chlorinated diphenyl ether was found only on the front filters (with LOD = 0.002 mg/m³). Filters enriched with 100 µg chlorinated diphenyl ether were analyzed after passing 100 L of air through them. The resulting recovery of the analyte was 99.75% with s_r = 0.017%. The recovery of chlorinated diphenyl ether from enriched filters through which no air was drawn was 1.012 in the range 23 to 90 µg per sample.

REFERENCES:

[1] 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.
[2] Patty, F. A. Industrial Hygiene and Toxicology, 2nd ed, Vol. 2, 1706-1707, Interscience, New York (1963).
[3] Documentation of the NIOSH Validation Tests, S119, 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.
[4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S119, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] Occupational Diseases, A Guide to Their Recognition, revised ed., 255-256, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-181 (1978).

METHOD REVISED BY: James E. Arnold, NIOSH/DPSE; S119 originally developed under NIOSH Contract CDC-99-74-45.

Table 1. Properties of chlorinated diphenyl ether [1,2].

Compound	BP, °C (8 mm Hg)	d, g/mL 25 °C	Vapor Pressure @ 25 °C Pa	mm Hg	mg/m³	1 ppm in mg/m³ @ NTP
Monochloro-	153	1.19	0.93	0.007	77	8.37
Dichloro-	168.2	1.32	0.08	0.0006	8	9.78
Hexachloro-	230 to 260	1.57 @ 20 °C	<0.008	<0.00006	<1	15.41

FORMULA: $ClCH_2COOH$

M.W.: 94.50

CHLOROACETIC ACID
METHOD: 2008
ISSUED: 8/15/87

OSHA: no standard
NIOSH: no recommended standard
ACGIH: no recommended standard
(1 ppm = 3.86 mg/m³ @ NTP)

PROPERTIES: solid; MP 61 to 63 °C; BP 189 °C; VP 138 Pa (1 mm Hg; 1300 ppm) @ 43 °C; flash point 126 °C

SYNONYMS: chloroethanoic acid; monochloroacetic acid; CAS #79-11-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(silica gel, 100 mg/50 mg, with glass wool plugs)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L @ 1 mg/m³
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C; 32 days refrigerated [1]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.35 to 29 mg/m³ [1,2] (3-L samples)

BIAS: not significant [1,2]

OVERALL PRECISION (s_r): 0.08 [1]

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: chloroacetate ion

DESORPTION: 2 mL deionized water

INJECTION LOOP VOLUME: 500 µL

ELUENT: 1.5 mM $NaHCO_3$; 2.3 mL/min

COLUMNS: anion guard (3 mm ID x 150 mm long); anion separators in tandem (3 mm ID x 250 mm and 3 mm ID x 500 mm) packed with low capacity anion exchange resin; anion suppressor (6 mm ID x 250 mm) packed with high capacity cation exchange resin

CALIBRATION: standard solutions of chloroacetic acid in deionized water

RANGE: 1 to 80 µg per sample [1]

ESTIMATED LOD: 0.04 µg per sample [2]

PRECISION (s_r): 0.016 [1]

APPLICABILITY: The working range is 0.3 to greater than 30 mg/m³ (0.09 to >115 ppm) for a 3-L air sample.

INTERFERENCES: Chloroacetyl chloride is a positive interferent since it is hydrolyzed to monochloroacetic acid by the measurement procedure and is efficiently collected by silica gel [3]. Particulate salts of the acid are positive interferents. The chromatograpic conditions given will separate acetate, chloride, dichloroacetate, fluoride, glycolate, and trichloroacetate ions from chloroacetate ion.

OTHER METHODS: This revises P&CAM 332 [2]. Recent improvements in IC column resins may eliminate the need for two separator columns in tandem and allow the use of a smaller injection volume.

REAGENTS:

1. Water, filtered, deionized. Specific conductance ≤10 µS/cm.
2. Sodium bicarbonate ($NaHCO_3$), reagent grade.
3. Chloroacetic acid, ≥99%.*
4. Eluent: 1.5 mM $NaHCO_3$. Dissolve 0.504 g $NaHCO_3$ in 4 L filtered, deionized water.
5. Calibration stock solution, 1000 µg/mL. Dissolve 100 mg chloroacetic acid in 100 mL filtered, deionized water.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, with plastic caps, containing two sections of 20/40 mesh silica gel (front = 100 mg; back = 50 mg) contained and separated by three silanized glass wool plugs. Pressure drop across the tube at 0.2 L/min is ca. 0.6 kPa (2.6 in. H_2O). Tubes are commercially available.
   NOTE: Chloroacetic acid is irreversibly adsorbed on urethane plugs. Use sorbent tubes with glass wool plugs.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Ion chromatograph (IC), anion separators and guard columns, anion suppressor (page 2008-1), conductivity detector, integrator, and strip chart recorder.
4. Ultrasonic bath.
5. Vials, 20-mL, glass, with aluminum-lined plastic screw caps.
6. Syringes, 3-mL, polyethylene with luer tip.
7. Filter holder, luer tip, 13-mm, with PTFE filter, 5-µm pore size.
8. Pipets, 10-µL to 2-mL.
9. Flasks, volumetric, 10- and 100-mL.

SPECIAL PRECAUTIONS: Chloroacetic acid is irritating to skin and mucous membranes [4]. Work with the concentrated material only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 to 0.2 L/min for a total sample size of 1 to 100 L.
4. Cap the samplers. Pack securely for shipment.
   NOTE: Store samples in the dark. Refrigerate samples if stored longer than 7 days.

SAMPLE PREPARATION:

5. Allow refrigerated samples to equilibrate to room temperature.
6. Transfer front sorbent section with front glass wool plug to vial. Place back sorbent section and other two glass wool plugs in separate vial.
7. Add 2.0 mL deionized water to each vial. Cap immediately.
8. Agitate vials in ultrasonic bath for 30 min at room temperature.
9. Draw sample extract through 13-mm PTFE filter with 3-mL syringe.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least five working standards.
    a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain chloroacetic acid concentrations in the range 0.02 to 40 µg/mL.
    b. Analyze together with samples and blanks (steps 13 through 15).
    c. Prepare calibration graph [peak height (mm or µS) vs. µg chloroacetic acid per sample].
11. Determine desorption efficiency (DE) for each batch of silica gel used for sampling in the calibration range. Prepare at least three tubes at each of five levels.
    a. Place silica gel from unused front section in vial.
    b. Inject a known amount (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, onto front sorbent section with a microliter syringe.
    c. Cap the vial. Allow to stand overnight.
    d. Desorb (steps 7 through 9) and analyze together with working standards (steps 13 through 15).
    e. Prepare graph of DE vs. µg chloroacetic acid recovered.
12. Analyze three quality control spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 2008-1.
14. Inject sample aliquot manually or use autosampler.
    a. Flush sample loop with 0.5-mL sample extract, then inject 0.5 mL sample.
    b. Rinse sample loop with 1 to 2 mL deionized water between determinations of separate samples.
    NOTE: All samples, eluents, and water flowing through the IC must be filtered to avoid plugging the system valves or columns.
15. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply appropriate dilution factor.

CALCULATIONS:

16. Determine 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.
17. Calculate concentration, C, of chloroacetic acid in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was developed and evaluated by Southern Research Institute [1] using dynamically-generated atmospheres of chloroacetic acid over the concentration range of 0.35 to 29 mg/m³ at 25 to 27 °C and at relative humidity ≥80%. Average recovery based on 18 samples, six at each of three levels, was 98% representing a negligible bias. Precision at 0.35 mg/m³ was inhomogeneous with those of higher levels; therefore, precisions were not pooled. Using this poorest precision (s_r = 0.064), the overall precision (s_r) was estimated to be ≤0.081.

The breakthrough volume of the 100-mg sorbent section was found to be >100 L at 0.2 L/min when sampling chloroacetic acid concentrations of 60 mg/m^3 at 42 °C and RH of 10 to 80% and 35 mg/m^3 at 27 °C and 10 to 90% RH. Samples stored at ambient temperature for 7 days had a mean recovery of 91% and a precision, s_r, of 0.047. Samples refrigerated after day 7, and stored for 32 days exhibited a mean recovery of 100% with a precision, s_r, of 0.085 based on samples analyzed on day 1.

REFERENCES:

[1] Dillon, H. K., D. W. Mason, and K. W. Boyd. Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for Monochloroacetic Acid, NIOSH Contract 210-78-0012, Southern Research Institute, Birmingham, AL (1980).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 322, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[3] McCullough, P. R. and J. W. Worley. "Sampling of Chloroacetyl Chloride in Air on Solid Support and Determination by Ion Chromatography," Anal. Chem., 51:1120-1122 (1979).

[4] Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).

METHOD REVISED BY: Mary Ellen Cassinelli, NIOSH/DPSE.

FORMULA: B_2H_6

M.W.: 27.67

DIBORANE

METHOD: 6006
ISSUED: 8/15/87

OSHA: 0.1 ppm
NIOSH: no recommended standard [1]
ACGIH: 0.1 ppm
(1 ppm = 1.131 mg/m³ @ NTP)

PROPERTIES: gas; vapor density (air = 1) 0.96;
BP -92.5 °C; MP -165.5 °C;
explosive range 0.8 to 98% v/v in air

SYNONYMS: boroethane; CAS #19287-45-7.

SAMPLING

SAMPLER: FILTER + SOLID SORBENT TUBE
(PTFE filter + oxidizer-impregnated charcoal, 100 mg/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 60 L @ 0.1 ppm
-MAX: 260 L

SHIPMENT: routine

SAMPLE STABILITY: 100% recovery after 7 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.05 to 0.22 mg/m³ (120-L samples) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.07 [2]

MEASUREMENT

TECHNIQUE: PLASMA EMISSION SPECTROMETRY

ANALYTE: boron

DESORPTION: 10 mL 3% H_2O_2; stand 30 min; ultrasonic bath 20 min

WAVELENGTH: 249.8 nm

ENTRANCE SLITS: 50 x 300 mm

CALIBRATION: aliquots of 1% (v/v) diborane adsorbed on impregnated charcoal

RANGE: 7 to 30 µg diborane per sample [2]

ESTIMATED LOD: 1 µg diborane per sample [2]

PRECISION (s_r): 0.063 @ 7 to 27 µg diborane per sample [2]

APPLICABILITY: The working range is 0.05 to 0.22 ppm (0.06 to 0.25 mg/m³) for a 120-L air sample.

INTERFERENCES: The filter removes boron-containing particulates. Avoid borosilicate glassware during sample preparation to prevent boron contamination of samples. Higher boranes (e.g., tetraborane) interfere but are not likely to be encountered in most samples.

OTHER METHODS: This revises P&CAM 341 [3]. The measurement can also be done by inductively-coupled plasma atomic emission spectrometry (e.g., Method 7300).

REAGENTS:

1. Diborane, 1% (v/v), certified gas mixture.*
2. Hydrogen peroxide (H_2O_2), 3% w/v in deionized water.
3. Calibration stock solution, 1000 µg B/mL, commercially available or dissolve 0.572 g boric acid (H_3BO_3) in deionized water to make 100 mL solution. Store in a polyethylene bottle.
4. Argon, for DC plasma excitation.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. PTFE membrane filter, 13-mm diameter, 1-µm pore size (e.g., Millipore FALP), in a plastic cassette (Millipore SX00013 or equivalent).
   b. Glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends with plastic caps, containing two sections (100 mg and 50 mg) of oxidizer-impregnated charcoal (#580-20, Barnebey-Cheney Co., Columbus, OH or equivalent); separated and retained by silylated glass wool plugs.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Plasma emission spectrometer with a DC plasma excitation source.
4. Pipets, plastic, 10-mL, and 5- to 50-µL.
5. Volumetric flasks, plastic, 10-mL.
6. Bottles, screw-top, plastic, 60-mL.
7. Syringe, plastic, 10-mL, fitted with 0.5-µm PTFE filter.
8. Vials, plastic, 7-mL, screw-on septum caps.
9. Ultrasonic bath.
10. Gas-tight syringes, 0.5- and 5-mL, graduated.

SPECIAL PRECAUTIONS: Diborane is very toxic and flammable, having an Immediately Dangerous to Life or Health (IDLH) level of 40 ppm. It is a strong irritant with a repulsive, sweet odor [1].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the charcoal tubes immediately before sampling. Attach the filter cassette in front of the charcoal tube with a short piece of tubing. Attach the outlet of the charcoal tube to the personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 60 to 260 L.
4. Separate the filter and the charcoal tube. Cap the charcoal tube. Pack securely for shipment.
   NOTE: The filters may be reused, if not heavily loaded, or discarded.

SAMPLE PREPARATION:

5. Pipet 10.0 mL 3% H_2O_2 into a series of plastic bottles. Quickly add the front and back charcoal sections to separate bottles and screw on the caps. Discard the glass wool plugs.
6. Allow to stand 30 min and then place in an ultrasonic bath for 20 min.
7. Draw the sample through a 0.5-µm PTFE membrane filter with a syringe.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to 3% H_2O_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain boron concentrations in the range 0.1 to 4 µg B/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (response vs. µg boron).
9. Determine desorption efficiency (DE) at least once for each lot of impregnated charcoal in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Place 100 mg impregnated charcoal (e.g., unused front sorbent section) in a vial and screw on the septum cap.
   b. Flush the gas-tight syringe with inert gas (e.g., N_2). Inject a known amount (0.1 to 5 mL) of diborane gas mixture with the syringe into the vial. Treat two parallel blanks in the same manner except that no diborane is added.
   c. Allow the vials to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg boron recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set spectrometer to conditions on page 6006-1 and as specified by the manufacturer.
12. Analyze standards and samples.
    NOTE: If response is above the range of the standards, dilute the sample solution with 3% H_2O_2, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of boron 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 diborane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 1.28}{V}, \text{ mg/m}^3$$

where: 1.28 = the stoichiometric conversion factor from boron to diborane.

EVALUATION OF METHOD:

The method was tested by analyzing 18 samples, prepared by spiking 100 mg of impregnated charcoal with 6.7, 13.4 or 26.8 µg of diborane gas representing the equivalent of 120-L air samples at 0.05, 0.1 and 0.2 ppm [2]. Desorption efficiency was determined to be 0.889, 0.964, and 0.994 at these three levels, respectively. After analysis, the precision at the three levels was 8.4, 4.0, and 3.8%, respectively. Test atmospheres at 0.05, 0.1, and 0.2 ppm were generated using diborane gas. The samples were collected at 1 L/min for 2 hours in charcoal tubes containing 100 mg impregnated charcoal. Eighteen samples were collected, and were desorbed one day later. The backup sections of the samples at the 0.2 ppm level were analyzed also. Six additional generated samples at the 0.1 ppm level were stored and analyzed seven days later. The average recovery of the 18 samples was 95.2%, pooled s_r = 2.7%. No trace of diborane (boron) was found in the backup section.

The seven-day storage stability samples indicated an average recovery of 101.6 ± 2.1%.

Breakthrough tests were conducted with a generated test atmosphere at 1.9 ppm with four impregnated charcoal tubes. The sample volume was 120 L. The average collection efficiency in the front sections was 99.8 ± 0.3%. Breakthrough occurred in only two samples indicating 0.6 and 0.2% breakthrough. An additional breakthrough study was conducted with a generated test atmosphere containing 0.34 ppm diborane at a relative humidity of 60 to 70%. Two impregnated charcoal tubes were collected after 60 min, two after 120 min, and two after 235 min. No breakthrough was detected in any sample. Therefore, the capacity of the charcoal tube is at least 80 µg diborane.

A filter sutdy was conducted with 12 samples collected simultaneously -- six with a prefilter and six without the prefilter -- at 0.1 ppm. The results indicated that the use of the PTFE filters does not affect the precision or accuracy of the method. Mixed cellulose ester membrane prefilters produced a loss of 7.5% in the collection efficiency and, therefore, are not recommended as prefilters.

REFERENCES:

[1] 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.
[2] Arthur D. Little, Inc., Backup Data Report for Diborane, prepared under NIOSH Contract No. 210-80-0099 (June 1, 1981).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 341, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).

METHOD WRITTEN BY: B. R. Belinky and J. Palassis, NIOSH/DPSE; and Arthur D. Little, Inc.

FORMULA: (1) CCl_2F_2; (2) $CClF_2CClF_2$

M.W.: (1) 120.91; (2) 170.92

(1) DICHLORODIFLUOROMETHANE and
(2) 1,2-DICHLOROTETRAFLUOROETHANE

METHOD: 1018
ISSUED: 8/15/87

OSHA: 1000 ppm
NIOSH: no recommended standard [1]
ACGIH: 1000 ppm
(1): (1 ppm = 4.94 mg/m³ @ NTP)
(2): (1 ppm = 6.99 mg/m³ @ NTP)

PROPERTIES: gases; BP (1) -29.8 °C, (2) 4.1 °C;
MP (1) -158 °C, (2) -94 °C
nonflammable (1) and (2)

SYNONYMS: (1) difluorodichloromethane; Refrigerant 12; CAS #75-71-8.
(2) cryofluorane; Refrigerant 114; CAS #76-14-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(two coconut shell charcoal tubes in series, 400 mg/200 mg and 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 1000 ppm
-MAX: 4 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 100% recovery after 7 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: (1) 2940 to 10,500 mg/m³
(2) 3500 to 14,100 mg/m³ [2]
(3-L air samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): (1) 0.064,
(2) 0.064 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dichlorodifluoromethane and
1,2-dichlorotetrafluoroethane

DESORPTION: 20 mL methylene chloride

INJECTION VOLUME: 5 µL

	(1)	(2)
TEMPERATURE-INJECTOR:	200 °C	240 °C
-DETECTOR:	260 °C	275 °C
-COLUMN:	110 °C	110 °C

CARRIER GAS: N_2, 25 mL/min

COLUMN: stainless steel, 1.2 m x 6 mm OD,
packed with 80/100 mesh Chromosorb 102

CALIBRATION: standard solutions of analytes in CH_2Cl_2

RANGE: (1) 5 to 30 mg per sample,
(2) 5 to 40 mg per sample [2]

ESTIMATED LOD: 0.03 mg per sample [2]

PRECISION (s_r): (1) 0.035 @ 7.4 to 30 mg,
(2) 0.038 @ 10 to 40 mg per sample [2]

APPLICABILITY: The working range is 340 to 2200 ppm (1670 to 11,000 mg/m³ dichlorodifluoromethane and 240 to 2100 ppm (1670 to 15,000 mg/m³) 1,2-dichlorotetrafluoroethane for a 3-L air sample.

INTERFERENCES: Methanol and acetone may interfere if present at high concentrations.

OTHER METHODS: This combines and revises Methods S111 and S108 [3].

REAGENTS:

1. Dichlorodifluoromethane, 99%.
2. 1,2-Dichlorotetrafluoroethane, 99%.
3. Methylene chloride (CH_2Cl_2), chromatographic quality.*
4. Nitrogen, purified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8 mm OD, 6 mm ID, followed by 7 cm long, 6 mm OD, 4 mm ID) connected in series with a short piece of tubing, flame-sealed ends and plastic end caps. Each tube contains two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg + 200 mg; back tube = 100 mg + 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes each front section and a 3-mm urethane foam plug follows each back section. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1018-1).
5. Bottles, glass, 30-mL, with PTFE-lined septum crimp caps.
6. Syringes, gas-tight, 10-µL and 1-, 2-, 5-, and 10-mL.
7. Pipet, TD, 20-mL.
8. DE apparatus. Glass tubing, through which nitrogen flows, with T-connection and septum.
9. Analytical balance, readable to 0.01 mg.

SPECIAL PRECAUTIONS: Methylene chloride is a suspect carcinogen [4].

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 with the smaller tube nearer the sampling pump.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 4 L.
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

NOTE: Refrigerate samples at -10 °C if not analyzed immediately.

5. Pipet 20.0 mL CH_2Cl_2 into a series of bottles.
6. Place, in order, the back and front sorbent sections of the front sampler tube into a bottle containing 20 mL CH_2Cl_2, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 hrs.
7. Perform step 6 for the back sampler tube.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Pipet 20.0 mL CH_2Cl_2 into each of a series of bottles. Cap, then weigh the bottles.
   b. Using a gas-tight syringe, add known amounts of analytes, e.g., 0.01 to 6 mL (0.0494 to 29.6 mg @ NTP) dichlorodifluoromethane or 0.01 to 6 mL (0.0699 to 41.9 mg @ NTP) 1,2-dichlorotetrafluoroethane by bubbling the gas slowly through the CH_2Cl_2. Gently shake the bottles.
   c. Reweigh the bottles.
   d. Analyze with samples and blanks (steps 11 and 12).
   e. Prepare calibration graph (peak area vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Using a gas-tight syringe, inject a known amount of analyte (0.01 to 6 mL) through the septum of the DE apparatus into a stream of nitrogen (ca. 20 mL/min) which carries the analyte into a large (400 mg/200 mg) sorbent tube. Allow the nitrogen to flow an additional 30 sec.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1018-1. 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 an aliquot of the desorbed liquid with CH_2Cl_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.
    NOTE: The order of elution is 1,2-dichlorotetrafluoroethane, dichlorodifluoromethane, and CH_2Cl_2 under these conditions.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and (B_b) sorbent tubes.
    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):

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

EVALUATION OF METHOD:

Dichlorodifluoromethane: Method S111 was issued September 30, 1976 [3], and validated using test atmospheres generated in air and monitored with a calibrated total hydrocarbon analyzer [2,5]. Average recovery for 18 samples was 98.2%. In breakthrough tests at 12 and 94% relative humidity (RH), the sampler contained 61 and 44 mg of dichlorodifluoromethane, respectively, when sampling at ca. 0.045 L/min from atmospheres containing ca. 10,000 mg/m³. Desorption efficiency averaged 0.97 in the range 7.4 to 30 mg per sample.

Dichlorotetrafluoroethane: Method S108 was issued October 29, 1976 [3], and validated using test atmospheres generated in air and monitored with a calibrated total hydrocarbon analyzer [2,4]. The average recovery for 18 samples was 99.8%. Breakthrough (effluent concentration = 5% of test concentration) occurred after 158 min when sampling 14,600 mg/m^3 at 90% RH at 0.046 L/min. Desorption efficiency averaged 0.99 in the range 10.7 to 42.8 mg per sample.

REFERENCES:

[1] 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.

[2] Backup Data Reports S111 (Dichlorodifluoromethane) and S108 (Dichlorotetrafluoroethane), prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB 271-712, from NTIS, Springfield, VA 22161.

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S111 and S108, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD WRITTEN BY: Y. T. Gagnon and K. J. Williams, NIOSH/DPSE.

FORMULA: BrH_2CCH_2Br; $C_2H_4Br_2$

M.W.: 187.88

ETHYLENE DIBROMIDE
METHOD: 1008
ISSUED: 2/15/84
REVISION #1: 8/15/87

OSHA: 0.1 ppm; C 0.5 ppm (proposed)
NIOSH: 1 mg/m³/15 min [1]
ACGIH: carcinogen (skin)
(1 ppm = 7.68 mg/m³ @ NTP)

PROPERTIES: liquid; d 2.169 g/mL @ 25 °C;
BP 131 °C; MP 10 °C;
VP 1.5 kPa (11 mm Hg; 1.4% v/v) @ 25 °C

SYNONYMS: EDB, 1,2-dibromoethane; CAS #106-93-4.

SAMPLING

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

FLOW RATE: 0.02 to 0.2 L/min

VOL-MIN: 0.1 L @ 0.1 ppm
-MAX: 25 L

SAMPLE STABILITY: refrigerated samples (-25 °C or below) may be stored 2 weeks [3,4]

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [3]

BIAS: not significant [4]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTE: ethylene dibromide

DESORPTION: 10 mL 99:1 benzene:methanol (v/v); stand 1 hr

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 175 °C
-DETECTOR: 315 °C
-COLUMN: 50 °C

CARRIER GAS: N_2, 35 mL/min

COLUMN: 1.8 m x 4 mm ID, borosilicate glass packed with 3% OV-210 on 80/100 Gas Chrom Q

CALIBRATION: ethylene dibromide in 99:1 benzene:methanol (v/v) with internal standard

RANGE: 0.1 to 0.5 µg per sample [3]

ESTIMATED LOD: 0.01 µg per sample [3,4]

PRECISION (s_r): 0.044 [5]

APPLICABILITY: The working range is 0.0003 to 1 ppm (0.002 to 8 mg/m³) for a 25-L air sample. The range of an ECD most useful for quantitation depends on the type of detector and chromatograph used. For reliable quantitation, the ECD must be optimized for the smallest possible amount of analyte.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems. An alternate chromatographic column packing is GP 20% SP-2100/0.1% Carbowax 1500 on 100/120 Chromosorb WHP [4].

OTHER METHODS: This revises P&CAM 260 [3] and Method 1008 (dated 2/15/84). Method S104 [2], which has not been revised, can also be used but uses the less sensitive flame ionization detector.

REAGENTS:

1. Benzene, pesticide quality.*
2. Methanol, pesticide quality.*
3. Ethylene dibromide, high purity (density=2.169 g/mL @ 25 °C).*
4. An appropriate internal standard such as 1,1,2,2-tetrachloroethane (density=1.587 g/mL @ 25 °C) or 1,2-dibromopropane (density= 1.923 g/mL @ 25 °C).
5. 99:1 benzene:methanol (v/v).
6. Eluent*: 99:1 benzene:methanol (v/v) containing 0.01 µg internal standard/mL.
7. Calibration stock solution, 10 ng/µL. Dissolve 50 mg ethylene dibromide in benzene to make 25 mL solution. Dilute 50 µL of this solution to 10 µL with benzene. Stable 3 weeks if refrigerated.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, 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.
2. Personal sampling pump, 0.02 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron-capture detector, integrator and column (see page 1008-1).
4. Syringe*, 10-µL, readable to 0.1 µL and 50 µL,readable to 1 µL.
5. Volumetric flasks, 10-mL, 25-mL, and 500 mL.
6. Pipet, 10-mL with pipet bulb.

SPECIAL PRECAUTIONS: Benzene and ethylene dibromide [1] are carcinogens and can be absorbed through the skin. Benzene and methanol are flammable. All work with these should be performed in a hood, while wearing gloves.

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 0.02 and 0.2 L/min for a total sample size of 0.1 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely in an insulated container with dry ice for shipment.

SAMPLE PREPARATION:

NOTE: Store the samplers at -25 °C or below until preparation begins.

5. Place the front and back sorbent sections of the sampler tube in separate 10-mL volumetric flasks. Discard the glass wool and foam plugs.
6. Add 10.0 mL eluent to each flask.
7. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 0.5 µg ethylene dibromide per sample.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).

c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. µg ethylene dibromide).

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 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 ethylene dibromide recovered.
10. Analyze three quality control blind spikes and five analyst spikes to ensure 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 1008-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Retention times under these conditions are: ethylene dibromide, 2.2 min; 1,2-dibromo propane, 2.9 min; and 1,1,2,2-tetrachloroethane, 4.1 min.
    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.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of ethylene dibromide 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 ethylene dibromide in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

P&CAM 260 [3] was evaluated with coconut shell charcoal (SKC Lot 106 and MSA Lot 6) fortified with solutions of ethylene dibromide. Average recoveries ranged from 0.85 to 0.93; overall precision (s_r) was 0.044 (31 samples, pooled) [5]. Samples based on 0.2- and 2-µg quantities of ethylene dibromide were stable on charcoal during storage below -20 °C for 13 and 12 days, respectively. Gasoline samples which contained ethylene dibromide were placed into U-tubes; ethylene dibromide vapor was collected with charcoal tubes (flow rate of air was 0.6 L/min). Recoveries were 0.91 and 0.93 for 0.2- and 2.4-µg quantities of ethylene dibromide, respectively. No significant breakthrough from front sections of charcoal occurred with 200-µg quantities of ethylene dibromide in the vapor phase (flow rate of air was 0.6 L/min); quantities of ethylene dibromide (if any) on the back sections of charcoal were less than 0.04 µg (<0.02%).

Breakthrough was determined for SKC Lot 105 charcoal [6]. At a concentration of 446 mg ethylene dibromide/m³ in dry air, the effluent concentration was 2% of the test concentration after 4 hrs of sampling (48 L air). Thus, the capacity of the charcoal was at least 21 mg ethylene dibromide under these conditions. In the analysis of a large set of field samples over a period of seven days, DE was found to vary day-to-day in the range of 0.76 to 0.87 at 0.1 µg ethylene dibromide per sample [7].

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Ethylene Dibromide, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-221 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] Ibid, V. 4, P&CAM 260, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] User check, UBTL, Inc., NIOSH Seq. #4585-R (unpublished, May 21, 1985)
[5] Tucker, S. P., J. J. Sweeney and A. W. Teass. "A Charcoal Tube Method for Determining 1,2-Dibromoethane in Air," NIOSH (unpublished, 1979).
[6] Documentation of the NIOSH Validation Tests, S104, U.S. Dept. Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[7] Report of NIOSH Seq. #5332-A (unpublished, May 5, 1986).

METHOD REVISED BY: K. J. Williams, NIOSH/DPSE.

FORMULA: $H_2C\!-\!CH_2$; C_2H_4O (O)

M.W. = 44.05

ETHYLENE OXIDE
METHOD: 1614
ISSUED: 8/15/87

OSHA: 1 ppm
NIOSH: <0.1 ppm; 5 ppm/10 min [1]
ACGIH: 1 ppm (suspect carcinogen) [2]
(1 ppm = 1.801 mg/m³ @ NTP)

PROPERTIES: gas; d (liquid) 0.8694 g/mL @ 20 °C;
BP 10.7 °C; MP -111 °C;
VP 146 kPa (1095 mm Hg) @ 20 °C;
explosive limits 3 to 100% (v/v) in air

SYNONYMS: 1,2-epoxyethane; oxirane; CAS #75-21-8.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(HBr-coated petroleum charcoal,
100 mg/50 mg)

FLOW RATE: 0.05 to 0.15 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: 90% recovery after 17 days
@ 25 °C in the dark [3]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.04 to 0.98 ppm
(24-L samples) [3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.13 [3]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, ECD
!
!ANALYTE: 2-bromoethylheptafluorobutyrate
!
!DESORPTION: 1 mL dimethylformamide; stand 5 min
!
!INJECTION VOLUME: 1 µL
!
!TEMPERATURE-INJECTION: 200 °C
! -DETECTOR: 300 °C
! -COLUMN: 100 °C
!
!CARRIER GAS: 5% CH_4 in Ar, 25 mL/min
!
!COLUMN: 3 m x 4 mm glass; 10% SP-1000 on 80/100
! Chromosorb WHP
!
!CALIBRATION: standard solutions of 2-bromo-
! ethanol in dimethylformamide
!
!RANGE: 2 to 42 µg EtO per sample
!
!ESTIMATED LOD: 1 µg EtO per sample [4]
!
!PRECISION (s_r): 0.028 @ 18 to 71 µg EtO
! per sample [3]
!

APPLICABILITY: The working range is 0.05 to 4.6 ppm (0.08 to 8.3 mg/m³) for a 24-L air sample. The method is applicable to short-term (10-min) samples.

INTERFERENCES: 2-Bromoethanol, if present in the sample, interferes. No other significant interferences have been found [3].

OTHER METHODS: This is a modification of OSHA Method 50 [3] and replaces NIOSH Methods 1607, which has smaller sample capacity, and S286 [5], which is useful for higher levels. Method 3702 describes field-readable gas chromatography for the determination of ethylene oxide.

REAGENTS:

1. N,N-Dimethylformamide (DMF), high purity.
2. Isooctane (2,2,4-trimethylpentane), reagent grade.
3. Benzene, reagent grade.*
4. N-Heptafluorobutyrylimidazole (HFBI; N-heptafluorobutanoylimidazole; Alfa Chemical #12214, Alfa Products, Danvers, MA 01923).
5. Water, high purity (e.g., deionized distilled).
6. 2-Bromoethanol (2-BrEt), 95 to 98%.
7. Sodium hydroxide (NaOH), reagent grade.
8. Potassium hydrogen phthalate (KHP), reagent grade, dried at 90 °C.
9. HCl, conc., reagent grade.*
10. Pyridine, reagent grade.
11. Phenolphthalein, 1% (w/v) in ethanol or methanol.
12. Hydrobromic acid (HBr), 48%, reagent grade.*
13. Charcoal, petroleum-based (SKC Lot 208 or equivalent, SKC, Eighty-Four, PA).
14. Ethylene oxide (EtO), liquid or gas, 99.7% purity.*
15. Sodium hydroxide, 0.5 N. Dissolve 20 g NaOH in distilled water to make 1 L of solution. Standardize with KHP to a phenolphthalein endpoint (APPENDIX B).
16. HCl in pyridine, 0.2 N. Dissolve 8.5 mL conc. HCl in pyridine to make 500 mL solution. Standardize (APPENDIX C).
17. Ethylene oxide stock solution,* ca. 40 µg/µL. Bubble EtO gas (or pipet 4 mL EtO liquid) into 85 mL benzene in a graduated cylinder until solution volume increases ca. 4 mL. Seal tightly and store in freezer. Standardize weekly (APPENDIX D).
18. 2% HFBI in isooctane. Dissolve 2 mL HFBI in isooctane to make 100 mL solution. Store in refrigerator.
19. 5% Methane in argon.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 6 mm OD x 4 mm ID x 45 mm glass tube, flame-sealed, with plastic caps, containing HBr-coated charcoal (see APPENDIX A), two sections, 100-mg front, 50-mg back, separated and contained with silanized glass wool plugs.
2. Gas chromatograph, electron capture detector, integrator, and column (page 1614-1).
3. Burette, 50-mL, 0.1-mL graduations.
4. Flask, round-bottom, 100-mL, with ground-glass joint.
5. Condenser, reflux, with ground-glass joint to fit round-bottom flask.
6. Heating mantle, with heat control, to fit round-bottom flask.
7. Graduated cylinder, glass, 100-mL, with stopper that seals tightly.
8. Vials, glass, 5-mL, with PTFE-lined screw caps.
9. Pipets, volumetric, 2- to 500-µL and 1-, 2-, 4-, and 40-mL, with pipet bulb.
10. Syringes.
11. Vials, glass, 2-mL, with PTFE-lined septum screw caps.
12. Flasks, Erlenmeyer, 125-mL.
13. Flasks, volumetric, 10- and 25-mL.
14. Gloves.
15. Fume hood.
16. File, triangular.
17. Evaporator, rotary.

SPECIAL PRECAUTIONS: Ethylene oxide and benzene are toxic and serious fire and explosion hazards; they are also suspect carcinogens [1,2].

Hydrobromic and hydrochloric acids are eye, skin, and inhalation hazards. Work with these substances only in a hood. Use protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.15 L/min for a total sample size of 1 to 24 L.
4. Cap each tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line. Remove and discard glass wool plug.
6. Transfer front and back sorbent sections to separate vials.
7. Add 1.0 mL DMF to each vial. Cap each vial.
8. Shake at least 10 sec. Allow to stand at least 5 min.
9. Pipet a 20-µL aliquot of the DMF solution to another 5-mL vial containing 2.0 mL 2% HFBI (v/v) in isooctane.
   NOTE: Pipet 20 µL of each working standard (step 13) into vials containing 2% HFBI at this step.
10. Cap and shake 1 min. Allow to stand at room temperature at least 5 min.
11. Add 2.0 mL high purity water. Mix 1 min to ensure complete hydrolysis of excess HFBI.
12. Transfer at least 1.0 mL of isooctane (top) layer to 2-mL vial.
    NOTE: If the sample concentration is higher than the standards, dilute an aliquot of sample with DMF, reanalyze starting at step 9, and apply the appropriate dilution factor in calculations. The desorbed sample (in DMF) keeps well in a freezer [3].

CALIBRATION AND QUALITY CONTROL:

13. Calibrate daily with at least six working standards over the range 1 to 42 µg EtO per sample. For example:
    a. Pipet 1.0 mL 2-BrEt (density 1.763 g/mL @ 20 °C) into a 10-mL volumetric flask. Dilute to volume with DMF. This is stock solution "A." Dilute 3 mL of "A" to 25 mL with DMF to give standard "B." Dilute 1 mL of "B" to 10 mL with DMF to give standard "C."
    NOTE: A sample calculation with 95% pure 2-BrEt (M.W. = 124.98) expressed as its equivalent weight in EtO (M.W. = 44.05) is:

Standard Solution "A":

$$\frac{1.763 \text{ g 2-BrEt}}{10 \text{ mL}} \cdot 0.95 \cdot \frac{44.05}{124.98} \cdot 1000 = 59{,}030 \text{ µg EtO/mL.}$$

Standard Solution "B":

$$3 \text{ mL} \cdot 59{,}030/25 \text{ mL} = 7084 \text{ µg EtO/mL.}$$

Standard Solution "C":

$$1 \text{ mL} \cdot 7084/10 \text{ mL} = 708.4 \text{ µg EtO/mL.}$$

b. Prepare working standards by injecting microliter volumes of "B" and "C" into vials containing 1.0 mL DMF. The following serial dilution scheme is suggested:

Working Standard	Aliquot added to 1.0 mL DMF	Final µg EtO/mL
D	2.5 µL "C"	1.77
E	5.0 µL "C"	3.52
F	10.0 µL "C"	7.01
G	2.5 µL "B"	17.7
H	3.5 µL "B"	24.7
I	5.0 µL "B"	35.2
J	6.0 µL "B"	42.2

Higher standards may be used if detector output remains acceptable. (Some detectors may become saturated at higher levels.)

c. Analyze working standards together with samples and blanks.

d. Prepare calibration graph (µg EtO per sample vs. peak area). Use a nonlinear (e.g., parabolic) least squares fit if necessary to obtain the best fit of the data.

14. Determine recovery (R) at least once for each batch of charcoal used for sampling in the concentration range of interest. Prepare three tubes at each level of interest plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (2 to 15 µL) of EtO stock solution or a serial dilution thereof directly onto the charcoal with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 9 through 12 and 16 and 17).
    e. Prepare a graph of R vs. µg EtO recovered.
15. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

16. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1614-1. Inject sample aliquot manually using solvent-flush technique or with autosampler.
17. Measure peak area.

CALCULATIONS:

18. Determine the mass, µg (corrected for R), of EtO 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.
19. Calculate concentration, C, of EtO in the air volume sampled, V (L):

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

EVALUATION OF METHOD:
This method uses HBr-coated charcoal to collect EtO and rapidly convert it to 2-bromoethanol. This method was evaluated at the OSHA Analytical Laboratory, Salt Lake City, UT, as OSHA Method 50 [3]. Fifteen-min and 30-min air samples were collected from a constant 5 ppm test atmosphere (80% relative humidity, ambient temperature) at 0.1 L/min with observed recoveries in the range 88 to 100%.

Fifteen pairs of side-by-side area samples were collected and analyzed by OSHA using this method and the Qazi-Ketcham method. The sampling rate was ca. 50 mL/min for 4 to 7.5 hrs. Results showed no statistical difference in the two methods, with no bias over the range 0.3 to 7 ppm EtO. Test atmospheres of 0.1, 0.5, 1.0, and 16 ppm at 70 to 80% relative humidity and ambient temperature were sampled for 4 hrs at 0.1 L/min with no breakthrough. The 5% breakthrough volume for sampling a 16-ppm atmosphere of EtO at 0.15 L/min was 39 L. No significant storage effects were observed for samples in the 0.1 to 16 ppm range at high humidity and stored at ambient temperature for a minimum of two weeks.

The precision, s_r, of chromatographic response of working standards in the range 18 to 71 µg EtO per sample was 0.028 [3]. Recovery of EtO spikes in NIOSH laboratories averaged 75% at 11, 22, 33, and 44 µg EtO per sample.

REFERENCES:
[1] NIOSH Testimony to USDOL at OSHA rulemaking hearing for ethylene oxide (July 20, 1983); also see Current Intelligence Bulletin 35, "Ethylene Oxide," U.S. Department of Health and Human Services, Publ. (NIOSH) 81-130 (May 22, 1981).
[2] Threshold Limit Values and Biological Exposure Indices for 1985-86, ACGIH, Cincinnati, OH (1985).
[3] Cummins, K. J. OSHA Method No. 50, "Ethylene Oxide," OSHA Analytical Laboratory, Salt Lake City, UT (unpublished, January, 1985).
[4] User check, DataChem, Inc., NIOSH Seq #5860-J (unpublished, May 15, 1987).
[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S286, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157C (1977); also cited in NIOSH Special Occupational Hazard Review with Control Recommendations - Use of Ethylene Oxide as a Sterilant in Medical Facilities, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-200 (1977).
[6] Siggia, S. and J. G. Hanna. Quantitative Organic Analysis via Functional Groups, 4th ed., Chapter 5, John Wiley & Sons, Inc., New York, NY (1979).

METHOD REVISED BY: George Williamson, NIOSH/DPSE.

APPENDIX A: PREPARATION OF SOLID SORBENT

Slowly add a mixture of 25 mL 48% hydrobromic acid and 125 mL acetonitrile to 75 g petroleum-based charcoal (SKC Inc., Lot 208) contained in a 500-mL round-bottom flask. Allow the slurry to cool to room temperature. Dry the coated charcoal by rotary evaporation using gentle heat and keep it overnight under vacuum at ambient temperature. The product is stable for four months when stored in a tightly sealed amber glass jar at room temperature [3]. Recovery may be lower as the sample medium ages.

APPENDIX B: STANDARDIZATION OF NaOH

1. Transfer duplicate, accurately weighed, ca. 1.5-gram portions of KHP (W, mg) to separate 125-mL Erlenmeyer flasks. Dissolve in 20 to 30 mL distilled water, warming if necessary.
2. Add one drop phenolphthalein solution to each flask.
3. Fill the burette with 0.5 N NaOH. Titrate, with constant mixing, to a pink endpoint in each flask. Record the volume, V (mL), of 0.5 N NaOH used.
4. Calculate the normality, N_b, of the NaOH solution:

$$N_b = W/(204.22 \cdot V).$$

APPENDIX C: STANDARDIZATION OF HCl IN PYRIDINE

1. Pipet 40.0 mL 0.2 N HCl-in-pyridine solution into a 100-mL round-bottom flask.
2. Add 4.0 mL benzene.
3. Attach the flask to a water-cooled condenser and heat flask with a heating mantle to boiling. Reflux for 20 min.
4. Cool to near room temperature. Add 5 mL distilled H_2O through condenser and collect washings in the flask.
5. Remove reflux condenser and add a drop of phenolphthalein solution to the flask.
6. Add, with mixing, 0.5 N NaOH from the burette to the flask to a pink endpoint. Record volume, V_b (mL),of NaOH used.
   NOTE: The phenolphthalein endpoint is not as sharp as in aqueous titrations.
7. Repeat steps 1 through 7 and average the results. Calculate the normality, N_o, of the HCl-pyridine solution using N_b from APPENDIX B:

$$N_o = N_b V_b/40.$$

APPENDIX D: STANDARDIZATION OF ETHYLENE OXIDE STOCK SOLUTION [6]

1. Pipet 20.0 mL standardized HCl-pyridine solution into a 100-mL round-bottom flask.
2. Add 2.0 mL EtO stock solution.
3. Attach the flask to the condenser. Reflux for 20 min.
   NOTE: The reaction is: EtO + $HCl_{(xs)}$ → chloroethanol. The excess HCl is back-titrated in step 6.
4. Cool to near room temperature. Add 5 mL distilled H_2O through condenser, collecting washings in the flask.
5. Remove condenser and add a drop of phenolphthalein solution to the flask.
6. Add, with mixing, 0.5 N NaOH from the burette to a pink endpoint. Record volume, V_c (mL), of NaOH used.
7. Calculate the normality, N_s, of the HCl-pyridine solution using N_b from APPENDIX B:

$$N_s = N_b V_c/20 \text{ mL}.$$

8. Repeat steps 1 through 7 to obtain an average of two titrations. Results should agree to within 1%. Rinse flask thoroughly before reuse.
9. Calculate the concentration of the EtO stock solution:

$$\frac{\text{mg EtO}}{\text{mL EtO stock solution}} = (N_o - N_s) \cdot \frac{20 \text{ mL}}{10^3 \text{ mL}} \cdot \frac{44.05 \text{ g}}{1 \text{ equivalent}} \cdot \frac{1}{2 \text{ mL}} \cdot \frac{10^3 \text{ mg}}{1 \text{ g}} = (N_o - N_s) \cdot 440.5.$$

FORMULA: $H_2C(O)CH_2$; C_2H_4O

M.W.: 44.05

ETHYLENE OXIDE

METHOD: 3702

ISSUED: 8/15/87

OSHA: 1 ppm [1]
NIOSH: 0.1 ppm; 5 ppm/10 min [2]
ACGIH: 1 ppm (suspect carcinogen) [3]
(1 ppm = 1.801 mg/m³ @ NTP)

PROPERTIES: gas; d (liq.) 0.8694 g/mL @ 20 °C;
BP 10.7 °C; MP -111 °C;
VP 146 kPa (1095 mm Hg) @ 20 °C;
explosive limits 3 to 100% (v/v) in air

SYNONYMS: 1,2-epoxyethane; oxirane; CAS #75-21-8.

SAMPLING

SAMPLER: AMBIENT AIR OR BAG SAMPLE

FLOW RATE: ≥ 0.02 L/min; spot samples possible (See Step 1)

SHIPMENT: calibration and carrier gas shipment must comply with hazardous materials shipment regulations

SAMPLE STABILITY: bag samples stable 24 hrs @ 25 °C [4]

FIELD BLANKS: clean air, either in bag or from non-work area

ACCURACY

RANGE STUDIED: 0.1 to 700 ppm [4]

BIAS: not significant [4]

OVERALL PRECISION (s_r): <0.05 [4]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: ethylene oxide

COLUMN: 1.2 m x 3 mm OD PTFE, packed with Carbopak BHT 40/100 mesh

CARRIER GAS: ultrapure air, 15 mL/min

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 0.001 to 1000 ppm

ESTIMATED LOD: 2.5 pg per injection @ .001 ppm (1-mL injection)

PRECISION (s_r): <0.07 @ 0.05 to 0.2 ppm [4]

APPLICABILITY: The working range is 0.001 to 1000 ppm in relatively non-complex atmospheres (e.g., sterilization facilities).

INTERFERENCES: Freon 12, carbon dioxide, and alcohols do not interfere. Other compounds with similar retention times under the same chromatographic conditions are potential interferences.

OTHER METHODS: This method complements Method 1614 which utilizes solid sorbent collection, derivatization, and gas chromatographic measurement for ethylene oxide.

REAGENTS:

1. Uncontaminated air for preparation of standards and purging samplers.
2. Carrier gas, air, ultra-pure.*
3. Ethylene oxide (EtO) for standards, pure or in known concentration (i.e., 88/12 Freon 12/EtO mixture).*
   NOTE: Commercial sterilant mixtures are sold on a weight/weight ratio. An 88/12 mixture is 27% EtO by volume.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC) with photoionization detector, column (page 3702-1), and (if appropriate) portable strip chart recorder or integrator, and battery chargers, regulators, and other peripherals necessary for individual instruments.
2. Personal sampling pump, 0.02 to 4 L/min or other rate suitable for filling bag, with flexible connecting tubing.
3. Syringes, gas-tight (0.01 to 1-mL, 1-L), for standards preparation, sample collection and sample injection.
4. Bags, inert plastic (e.g., aluminized polyester or Tedlar), 2- to 20-L, for standard preparation, and (if needed) sample collection.
   NOTE: Care must be taken to assure that the pump, bag, and tubing are all inert and impermeable to the analyte (step 3).

SPECIAL PRECAUTIONS: Ethylene oxide is flammable. Shipment of compressed calibration gas and carrier gas must comply with 49 CFR regulations on shipment of hazardous materials.

SAMPLING:

1. Collect samples by one of the following methods:
   NOTE: Other techniques such as liquid displacement or use of an evacuated vessel may be adaptable to this method but have not been evaluated.
   a. Draw air directly into a syringe. Collect syringe samples by first purging a gas-tight syringe several times with clean air to remove any residual ethylene oxide from previous samples, then draw air into the syringe at the time and location of interest.
      NOTE: This technique requires less equipment and also has the advantage of allowing for a grab sample. It is not easily applied to TWA measurements. Since this is a one-time analysis, the concentration of the sample must be estimated in advance so that the proper size sample can be collected. An injection volume as small as ten microliters can be used if the concentration is expected to be several hundred ppm, while a 1.0- mL syringe is more appropriate if a concentration on the order of 0.01 ppm is expected.
   b. Bag samples for TWA.
      (1) Evacuate the sampling bag.
      (2) Allow the pump to be purged with sample air before opening the valve on the sampling bag. Collect bag sample by using pump to pull air from a point of interest and push it into the bag.
      NOTE: This technique can obtain a sample in a relatively short time (e.g., at 4 L/min, a few seconds sampling time will yield the fraction of a liter necessary for several replicate analyses). By selecting a low flow rate and larger bag (i.e., 10 mL/min flow and 5 L bag), an 8-hr TWA sample can be obtained. A few mL will allow for replicate injections of 1 mL or less, although in practice several hundred mL to 1 L is a more reasonable minimum. The maximum volume is limited only by the size of bags available and space in which to store them.

CALIBRATION AND QUALITY CONTROL:

2. Calibrate the GC daily in the field.
   a. Prepare bag standards by adding a known volume of EtO to a known volume of clean air in a bag. This creates a standard of known concentration in ppm (µL EtO/L air).
      (1) Evacuate a 5- to 10-L bag completely by drawing the air out with a large (1- to 2-L) syringe.
      (2) Draw clean air (or oxygen or nitrogen) from a supply cylinder into the syringe for measured transfer into the bag. Alternately, if a clean air supply is not available, draw room air through charcoal sorbent into the syringe. Repeat until the bag contains 5 L of air.
      (3) Add a known amount of pure EtO or standard EtO mixture to the bag by means of gas-tight syringe.
      Example: Using a gas-tight syringe, take 50 µL from a cylinder of pure EtO and inject it into 5 L of air to create a 10 ppm standard. Alternately, 200 µL of a 27% v/v EtO mixture (i.e., 88/12 w/w Freon 12 and EtO) can be added to the 5 L of air to obtain a 10.8 ppm standard.
      (4) Allow the bag to equilibrate, with occasional kneading, for at least 5 min.
   b. Analyze aliquots of various sizes to establish a calibration graph (steps 4 and 5). Analyze three or more replicates at each point.
      NOTE: On a high instrument attenuation (low sensitivity), injections of 0.2, 0.4, 0.6, 0.8 and 1.0 mL might be possible. This would correspond to injections of 2, 4, 6, 8, and 10 nL. On a more sensitive attenuation, injections of 0.02, 0.04, 0.06, 0.08 and 0.10 mL would be typical. Results will vary from instrument to instrument, and from time to time on the same instrument.
   c. Plot nL EtO vs. peak height or area. This plot should be a straight line.
   d. Periodically throughout the day, check calibration by repeating some of these injections of standards. Ideally, each sample would be bracketed, before and after, with injections of standards, although this is seldom practical.
3. Check the sampling equipment to prevent contamination.
   a. Use different syringes for sampling and for standard preparation. Identify each syringe with a unique number.
      NOTE 1: So called gas-tight syringes appear to be so only when new. Leakage results in injections less than indicated, resulting in inaccurate reporting of the actual concentration.
      NOTE 2: Even after more than a dozen purges, a syringe used to transfer pure ethylene oxide continues to elute small amounts of EtO.
   b. Bag sampling.
      (1) Check inertness and impermeability of the entire sampling train. This is best accomplished in the laboratory before going to the field. Purge a bag of the type to be used for sampling with clean air, and then fill it with clean air and an amount of EtO to create a concentration in the range of interest. Take replicate samples from that bag and inject them into the GC. Measure peak heights. Pump the contents of this bag through a sampling train of the type to be used in the field, into a second bag. Analyze replicate samples from the second bag immediately after transfer and hourly thereafter. If the concentrations found immediately after transfer are equal to those prior to transfer, the sampling train is not altering the EtO concentration (i.e., is inert). If the concentrations do not change over time, the bags are inert.

(2) Consider any residual analyte which may remain in a bag after use, since practicality dictates reuse of bags. One or two purges with clean air are usually sufficient to remove residual EtO unless the concentration of the previous sample was extremely high. Analyze a sample of "clean" air taken from the bag during its final purge. If no measurable EtO is found, the bag is ready for reuse.
NOTE: Some bags continue to show traces of analyte, even after several purges, and these bags should be discarded.

(3) Segregate bags used for sample collection from those used for calibration standards.

MEASUREMENT:

4. Fill a gas-tight syringe, purged several times with sample, from the sample bag. Then empty it to the desired volume, and inject that volume into the chromatograph with a quick firm motion. Record identity of syringe. Use replicate analyses to determine the repeatability of the analysis.
NOTE 1: If no estimate of concentration is available, use an injection volume of 10 to 25 µL at a high attenuation to reduce the possibility of column and detector overload. Depending on the results of this injection, larger volumes and/or more sensitive attenuations may be selected.
NOTE 2: The procedure for analysis of samples collected directly in a gas tight syringe is the same as for bag samples, with the obvious elimination of the step where the sample is withdrawn from the bag.
5. Along with the sample identification, record the injection volume (mL), the instrument attenuation, and the resultant peak height or area.

CALCULATIONS:

6. Divide the EtO volume (nL) from the calibration graph, by the injection volume (mL) to calculate sample EtO concentration (ppm):

$$ppm = \frac{\mu L\ (gas)}{L\ (gas)} = \frac{nL\ (gas)}{mL\ (gas)}.$$

EVALUATION OF METHOD: This method was evaluated in the laboratory where the accuracy and precision were determined by a comparison of measured values with accepted concentractions from a dynamic (permeation tube) generation system with confirmation by lab G.C. with flame ionization detector [4]. Field evaluations were conducted in hospital and manufacturing sterilization facilities which used commercial mixtures of EtO with Freon 12 and carbon dioxide, respectively.

REFERENCES:

[1] U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Safety and Health Standards (29 CFR 1910).
[2] Statement of the National Institute for Occupational Safety and Health, OSHA Proposed Rule, Occupational Exposure to Ethylene Oxide (July 20, 1983); also see Current Intelligence Bulletin 35, "Ethylene Oxide," U.S. Department of Health and Human Services, Publ. (NIOSH) 81-130 (May 22, 1981).
[3] Threshold Limit Values and Biological Exposure Indices for 1985-86, American Conference of Governmental Industrial Hygienists, Cincinnati, OH.
[4] Burroughs G. E., and Busch, K. A., "Field Validation of Direct-Reading Instrumental Methods for the Sampling and Analysis of Environmental Contaminants," submitted for publication.

METHOD WRITTEN BY: G. E. Burroughs, NIOSH/DPSE.

FORMULA: various

M.W.: various

FIBERS

METHOD: 7400
ISSUED: 2/15/84
REVISION #2: 8/15/87

OSHA: 0.2 asbestos fibers (> 5 µm long)/mL [1]
NIOSH: 0.1 asbestos f/mL [1]; 3 glass fibers (>10 µm x <3.5 µm)/mL [3]
ACGIH: 0.2 crocidolite; 0.5 amosite; 2 chrysotile and other asbestos, f/mL

PROPERTIES: solid, fibrous

SYNONYMS: actinolite asbestos [CAS #13768-00-8], grunerite asbestos (amosite) [CAS #12172-73-5], anthophyllite asbestos [CAS #17068-78-9], chrysotile asbestos [CAS #12001-29-5], crocidolite asbestos [CAS #12001-28-4], tremolite asbestos [CAS #14567-73-8]; fibrous glass.

SAMPLING	MEASUREMENT
SAMPLER: FILTER (0.8- to 1.2- µm cellulose ester membrane, 25-mm diameter; conductive cowl on cassette)	TECHNIQUE: LIGHT MICROSCOPY, PHASE CONTRAST
FLOW RATE*: 0.5 to 16 L/min (see step 4)	ANALYTE: fibers (manual count)
VOL-MIN*: 400 L @ 0.1 fiber/mL (see step 4) -MAX*: (see step 4) *Adjust for 100 to 1300 fibers/mm² (step 4)	SAMPLE PREPARATION: acetone/triacetin "hot block" method [5]
SHIPMENT: routine (securely packed to reduce shock)	COUNTING RULES: Set A (required by OSHA; [1,4]) or Set B (modified CRS [6])
SAMPLE STABILITY: stable	EQUIPMENT: 1. positive phase-contrast microscope 2. Walton-Beckett graticule (100-µm field of view): A Rules use Type G-22; B Rules use Type G-24 3. phase-shift test slide (HSE/NPL)
FIELD BLANKS: 10% (≥2) of samples	CALIBRATION: HSE/NPL test slide
ACCURACY	RANGE: 100 to 1300 fibers/mm² filter area
RANGE STUDIED: 80 to 100 fibers counted	ESTIMATED LOD: 7 fibers/mm² filter area
BIAS: see EVALUATION OF METHOD	PRECISION: 0.10 to 0.12 (A Rules) [3] (see Evaluation of Method:B)
OVERALL PRECISION (s_r): 0.115 to 0.13 (A Rules) [3]	

APPLICABILITY: The method gives an index of airborne fibers in workplace atmospheres. Phase contrast microscopy will not differentiate between asbestos and other fibers; use this method in conjunction with electron microscopy (e.g., Method 7402) for positive identification. Fibers < ca. 0.25 µm diameter will not be detected by this method [7].

INTERFERENCES: Any other airborne fiber may interfere since all particles meeting the counting criteria are counted. Chain-like particles may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

OTHER METHODS: This method introduces changes for improved sensitivity and reproducibility. It replaces P&CAM 239 [4,8] and Method 7400, Revision #1 (dated 5/15/85).

REAGENTS:

1. Acetone.*
2. Triacetin (glycerol triacetate), reagent grade.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: field monitor, 25-mm, three-piece cassette with ca. 50-mm electrically-conductive extension cowl and cellulose ester filter, 0.8- to 1.2-µm pore size, and backup pad.
   NOTE 1: Analyze representative filters for fiber background before use. Discard the filter lot if mean is ≥ 5 fibers per 100 graticule fields. These are defined as laboratory blanks.
   NOTE 2: Use an electrically-conductive extension cowl to reduce electrostatic effects. Ground the cowl when possible during sampling.
2. Personal sampling pump, 0.5 to 16 L/min (see step 4 for flow rate), with flexible connecting tubing.
3. Microscope, positive phase contrast, with green or blue filter, 8 to 10X eyepiece, and 40 to 45X phase objective (total magnification ca. 400X); numerical aperture = 0.65 to 0.75.
4. Slides, glass, frosted-end, pre-cleaned, 25 x 75 mm.
5. Cover slips, 22 x 22 mm, No. 1-1/2, unless otherwise specified by microscope manufacturer.
6. Lacquer or nail polish.
7. Knife, #10 surgical steel, curved blade.
8. Tweezers.
9. Heated aluminum block for clearing filters on glass slides (see ref. [5] for instructions on manufacture).
10. Micropipets, 5-µL and 100- to 500-µL.
11. Graticule, Walton-Beckett type with 100-µm diameter circular field (area = 0.00785 mm^2)at the specimen plane (Type G-22 for A Rules; Type G-24 for B Rules). Available from PTR Optics Ltd., 145 Newton Street, Waltham, MA 02154 [phone (617) 891-6000] and McCrone Accessories and Components, 850 Pasquinelli Drive, Westmont, IL 60559 [phone (312) 887-7100].
    NOTE: The graticule is custom-made for each microscope. Specify disc diameter needed to fit exactly the ocular of the microscope and the diameter (mm) of the circular counting area (see APPENDIX A).
12. HSE/NPL phase contrast test slide, Mark II. Available from PTR Optics Ltd. (address above).
13. Telescope, ocular phase-ring centering.
14. Stage micrometer (0.01-mm divisions).
15. Wire, multi-stranded, 22-gauge.

SPECIAL PRECAUTIONS: Acetone is extremely flammable. Take precautions not to ignite it. Heating of acetone in volumes greater than 1 mL must be done in a ventilated laboratory fume hood using a flameless, spark-free heat source.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.

2. For personal sampling, fasten sampler to the worker's lapel near the worker's mouth. Remove top cover from cowl extension (open face) and orient face down. Wrap joint between cowl and monitor body with shrink tape to prevent air leaks.
   NOTE: If possible, ground the cassette to remove any surface charge, using a wire held in contact (e.g., with a hose clamp) with the conductive cowl and a non-electrical metal fixture, or a cold-water pipe.
3. Submit at least two field blanks (or 10% of the total samples, whichever is greater) for each set of samples. Remove top covers from the field blank cassettes and store top covers and cassettes in a clean area (bag or box) with the top covers from the sampling cassettes during the sampling period. Replace the top covers in the cassettes after sampling.
4. Sample at 0.5 L/min or greater [9]. Adjust sampling flow rate, Q (L/min), and time, t (min), to produce a fiber density, E, of 100 to 1300 fibers/mm^2 ($3.85 \cdot 10^4$ to $5 \cdot 10^5$ fibers per 25-mm filter with effective collection area A_c= 385 mm^2) for optimum accuracy. These variables are related to the action level (one-half the current standard), L (fibers/mL), of the fibrous aerosol being sampled by:

$$t = \frac{(A_c)(E)}{(Q)(L)10^3}.$$

   NOTE 1: The purpose of adjusting sampling times is to obtain optimum fiber loading on the filter. A sampling rate of 1 to 4 L/min for 8 hrs is appropriate in non-dusty atmospheres containing ca. 0.1 fiber/mL. Dusty atmospheres require smaller sample volumes ($\leq$400 L) to obtain countable samples. In such cases take short, consecutive samples and average the results over the total collection time. For documenting episodic exposures, use high flow rates (7 to 16 L/min) over shorter sampling times. In relatively clean atmospheres, where targeted fiber concentrations are much less than 0.1 fiber/mL, use larger sample volumes (3000 to 10000 L) to achieve quantifiable loadings. Take care, however, not to overload the filter with background dust. If $\geq$ 50% of the filter surface is covered with particles, the filter may be too overloaded to count and will bias the measured fiber concentration.
   NOTE 2: OSHA regulations specify a maximum sampling rate of 2.5 L/min [1].
5. At the end of sampling, replace top cover and small end caps.
6. Ship samples with conductive cowl attached in a rigid container with packing material to prevent jostling or damage.
   NOTE: Do not use untreated polystyrene foam in shipping container because electrostatic forces may cause fiber loss from sample filter.

SAMPLE PREPARATION:

NOTE: The object is to produce samples with a smooth (non-grainy) background in a medium with refractive index $\leq$ 1.46. This method collapses the filter for easier focusing and produces permanent mounts which are useful for quality control and interlaboratory comparison. The aluminum "hot block" technique may be used outside the laboratory [5]. Other mounting techniques meeting the above criteria may also be used (e.g., the laboratory fume hood procedure for generating acetone vapor as described in Method 7400 - revision of 5/15/85, or the non-permanent field mounting technique used in P&CAM 239 [2,4,8,22]). A videotape of the mounting procedure is available from the NIOSH Publication Office [20].

7. Ensure that the glass slides and cover slips are free of dust and fibers.
8. Adjust the rheostat to heat the "hot block" to ca. 70 °C [5].
   NOTE: If the "hot block" is not used in a fume hood, it must rest on a ceramic plate and be isolated from any surface susceptible to heat damage.

9. Mount a wedge cut from the sample filter on a clean glass slide.
   a. Cut wedges of ca. 25% of the filter area with a curved-blade steel surgical knife using a rocking motion to prevent tearing. Place wedge, dust side up, on slide.
      NOTE: Static electricity will usually keep the wedge on the slide.
   b. Insert slide with wedge into the receiving slot at base of "hot block". Place tip of a micropipet containing ca. 250 µL acetone into the inlet port of the PTFE cap on top of the "hot block". Inject the acetone into the vaporization chamber with a slow, steady pressure on the plunger button while holding pipet firmly in place. After waiting 3 to 5 sec for the filter to clear, remove pipet and slide from their ports.
      CAUTION: Although the volume of acetone used is small, use safety precautions. Work in a well-ventilated area (e.g., laboratory fume hood). Take care not to ignite the acetone. Continuous, frequent use of this device in an unventilated space may produce explosive acetone vapor concentrations.
   c. Using the 5-µL micropipet, immediately place 3.0 to 3.5 µL triacetin on the wedge. Gently lower a clean cover slip onto the wedge at a slight angle to reduce bubble formation.
      NOTE: If too many bubbles form or the amount of triacetin is insufficient, the cover slip may become detached within a few hours. If excessive triacetin remains at the edge of the filter under the cover slip, fiber migration may occur.
   d. Glue the edges of the cover slip to the slide using lacquer or nail polish [10] Counting may proceed immediately after clearing and mounting are completed.
      NOTE: If clearing is slow, warm the slide on a hotplate (surface temperature 50 °C) for up to 15 min to hasten clearing. Heat carefully to prevent gas bubble formation.

CALIBRATION AND QUALITY CONTROL:

10. Microscope adjustments. Follow the manufacturers instructions. At least once daily use the telescope ocular supplied by the manufacturer to ensure that the phase rings (annular diaphragm and phase-shifting elements) are concentric. With each microscope, keep a logbook in which to record the dates of microscope cleanings, adjustments, and calibrations.
   a. Each time a sample is examined, do the following:
      (1) Adjust the light source for even illumination across the field of view at the condenser iris. With some microscopes, the illumination may have to be set up with bright field optics rather than phase contract optics.
          NOTE: Use Köhler illumination if available.
      (2) Focus on the particulate material to be examined.
      (3) Make sure that the field iris is in focus, centered on the sample, and open only enough to fully illuminate the field of view.
   b. Check the phase-shift detection limit of the microscope periodically for each analyst/microscope combination:
      (1) Center the HSE/NPL phase-contrast test slide under the phase objective.
      (2) Bring the blocks of grooved lines into focus in the graticule area.
          NOTE: The slide contains seven blocks of grooves (ca. 20 grooves per block) in descending order of visibility. For asbestos counting the microscope optics must completely resolve the grooved lines in block 3 although they may appear somewhat faint, and the grooved lines in blocks 6 and 7 must be invisible when observing them in the center of the graticule area. Blocks 4 and 5 must be at least partially visible but may vary slightly in visibility between microscopes. A microscope which fails to meet these requirements has resolution either too low or too high for fiber counting.
      (3) If image quality deteriorates, clean the microscope optics. If the problem persists, consult the microscope manufacturer.

11. Document the laboratory's precision for each counter for replicate fiber counts.
    a. Maintain as part of the laboratory quality assurance program a set of reference slides to be used on a daily basis. These slides should consist of filter preparations including a range of loadings and background dust levels from a variety of sources including both field and PAT samples. The Quality Assurance Officer should maintain custody of the reference slides and should supply each counter with a minimum of one reference slide per workday. Change the labels on the reference slides periodically so that the counter does not become familiar with the samples.
    b. From blind repeat counts on reference slides, estimate the laboratory intra- and intercounter s_r (see step 21). Obtain separate values of relative standard deviation for each sample matrix analyzed in each of the following ranges: 5 to 20 fibers in 100 graticule fields, 21 to 50 fibers in 100 graticule fields, 51 to 100 fibers in 100 graticule fields, and 100 fibers in less than 100 graticule fields. Maintain control charts for each of these data files.
    NOTE 1: Since fiber counting is the measurement of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will result in approximately normally distributed data.
    NOTE 2: Certain sample matrices (e.g., asbestos cement) have been shown to give poor precision [6]
12. Prepare and count field blanks along with the field samples. Report counts on each field blank.
    NOTE 1: The identity of blank filters should be unknown to the counter until all counts have been completed.
    NOTE 2: If a field blank yields greater than 7 fibers per 100 graticule fields, report possible contamination of the samples.
13. Perform blind recounts by the same counter on 10% of filters counted (slides relabeled by a person other than the counter). Use the following test to determine whether a pair of counts by the same counter on the same filter should be rejected because of possible bias: Discard the sample if the difference between the two counts exceeds $2.77\ (X)s_r$, where X = average of the two fiber counts and s_r = intracounter relative standard deviation from step 11.
    NOTE: If a pair of counts is rejected by this test, recount the remaining samples in the set and test the new counts against the first counts. Discard all rejected paired counts. It is not necessary to use this statistic on blank counts.
14. Enroll each new counter in a training course which compares performance of counters on a variety of samples using this procedure.
    NOTE: All laboratories engaged in asbestos counting should participate in a proficiency testing program such as the AIHA-NIOSH Proficiency Analytical Testing (PAT) Program and routinely exchange field samples with other laboratories to compare performance of counters.

MEASUREMENT:

15. Center the slide on the stage of the calibrated microscope under the objective lens. Focus the microscope on the plane of the filter.
16. Adjust the microscope (Step 10) [7].
    NOTE: Calibration with the HSE/NPL test slide determines the minimum detectable fiber diameter (ca. 0.25 µm).
17. Select one of the following sets of counting rules:
    NOTE: The two sets of rules have produced approximately equivalent mean counts on a variety of asbestos sample types [6]. OSHA regulations require the use of the A rules [1]. In either case, the rules must be strictly followed to obtain valid results. No hybridizing of the two sets of rules is permitted.

a. A Rules (same as P&CAM 239 rules [2,4,8]; see APPENDIX B).
   1. Count only fibers longer than 5 µm. Measure length of curved fibers along the curve.
   2. Count only fibers with a length-to-width ratio equal to or greater than 3:1.
   3. For fibers which cross the boundary of the graticule field:
      a. Count any fiber longer than 5 µm which lies entirely within the graticule area.
      b. Count as 1/2 fiber any fiber with only one end lying within the graticule area, provided that the fiber meets the criteria of rules a.1. and a.2.
      c. Do not count any fiber which crosses the graticule boundary more than once.
      d. Reject and do not count all other fibers.
   4. Count bundles of fibers as one fiber unless individual fibers can be identified by observing both ends of a fiber.
   5. Count enough graticule fields to yield 100 fibers. Count a minimum of 20 fields. Stop at 100 graticule fields regardless of count.

b. B Rules (see APPENDIX B)
   1. Count only ends of fibers. Each fiber must be longer than 5 µm and less than 3 µm diameter.
   2. Count only ends of fibers with a length-to-width ratio equal to or greater than 5:1.
   3. Count each fiber end which falls within the graticule area as one end, provided that the fiber meets rules b.1 and b.2. Add split ends to the count as appropriate if the split fiber segment also meets the criteria of rules b.1 and b.2.
   4. Count visibly free ends which meet rules b.1 and b.2 when the fiber appears to be attached to another particle, regardless of the size of the other particle. Count the end of a fiber obscured by another particle if the particle covering the fiber end is less than 3 µm in diameter.
   5. Count free ends of fibers emanating from large clumps and bundles up to a maximum of 10 ends (5 fibers), provided that each segment meets rules b.1 and b.2.
   6. Count enough graticule fields to yield 200 ends. Count a minimum of 20 graticule fields. Stop at 100 graticule fields, regardless of count.
   7. Divide total end count by 2 to yield fiber count.

18. Start counting from the tip of the filter and progress along a radial line to the outer edge. Shift up or down on the filter, and continue in the reverse direction. Select graticule fields randomly by looking away from the eyepiece briefly while advancing the mechanical stage. Ensure that, as a minimum, each analysis covers one radial line from the filter center to the outer edge of the filter. When an agglomerate covers ca. 1/6 or more of the graticule field, reject the graticule field and select another. Do not report rejected graticule fields in the total number counted.

NOTE 1: When counting a graticule field, continuously scan a range of focal planes by moving the fine focus knob to detect very fine fibers which have become embedded in the filter. The small-diameter fibers will be very faint but are an important contribution to the total count. A minimum counting time of 15 seconds per field is appropriate for accurate counting.

NOTE 2: This method does not allow for differentiation of fibers based on morphology. Although some experienced counters are capable of selectively counting only fibers which appear to be asbestiform, there is presently no accepted method for ensuring uniformity of judgment between laboratories. It is, therefore, incumbent upon all laboratories using this method to report total fiber counts. If serious contamination from non-asbestos fibers occurs in samples, other techniques such as transmission electron microscopy must be used to identify the asbestos fiber fraction present in the sample (see NIOSH Method 7402). In some cases (i.e., for fibers with diameters > 1 µm), polarized light microscopy (e.g., NIOSH Method 7403) may be used to identify and eliminate interfering non-crystalline fibers.

CALCULATIONS AND REPORTING OF RESULTS:

19. Calculate and report fiber density on the filter, E (fibers/mm^2), by dividing the total fiber count per graticule field, F/n_f, minus the mean field blank count per graticule field, B/n_b, by the graticule field area, A_f (0.00785 mm^2 for a properly calibrated Walton-Beckett graticule):

$$E = \frac{(\frac{F}{n_f} - \frac{B}{n_b})}{A_f}, \text{ fibers/mm}^2.$$

NOTE: Fiber counts above 1300 fibers/mm^2 and fiber counts from samples with > 50% of filter area covered with particulate should be reported as "uncountable" or "probably biased."

20. Calculate and report the concentration, C (fibers/mL), of fibers in the air volume sampled, V (L), using the effective collection area of the filter, A_c (385 mm^2 for a 25-mm filter):

$$C = \frac{(E)(A_c)}{V \cdot 10^3}.$$

NOTE: Periodically check and adjust the value of A_c, if necessary.

21. Report intralaboratory and interlaboratory relative standard deviations (from Step 11) with each set of results.

NOTE: Precision depends on the total number of fibers counted [4,11]. Relative standard deviation (also called coefficient of variation) is documented in references [4,11,12,13] for fiber counts up to 100 fibers in 100 graticule fields. Comparability of interlaboratory results is discussed below. As a first approximation, use 213% above and 49% below the count as the upper and lower confidence limits for fiber counts greater than 20 (Fig. 1).

EVALUATION OF METHOD:

A. This method is a revision of P&CAM 239 [2,4,8]. A summary of the revisions is as follows:

1. Sampling:
   The change from a 37-mm to a 25-mm filter improves sensitivity for similar air volumes. The change in flow rates allows for 2-m^3 full-shift samples to be taken, providing that the filter is not overloaded with non-fibrous particulates. The collection efficiency of the sampler is not a function of flow rate in the range 0.5 to 16 L/min [9].
2. Sample Preparation Technique:
   The acetone vapor-triacetin preparation technique is a faster, more permanent mounting technique than the dimethyl phthalate/diethyl oxalate method of P&CAM 239 [2,4,5,8,14]. The aluminum "hot block" technique minimizes the amount of acetone needed to prepare each sample.
3. Measurement:
   a. The Walton-Beckett graticule standardizes the area observed [14,15].
   b. The HSE/NPL test slide standardizes microscope optics for sensitivity to fiber diameter [7,14].

c. An international collaborative study involved 16 laboratories using prepared slides from the asbestos cement, milling, mining, textile, and friction material industries [6]. The modified CRS (NIOSH B) Rules were found to yield equivalent counts but were more precise than the AIA (NIOSH A)* Rules. The relative standard deviations (s_r) varied with sample type and laboratory. The ranges were:

	s_r		
	Intralaboratory	Interlaboratory	Overall
AIA (NIOSH A Rules)*	0.12 to 0.40	0.27 to 0.85	0.46
Modified CRS (NIOSH B Rules)	0.11 to 0.29	0.20 to 0.35	0.25

*Under AIA rules, only fibers having a diameter less than 3 μm are counted and fibers attached to particles larger than 3 μm are not counted. NIOSH A Rules are otherwise similar to the AIA rules.

d. The B Rules have also been favorably received by analysts as less ambiguous and simpler to use; these rules also showed the least bias relative to AIA rules in the collaborative study. An independent NIOSH laboratory study using amosite fibers reported a relative standard deviation, including within- and between-sample variability, of 0.16 for the B Rules [16]. Another NIOSH study was conducted using field samples of asbestos [19]. This study indicated intralaboratory s_r in the range 0.17 to 0.25 and an interlaboratory s_r of 0.45. This agrees well with other recent studies [6,11,13].

e. Because of past inaccuracies associated with low fiber counts, the minimum recommended loading has been increased to 100 fibers/mm^2 filter area (80 fibers total count). This level should yield intracounter s_r in the range of 0.13 to 0.17 [4,8,16,19].

B. Interlaboratory Comparability:

At this time, there is no independent method for assessing the overall accuracy of this method. One measure of reliability is to estimate how well the count for a single sample agrees with the mean count from a large number of laboratories. The following discussion indicates how this estimation can be carried out based on measurements of the interlaboratory variability, as well as showing how the results of this method relate to the theoretically attainable counting precision and to measured intra- and interlaboratory s_r.

Theoretically, the process of counting randomly (Poisson) distributed fibers on a filter surface will give an s_r that depends on the number, N, of fibers counted:

$$s_r = 1/(N)^{1/2} \qquad (1)$$

Thus s_r is 0.1 for 100 fibers and 0.32 for 10 fibers counted. The actual s_r found in a number of studies is greater than these theoretical numbers [6,11,12,13].

An additional component of variability comes primarily from subjective laboratory-to-laboratory differences. In a study of ten counters in a continuing sample exchange program, Ogden [11] found this subjective component of intralaboratory s_r to be approximately 0.2 and estimated the overall s_r by the term:

$$\frac{(N + (0.2 \cdot N)^2)^{1/2}}{N} \qquad (2)$$

Ogden found that the 90% confidence interval of the individual intralaboratory counts in relation to the means were +2 s_r and - 1.5 s_r. In this program, one sample out of ten was a quality control sample. For laboratories not engaged in an intensive quality assurance program, the subjective component of variability can be higher.

In a study of field sample results in 46 laboratories, the Asbestos Information Association [13] also found that the variability had both a constant component and one that depended on the fiber count. These results gave a subjective interlaboratory component of s_r (on the same basis as Ogden's) for field samples of ca. 0.45. A similar value was obtained for 12 laboratories analyzing a set of 24 field samples [19]. This value falls slightly above the range of s_r (0.25 to 0.42 for 1984-85) found for 80 reference laboratories in the NIOSH Proficiency Analytical Testing (PAT) program for laboratory-generated samples [12].

A number of factors influence s_r for a given laboratory, such as that laboratory's actual counting performance and the type of samples being analyzed. In the absence of other information, such as from an interlaboratory quality assurance program using field samples, the value for the subjective component of variability is chosen as 0.45. Note that, though based on at least two studies, this is a somewhat arbitrary choice. It is hoped that by the use of this number in the absence of other information, laboratories will carry out the recommended interlaboratory quality assurance programs to improve their performance and thus reduce the s_r.

The above relative standard deviations apply when the population mean has been determined. It is more useful, however, for laboratories to estimate the 90% confidence interval on the mean count from a single sample fiber count (Figure 1). These curves assume similar shapes of the count distribution for interlaboratory and intralaboratory results [11].

For example, if a sample yields a count of 24 fibers, Figure 1 indicates that the mean interlaboratory count will fall within the range of 227% above and 52% below that value 90% of the time. We can apply these percentages directly to the air concentrations as well. If, for instance, this sample (24 fibers counted) represented a 500-L volume, then the measured concentration is 0.02 fibers/mL (assuming 100 fields counted, 25-mm filter, 0.00785 mm^2 counting field area). If this same sample were counted by a group of laboratories, there is a 90% probability that the mean would fall between 0.01 and 0.08 fiber/mL. These limits should be reported in any comparison of results between laboratories.

Note that the s_r of 0.45 used to derive Figure 1 is used as an estimate for a random group of laboratories. If several laboratories belonging to a quality assurance group can show that their interlaboratory s_r is smaller, then it is more correct to use that smaller s_r. However, the estimated s_r of 0.45 is to be used in the absence of such information. Note also that it has been found that s_r can be higher for certain types of samples, such as asbestos cement.

Quite often the estimated airborne concentration from an asbestos analysis is used to compare to a regulatory standard. For instance, if one is trying to show compliance with an 0.5 fiber/mL standard using a single sample on which 100 fibers have been counted, then Figure 1 indicates that the 0.5 fiber/mL standard must be 213% higher than the measured air concentration. This indicates that if one measures a fiber concentration of 0.16 fiber/mL (100 fibers counted), then the mean fiber count by a group of laboratories (of which the compliance laboratory might be one) has a 95% chance of being less than 0.5 fibers/mL; i.e., 0.16 + 2.13 x 0.16 = 0.5.

It can be seen from Figure 1 that the Poisson component of the variability is not very important unless the number of fibers counted is small. Therefore, a further approximation is to simply use +213% and -49% as the upper and lower confidence values of the mean for a 100-fiber count.

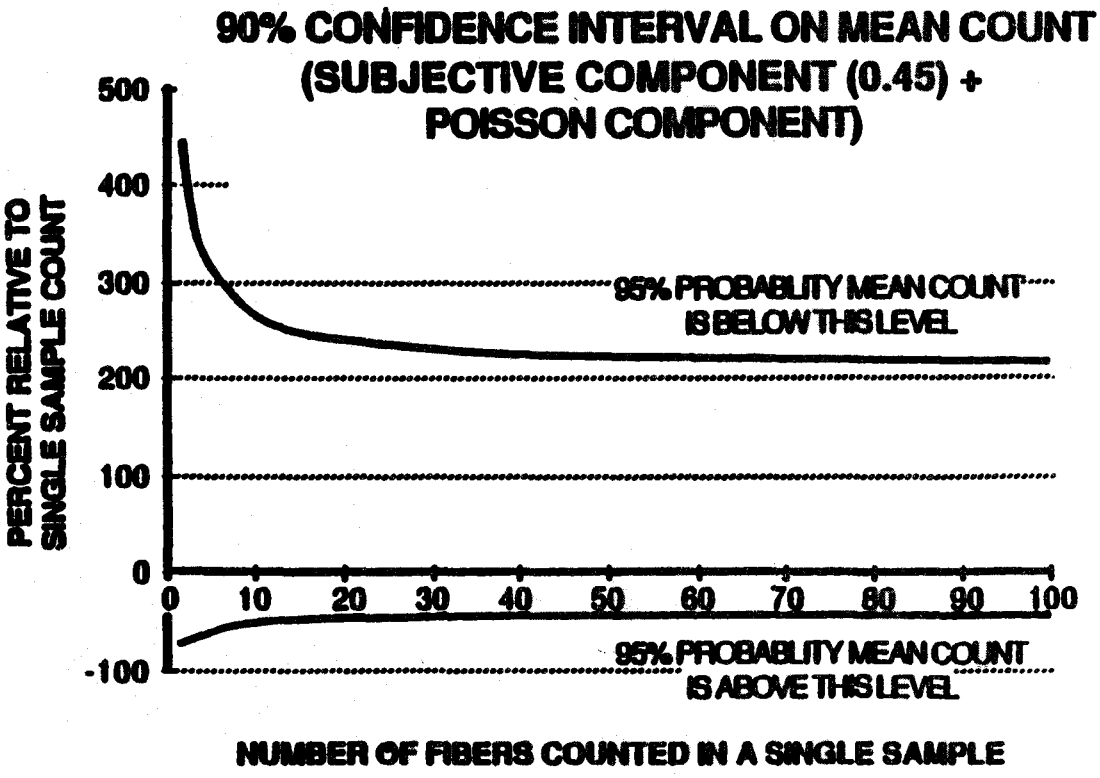


Figure 1. Interlaboratory Precision of Fiber Counts

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APPENDIX A: CALIBRATION OF THE WALTON-BECKETT GRATICULE:

Before ordering the Walton-Beckett graticule, the following calibration must be done to obtain a counting area (D) 100 µm in diameter at the image plane. The diameter, d_c (mm), of the circular counting area and the disc diameter must be specified when ordering the graticule.

1. Insert any available graticule into the eyepiece and focus so that the graticule lines are sharp and clear.
2. Set the appropriate interpupillary distance and, if applicable, reset the binocular head adjustment so that the magnification remains constant.

3. Install the 40 to 45X phase objective.
4. Place a stage micrometer on the microscope object stage and focus the microscope on the graduated lines.
5. Measure the magnified grid length of the graticule, L_o (µm), using the stage micrometer.
6. Remove the graticule from the microscope and measure its actual grid length, L_a (mm). This can best be accomplished by using a stage fitted with verniers.
7. Calculate the circle diameter, d_c (mm), for the Walton-Beckett graticule:

$$d_c = \frac{L_a}{L_o} \times D.$$

Example: If L_o = 112 µm, L_a = 4.5 mm and D = 100 µm, then d_c = 4.02 mm.

8. Check the field diameter, D (acceptable range 100 µm ± 2 µm) with a stage micrometer upon receipt of the graticule from the manufacturer. Determine field area (acceptable range 0.00785 mm² ± 0.00032 mm²).

APPENDIX B: COMPARISON OF COUNTING RULES:

Figure 2 shows a Walton-Beckett graticule as seen through the microscope. Although the graticule incorporates the 3:1 aspect ratio, both the "A" and "B" rules will be discussed as they apply to the labeled fibers in the figure.

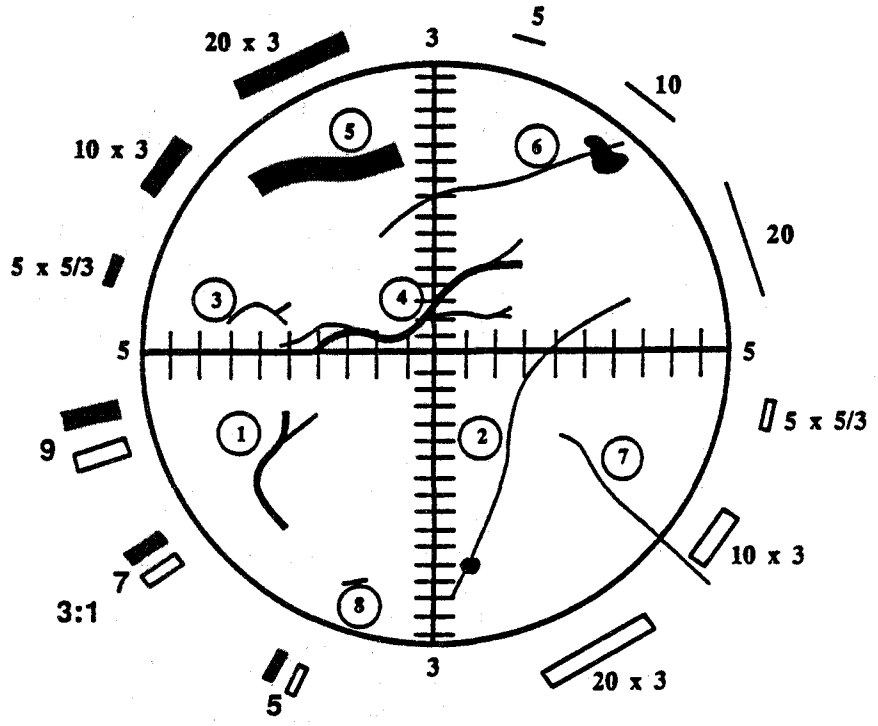

Figure 2. Walton-Beckett graticule with fibers.

Fiber	FIBER COUNT A Rules	FIBER COUNT B Rules	DISCUSSION
1	1 fiber	3 ends	(A)"A" rules do not allow for split ends; therefore, count one fiber. (B) Under 'B' rules, first detemine whether the fiber meets dimensional criteria, (i.e., >5 µm, >5:1 aspect ratio, <3 µm diameter). Next determine and count which two ends are the main trunk of the fiber. Finally, count all split ends >5 µm as one end. Fiber #1 is counted as 3 ends.
2	1 fiber	2 ends	(A) Single fiber with small particle attached. The particle is treated as if it does not exist by the "A" rules. (B) The particle is <3 µm diameter and therefore ignored under "B" rules.
3	1 fiber	2 ends	(A) As with Fiber 1, count one fiber under "A" rules because it meets the >3:1 aspect ratio, >5 µm criteria. (B) The split end is <5 µm long so it is not counted under "B" rules.
4	1 fiber	5 ends	(A) Fiber ends all attached to a central large fiber or bundle; therefore, count one fiber under "A" rules. (B) Count two ends as belonging to the main fiber. Three of the remaining four split ends are >5 µm, giving a total of 5 ends.
5	1 fiber	Do not count	(A) No diameter limit under "A" rules; therefore count this thick fiber because it meets the >3:1, >5 µm counting criteria. (B) The fiber is >3 µm diameter; therefore not counted under "B" rules.
6	1 fiber	1 end	(A) Ignore non-fibrous particulate matter under the "A" rules; count this as a whole fiber. (B) The short end of the fiber is <5 µm long and obscured by a particle >3 µm in diameter; therefore, not counted under "B" rules.
7	1/2 fiber	1 end	(A) Fibers which meet rules a.1. and a.2. and cross the graticule boundary are counted as 1/2 fiber under "A" rules unless the fiber crosses the graticule boundary more than once, in which case the fiber is not counted no matter how many ends lie within the graticule area. (B) Fiber ends lying inside the graticule boundary are counted as one end provided that the entire fiber meets rules b.1. and b.2. and each end is >5 µm. The portion of the fiber lying outside the graticule boundary must be considered in order to make this determination. Under "B" rules, it does not matter how often the fiber crosses the graticule boundary.
8	Do not count	Do not count	The fiber is <5 µm long.

FORMULA:  ; $C_5H_4O_2$

M.W.: 96.09

FURFURAL

METHOD: 2529

ISSUED: 8/15/87

OSHA: 5 ppm (skin)
NIOSH: no recommended standard [1]
ACGIH: 2 ppm (skin)
(1 ppm = 3.93 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.160 g/mL @ 20 °C;
BP 162 °C; MP -36 °C;
VP 0.26 kPa (2 mm Hg; 2600 ppm) @ 20 °C;
explosive range 2.1 to 19.3% (v/v) in air

SYNONYMS: 2-furaldehyde; 2-furancarboxaldehyde; CAS #98-01-1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(10% 2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C

FIELD BLANKS: 10% of samples
MEDIA BLANKS: 18 per set (for DE)

ACCURACY

RANGE STUDIED: 2.6 to 40 mg/m³ [2]
(15-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.076 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of furfural

DESORPTION: 2 mL toluene; 30 min ultrasonic

INJECTION VOLUME: 1 µL, splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 1 min @ 70 °C; 20 °C/min; hold 2 min @ 290 °C

CARRIER GAS: He, 20 cm/sec

COLUMN: 10 m x 0.25 mm, 1 µm DB5

CALIBRATION: furfural standards spiked on sampler

RANGE: 16 to 640 µg per sample [2]

ESTIMATED LOD: 5 µg per sample [2]

PRECISION (s_r): 0.057 [2]

APPLICABILITY: The working range is 0.3 to 5.5 ppm (1.3 to 22 mg/m³) for a 12-L air sample. The method is suitable for the simultaneous determination of furfural and glutaraldehyde.

INTERFERENCES: None have been observed.

OTHER METHODS: Method S17 [3] is an alternate, less sensitive method for furfural which uses bubbler collection and derivatization with Girard T reagent.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas) or equivalent. Extract 4 hrs in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Furfural,* freshly distilled under N_2 to remove impurities. Store at 0 °C.
5. Calibration stock solution, 100 µg/µL. Add 1 g furfural to toluene and dilute to 10 mL. Prepare in duplicate.
6. Furfural oxazolidine (see APPENDIX) stock solution, 2.5 mg/mL. Add 25 mg to toluene and dilute to 10 mL.
7. Water, deionized, then distilled.
8. Hydrogen, prepurified.
9. Air, filtered.
10. Helium, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm x 4 mm ID, flame-sealed, with plastic caps, containing a 120-mg front section and a 60-mg back-up section of the 2-(hydroxymethyl)piperidine-coated XAD-2 (see APPENDIX) with flame-sealed ends. Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 756 Pa. Tubes are commercially available (Supelco ORBO 23 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2529-1).
4. Ultrasonic bath.
5. Vials, glass, 4-mL, with septum and plastic screw caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Pipets, disposable, 2-mL.
9. Syringes, 10-µL (readable to 0.1 µL), 25-, and 50-µL.
10. File.
11. Beakers, 50-mL.
12. Magnetic stirrer.
13. Flasks, round-bottomed, 100-mL.
14. Soxhlet extraction apparatus.
15. Vacuum oven.
16. Distillation apparatus.

SPECIAL PRECAUTIONS: Furfural can irritate the mucous membranes and act on the central nervous system [1,4]. Work with this compound only in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break 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 0.05 L/min for a total sample size of 1 to 12 L.

   NOTE: Furfural reacts with 2-(hydroxymethyl)piperidine to form an oxazolidine derivative during sampling. Sampling rate is limited by the speed of this reaction; rates above 0.05 L/min may cause breakthrough due to incomplete reaction.

SAMPLE PREPARATION:

4. Score each sampler with a file in back of the rear sorbent section.
5. Break sampler at score line. Remove and place rear glass wool plug and rear sorbent section in a vial.
6. Transfer front section with remaining glass wool plugs to a second vial.

7. Add 2.0 mL toluene to each vial. Screw cap tightly onto each vial.
8. Agitate vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Prepare oxazolidine standard solutions.
   a. Add known amounts of furfural oxazolidine stock solution (equivalent to the range of the samples) to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze (steps 12 and 13) with samples and blanks for qualitative identification of derivative peaks.
10. Calibrate daily with at least five working standards covering the range of the samples.
   a. Weigh 120-mg portions of unused sorbent into vials.
   b. Add aliquots of calibration stock solution or dilutions thereof. Cap vials and allow them to stand overnight at room temperature.
   c. Desorb (steps 7 and 8) and analyze (steps 12 and 13) with samples and blanks.
   d. Prepare calibration graph (peak area vs. µg furfural).
   NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary.
11. Analyze three quality control blind spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2529-1. Inject 1-µL sample aliquot.
   NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene and apply the appropriate dilution factor in calculations.
13. Measure total peak area of the two analyte peaks.
   NOTE: On the DB-5 column, the oxazolidine derivative of furfural gives two peaks, since the diastereoisomers are resolved. t_r for the furfural derivative = 5.0 and 5.3 min; glutaraldehyde derivative = 9.4 and 9.7 min; and t_r for 2-(hydroxymethyl)piperidine = 2.6 min for these conditions.

CALCULATIONS:

14. Determine the mass, µg of furfural found in the sample front (W_f) and back (W_b) sorbent sections.
   NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of furfural in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Atmospheres were generated by flash vaporization of an aqueous furfural solution into a stream of air flowing at a fixed rate [2]. Relative humidity during generation was 80% ±5%. The generator and sampling manifold system have been described previously [5]. Concentration of furfural vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [6]. The method was studied over the range of 2.6 to 40 mg/m³ using 15-L samples. Desorption efficiencies on statically-spiked samples averaged 94% in the range 16 to 640 µg per sample. Recovery of dynamically-generated samples was 93%, due to breakthrough of furfural at the highest level studied (40 mg/m³). Recovery was quantitative at lower levels.

REFERENCES:
[1] 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.
[2] E. R. Kennedy, Y. T. Gagnon, J. R. Okenfuss and A. W. Teass, "Air sampling and analytical method for the determination of selected low-molecular weight aldehydes as their oxazolidines by capillary gas chromatography." Appl. Ind. Hyg., in press.
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METHOD WRITTEN BY: Julie R. Okenfuss and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

APPENDIX:

SORBENT PREPARATION (optional if commercially prepared tubes are used):
Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent. Allow this mixture to stand 1 hr with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 hr. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze (steps 7 through 13). No blank peak is expected for furfural.

SYNTHESIS OF FURFURAL OXAZOLIDINE:
Place a solution of 0.58 g (0.5 mL; 6 mmol) freshly distilled furfural in 10 mL toluene in a 50-mL round-bottomed flask. Add 2.5 g magnesium sulfate to the flask to remove water which forms during the reaction. Add a solution of 0.61 g (5.3 mmol) purified 2-hydroxymethylpiperidine in 10 mL toluene dropwise with stirring over 1 hr. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation. The product is a yellow viscous oil.

DESORPTION EFFICIENCY:
The determination of desorption efficiency (DE) is not necessary when using the calibration procedure in step 10. If desired, the following procedure can be used to determine DE:
a. Prepare and analyze a set of oxazolidine standard solutions (step 9.a) and a set of working standards (step 10) including media blanks.
b. Treating the working standards as unknowns, read the mass (µg) of oxazolidine found in each working standard (W), and in the average media blank (B).
c. Using the mass of furfural, µg, spiked onto the working standard (W_0) and the stoichiometric conversion factor between furfural and furfural oxazolidine (2.01), calculate the desorption efficiency:

$$DE = \frac{W - B}{W_0 \cdot 2.01} .$$

d. Prepare a graph of DE vs. µg furfural recovered per sample [(W - B)/2.01].

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/15/84
REVISION #1: 8/15/87

COMPOUNDS: (synonyms in Table 1)

benzyl chloride	chlorobromomethane	1,1-dichloroethane	methylchloroform
bromoform	chloroform	1,2-dichloroethylene	tetrachloroethylene
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 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): 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

TEMPERATURES: Table 3

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 3; 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 3

ESTIMATED LOD: 0.01 mg per sample [2]

PRECISION (s_r): see EVALUATION OF METHOD [1]

APPLICABILITY: See Table 2 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-hexane.
   c. o-dichlorobenzene, 200 mg/mL in acetone.
   d. p-dichlorobenzene, 300 mg/mL in acetone.
   e. 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 at step 8.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five 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 levels 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 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):

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

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	Precision (s_r) Overall	Precision (s_r) Measurement	Desorption Efficiency	Ref.
Benzyl chloride	2–8	10 L	0.096	0.031	0.90 @ 0.03–0.1 mg	[8]
Bromoform	3–10	10 L	0.071	0.043	0.80 @ 0.025 mg	[7]
Carbon tetrachloride	65–299	15 L	0.092	0.037	0.96 @ 1.3–4.8 mg	[16]
Chlorobenzene	183–736	10 L	0.056	0.025	0.91 @ 1.8–7.1 mg	[12]
Chlorobromomethane	640–2655	5 L	0.061	0.051	0.94 @ 3.3–13 mg	[6]
Chloroform	100–416	15 L	0.057	0.047	0.97 @ 1.8–7.4 mg	[19]
o-Dichlorobenzene	150–629	3 L	0.068	0.013	0.86 @ 0.5–1.9 mg	[14]
p-Dichlorobenzene	183–777	3 L	0.052	0.022	0.91 @ 0.7–2.7 mg	[15]
1,1-Dichloroethane	212–838	10 L	0.057	0.011	1.01 @ 1.9–8 mg	[10]
1,2-Dichloroethylene*	475–1915	3 L	0.052	0.017	1.00 @ 2.4–9.5 mg	[5]
Ethylene dichloride	195–819	3 L	0.079	0.012	0.96 @ 0.6–2.5 mg	[9]
Hexachloroethane	5–25	10 L	0.121	0.014	0.98 @ 0.05–0.2 mg	[4]
Methyl chloroform	904–3790	3 L	0.054	0.018	0.99 @ 2.9–11 mg	[17]
Tetrachloroethylene	655–2749	3 L	0.052	0.013	0.96 @ 2.1–8 mg	[18]
1,1,2-Trichloroethane	26–111	10 L	0.057	0.010	0.97 @ 0.3–1.2 mg	[13]
1,2,3-Trichloropropane	163–629	10 L	0.068	0.027	0.95 @ 1.5–6 mg	[11]

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

REFERENCES:
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[5] Ibid., S110.
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[8] Ibid., S115.
[9] Ibid., S122.
[10] Ibid., S123.
[11] Ibid., S126.
[12] Ibid., S133.
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[15] Ibid., S281.
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[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 REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. General information.

Compound	M.W.	mg/m³ = 1 ppm @ NTP	Synonyms	OSHA/NIOSH/ACGIH (ppm)
Benzyl chloride* ($C_6H_5CH_2Cl$)	126.58	5.17	(chloromethyl) benzene; α-chlorotoluene; CAS #100-44-7	1/—/1 [20,23]
Bromoform ($CHBr_3$)	252.75	10.33	tribromomethane; CAS #75-25-2	0.5/—/0.5 (skin) [20]
Carbon tetrachloride* (CCl_4)	153.84	6.29	tetrachloromethane; CAS #56-23-5	10, C 25/C 2/5 (skin) [20,24]
Chlorobenzene (C_6H_5Cl)	112.56	4.60	monochlorobenzene; phenyl chloride; CAS #108-90-7	75/—/75 [20]
Chlorobromomethane (CH_2BrCl)	129.39	5.29	bromochloromethane; Halon 1011; CAS #74-97-5	200/—/200, STEL 250 [20]
Chloroform* ($CHCl_3$)	119.39	4.88	trichloromethane; CAS #67-66-3	C 50/C 2/10 [20,25]
o-Dichlorobenzene ($1,2-C_6H_4Cl_2$)	147.00	6.01	1,2-dichlorobenzene; CAS #95-50-1	50/—/C 50 [20]
p-Dichlorobenzene ($1,4-C_6H_4Cl_2$)	147.00	6.01	1,4-dichlorobenzene; CAS #106-46-7	75/—/75, STEL 110 [20]
1,1-Dichloroethane (CH_3CHCl_2)	98.96	4.05	ethylidene chloride; CAS #75-34-3	100/100/200, STEL 250 [20,21]
1,2-Dichloroethylene ($ClCH=CHCl$)	96.94	3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200/—/200, STEL 250 [20]
Ethylene dichloride* ($ClCH_2CH_2Cl$)	98.96	4.05	1,2-dichloroethane; CAS #107-06-2	50, C 100/5, C 15/10 [20,21,26]
Hexachloroethane* (CCl_3CCl_3)	236.74	9.68	perchloroethane; CAS #67-72-1	1 (skin)/—/10 [20,21]
Methylchloroform (CH_3CCl_3)	133.42	5.45	1,1,1-trichloroethane; CAS #71-55-6	350/C 350/350, STEL 450 [20,21,27]
Tetrachloroethylene ($Cl_2C=CCl_2$)	165.83	6.78	perchloroethylene; CAS #127-18-4	100, C 200, P 300/—/ 50, STEL 200 [20,28]
1,1,2-Trichloroethane (Cl_2CHCH_2Cl)	133.41	5.45	vinyl trichloride; CAS #79-00-5	10 (skin)/—/10 (skin) [20,21]
1,2,3-Trichloropropane ($CH_2ClCHClCH_2Cl$)	147.43	6.03	allyl trichloride; glycerol trichlorohydrin; CAS #96-18-4	50/—/50, STEL 75 [20]

*Suspect carcinogen [20,21,22].

Table 2. Sampling limits.

Compound	Air Sample Volume (L) Min	Max	Target	Working Range, ppm, at Max Sample Volume
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
Methylchloroform	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 3. Measurement parameters.

Compound	Column*	t (°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
Methylchloroform	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.

FORMULA: I_2

M.W.: 253.81

IODINE

METHOD: 6005
ISSUED: 8/15/87

OSHA: C 0.1 ppm
NIOSH: Group I Pesticide [1]
ACGIH: C 0.1 ppm
(1 ppm = 10.38 mg/m³ @ NTP)

PROPERTIES: solid; d 4.93 g/mL;
MP 113.5 °C; BP 184.3 °C;
VP 40 Pa (0.3 mm Hg; 395 ppm) @ 25 °C;
not combustible

SYNONYMS: CAS #7553-56-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(alkali-treated charcoal,
100 mg/50 mg)

FLOW RATE: 0.5 to 1 L/min

VOL-MIN: 15 L @ 0.05 ppm
-MAX: 225 L

SHIPMENT: routine

SAMPLE STABILITY: 100% recovered after 8 days @ room temperature [2]

FIELD BLANKS: 10% of samples

MEDIA BLANKS: 6 per sample set + 15 per lot of charcoal

ACCURACY

RANGE STUDIED: 0.74 to 2.1 mg/m³ [2]
(15-L air samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.085 [2]

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: iodide ion (I^-)

DESORPTION: 3 mL 10 mM Na_2CO_3

INJECTION LOOP VOLUME: 100 µL

ELUENT: 10 mM Na_2CO_3; 3 mL/min

COLUMNS: AS3 anion separator, fast run; AG3 anion guard, fast run; anion suppressors (in tandem); ASC-2 (6-mm ID x 250 mm); ASC-1 (6-mm ID x 75 mm)

CONDUCTIVITY SETTING: 3µS full scale

CALIBRATION: standard solutions of KI in eluent

RANGE: 0.008 to 0.2 mg I_2 per sample [2]

ESTIMATED LOD: 0.001 mg I_2 per sample [2]

PRECISION (s_r): 0.071 @ 0.01 to 0.03 mg I_2 per sample [2]

APPLICABILITY: The working range is 0.05 to 5 ppm (0.5 to 50 mg/m³) for a 15-L air sample. The method is applicable to 15-min ceiling measurements.

INTERFERENCES: Particulate iodide salts, HI, or organic iodides may give positive interferences, but collection of these compounds on treated charcoal has not been investigated. Iodate, other halogens, nitrate, phosphate, and sulfate do not interfere.

OTHER METHODS: Better sensitivity (ppb range) has been found using amperometric detection (AS1 column [3] or AG2 and AS2 columns [4]). An AS5 column using 6 mM Na_2CO_3/0.8 mM paracyanophenol in 2% acetonitrile as eluent and either conductometric or amperometric detection yielded the best sensitivity [3].

REAGENTS:

1. Deionized, filtered water with specific conductance ≤10 µS/cm.
2. Sodium carbonate (Na_2CO_3), reagent grade.
3. Potassium iodide (KI), reagent grade.
4. Iodine (I_2), reagent grade.*
5. Toluene, distilled in glass.
6. Eluent: 10 mM Na_2CO_3. Dissolve 4.240 g Na_2CO_3 in 4 L filtered, deionized water.
7. Calibration stock solution, 1000 µg I^-/mL. Dissolve 0.1308 g KI in filtered, deionized water to make 100 mL solution.
8. DE stock solution, 50 µg/µL. Dissolve 500 mg I_2 in toluene to make 10 mL solution.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends and plastic caps, containing two sections of 20/40 mesh alkali-treated charcoal (Barnebey-Cheney Type 580-19) (front = 100 mg; back = 50 mg) separated by 2-mm urethane foam plug. A glass wool plug and metal retaining spring precede the front section and a 3-mm foam plug follows the back section. Pressure drop <2.1 kPa across the tube at 1.2 L/min airflow. Tubes are commercially available (SKC No. 226-67, SKC, Inc., Eighty-Four, PA, or equivalent).
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Ion chromatograph (IC), anion separator and guard columns, anion suppressors (page 6005-1), conductivity detector, integrator (optional) and strip chart recorder.
4. File, triangular.
5. Ultrasonic bath.
6. Vials, 20-mL, glass, with PTFE-lined screw caps.
7. Syringes, 3-mL, polyethylene with luer tip.
8. Filters, luer tip, with PTFE filter, 13-mm diameter, 5-µm pore size.
9. Volumetric flasks, 10-, 50-, and 100-mL.
10. Bottles, polyethylene, 100-mL.
11. Pipets, 0.05- to 3-mL.
12. Syringe, 5-µL, readable to 0.1 µL.

SPECIAL PRECAUTIONS: Iodine is a severe irritant to the eyes and respiratory system and, to a lesser extent, the skin [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.0 L/min for a total sample size of 15 to 225 L.
4. Cap samplers. Pack securely for shipment.
   NOTE: Refrigerate samples if stored longer than 7 days.

SAMPLE PREPARATION:

5. Allow refrigerated samples to equilibrate at room temperature.
6. Score sampler with a file in front of primary sorbent section. Break sampler at score line.
7. Transfer front sorbent section with glass wool plug to vial.
8. Place back sorbent section with foam plugs in separate vial.
9. Add 3.0 mL eluent to each vial. Cap immediately.
10. Agitate vials in ultrasonic bath for 2 min at room temperature.

11. Draw sample extract through 13-mm PTFE filter attached to 3-mL syringe.
    NOTE: All samples, eluents and water flowing through the IC must be filtered to avoid plugging the system valves or columns.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least five working standards.
    a. Add known aliquots of calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to prepare solutions containing 1 to 60 µg I^-/mL (equivalent to 1.2 to 72 µg I_2/mL). Store in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
    b. Analyze working standards with samples and blanks (steps 15 through 17).
    c. Prepare calibration graph [peak height (mm or µS) vs. mg].
13. Determine desorption efficiency (DE) for each lot of charcoal used for sampling in the calibration range. Prepare at least three tubes at each of five levels.
    a. Place treated charcoal from unused front sorbent section in vial. Discard glass wool and backup section.
    b. Inject a known amount (2 to 5 µL) of DE stock solution, or a serial dilution thereof, onto charcoal with microliter syringe.
    c. Cap the vial. Allow to stand overnight.
    d. Desorb (steps 9 through 11) and analyze together with standards (steps 15 through 17).
    e. Prepare a graph of DE vs. mg I_2 recovered.
14. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

15. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 6005-1.
16. Inject sample aliquot. For manual operation, inject 1 to 2 mL of sample to ensure complete rinse of sample loop, or use autosampler.
17. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply appropriate dilution factor in calculations.

CALCULATIONS:

18. Determine 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.
19. Calculate concentration, C, of iodine in the air volume sampled, V (L):

$$C = \frac{1.2 \cdot (W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3$$

where: 1.2 = the stoichiometric factor arising from conversion of iodine to iodide on the sampler ($3I_2 + 6OH^- \rightarrow 3H_2O + 5I^- + IO_3^-$).

EVALUATION OF METHOD:

This method was optimized and evaluated by Southern Research Institute [2] and is based on a method developed by Kim et al. [6]. The method was evaluated over the range 0.74 to 2.11 mg/m³ iodine in 15-L air samples with a pooled sampling and measurement precision, s_r, of 0.062. The capacity of the 100-mg charcoal front section was at least 6 mg of iodine vapor. The total variance, including pump error, was 0.085. Overall average recovery based on

18 samples, six at each of three levels, was 90.8%. When corrected for desorption efficiency (0.962 in the range 0.0088 to 0.03 mg I_2 per sample), the recovery was 94.3%, representing an insignificant bias. Samples stored at ambient temperature for eight days were stable with recovery of 101.6% and a precision, s_r, of 0.103 based on samples analyzed on day one.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978), available as PB81-227001 from NTIS, Springfield, VA 22161.

[2] Dillon, H. K., M. L. Bryant and W. K. Fowler. Methods Development for Sampling and Analysis of Chlorine, Chlorine Dioxide, Bromine and Iodine: Research Report for Iodine, Contract 210-80-0067, Southern Research Institute, Birmingham, AL, (1983), available as PB83-246595 from NTIS, Springfield, VA 22161 .

[3] The Determination of Iodide by Ion Chromatography, Application Note 37, Dionex Corporation, Sunnyvale, CA (February, 1982).

[4] Han, K., W. F. Koch and K. W. Pratt. Improved Procedure for the Determination of Iodide by Ion Chromatography with Electrochemical Detection, Anal. Chem. 59, 731-736(1987).

[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.

[6] Kim, W. S., J. D. McGlothlin and R. E. Kupel. Sampling and Analysis of Iodine in the Industrial Atmosphere, Am. Ind. Hyg. Assoc. J., 43, 187-190 (1981).

METHOD REVISED BY: Mary Ellen Cassinelli, NIOSH/DPSE.

FORMULA: CH_3Cl

M.W.: 50.49

METHYL CHLORIDE

METHOD: 1001

ISSUED: 8/15/87

OSHA: 100 ppm; C 200 ppm; P 300 ppm
NIOSH: suspect carcinogen and teratogen [1]
ACGIH: 50 ppm; STEL 100 ppm
(1 ppm = 2.06 mg/m³ @ NTP)

PROPERTIES: gas; vapor density 1.8 (air = 1); BP -24.2 °C; MP -97.7 °C; VP 575 kPa (4300 mm Hg) @ 25 °C; explosive range 7.6 to 19% v/v air [2]

SYNONYMS: chloromethane; CAS #74-87-3.

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(two coconut shell charcoal tubes in series, 400 mg/200 mg and 100 mg/50 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 0.4 L @ 100 ppm
-MAX: 3 L

SHIPMENT: refrigerated

SAMPLE STABILITY: 95% recovery after 7 days @ 25 °C [3]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 110 to 460 mg/m³ (1.5-L air samples); 300 to 1200 mg/m³ (0.5-L air samples) [3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.052 [3]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl chloride

DESORPTION: 3 mL CH_2Cl_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 260 °C
-COLUMN: 100 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.2 m x 6 mm OD, packed with 80/100 mesh Chromosorb 102

CALIBRATION: standard solutions of methyl chloride in CH_2Cl_2

RANGE: 0.1 to 1 mg per sample

ESTIMATED LOD: 0.01 mg per sample [4]

PRECISION (s_r): 0.017 @ 0.16 to 0.62 mg per sample [3]

APPLICABILITY: The working range is 31 to 320 ppm (66 to 670 mg/m³) for a 1.5-L air sample. The method is applicable to 5-min peak determinations.

INTERFERENCES: None reported. An alternate GC column is fused silica capillary, 30 m x 0.315 mm, coated with 0.25 µm Durawax DX-4 at 45 °C [4].

OTHER METHODS: This combines and revises Methods S99 [5] and P&CAM 201 [6].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality, methyl chloride-free.*
2. Methyl chloride, 99.5%.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two glass tubes (9 cm long, 8 mm OD, 6 mm ID, followed by 7 cm long, 6 mm OD, 4 mm ID) connected in series with a short piece of tubing, flame-sealed ends and plastic end caps. Each tube contains two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front tube = 400 mg + 200 mg; back tube = 100 mg + 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes each front section and a 3-mm urethane foam plug follows each back section. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., "Blue Ice") and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1001-1).
5. Bottles, glass, 15-mL, with PTFE-lined septum crimp caps.
6. Syringes, gas-tight, 10-µL, and a 0.1- to 1-mL.
7. Pipet, TD, 3-mL.
8. DE apparatus. Glass tubing, through which nitrogen flows at ca. 30 mL/min, with T-connection and septum.

SPECIAL PRECAUTIONS: Methyl chloride has poor warning properties and is a narcotic and a suspect carcinogen and teratogen [1,2]. Methylene chloride is a suspect carcinogen [7].

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, with the smaller tube nearer the sampling pump.
3. Sample at an accurately known flow rate between 0.01 and 0.1 L/min for a total sample size of 0.4 to 3 L (e.g., at 0.1 L/min for 5 min for peak measurement and 0.01 L/min for 50 to 300 min for TWA measurement).
4. Separate and cap the tubes. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Pipet 3.0 mL CH_2Cl_2 into several bottles.
6. Place, in order, the back and front sorbent sections of the front sampler tube into a bottle, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 hrs.
7. Place, in order, the back and front sorbent sections of the back sampler tube into another bottle, discarding the glass wool and foam plugs. Immediately cap and gently shake the bottle. Analyze within 6 hrs.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Pipet 3.0 mL CH_2Cl_2 into each of a series of bottles. Cap the bottles.
   b. Using a gas-tight syringe, add known amounts of methyl chloride (0.005 to 0.5 mL; 0.01 to 1 mg at NTP) by bubbling the gas slowly through the CH_2Cl_2. Gently shake the bottles.
   c. Analyze with samples and blanks (steps 10 and 11).
   d. Prepare calibration graph (peak area vs. mg methyl chloride).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Using a gas-tight syringe, slowly inject a known amount of methyl chloride (0.005 to 0.5 mL) through the septum of the DE apparatus into a stream of nitrogen which carries the analyte into a large (400 mg/200 mg) sorbent tube. Allow the nitrogen to flow an additional 1 min.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 10 and 11).
   d. Prepare a graph of DE vs. mg methyl chloride recovered.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1001-1. 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 an aliquot of the desorbed liquid with CH_2Cl_2, reanalyze and apply the appropriate dilution factor in calculations.
11. Measure peak area.
    NOTE: Methyl chloride elutes before CH_2Cl_2 under these conditions.

CALCULATIONS:

12. Determine the mass, mg (corrected for DE) of methyl chloride 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.
13. Calculate concentration, C, of methyl chloride in the air volume sample, V (L):

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

EVALUATION OF METHOD:

Method S99 was issued on March 18, 1977 [5], and validated with generated atmospheres monitored by total hydrocarbon analyzer [3, 8]. Average recovery was 105% with $s_r = 0.05$ for eighteen 1.5-L samples in the range 110 to 460 mg/m³ and 101% with $s_r = 0.05$ for eighteen 0.5-L samples in the range 300 to 1200 mg/m³. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 135 min at 0.0235 L/min from an atmosphere containing 410 mg/m³ methyl chloride in air at 80% RH, and at 24.4 min when sampling at 0.105 L/min from an atmosphere containing 1425 mg/m³ at 84% RH. Desorption efficiency for 18 samples in the range 0.16 to 0.62 mg methyl chloride averaged 0.99 with $s_r = 0.02$. Desorption with carbon disulfide, chloroform, or ethanol as eluent gave lower recoveries. Samples stored in the laboratory for seven days gave a mean recovery of 95% relative to samples analyzed immediately after collection.

REFERENCES:
[1] NIOSH Current Intelligence Bulletin 43, Monohalomethanes, U.S. Department of Health and Human Services, Publ. (NIOSH) 84-117 (September 27, 1984).
[2] 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.
[3] Backup Data Report S99, available at "Ten NIOSH Analytical Methods, Set 2," Order No. PB 271-464, from NTIS, Springfield VA 22161.
[4] UBTL report for Sequence #4131-L,M (NIOSH, unpublished, November 28, 1983).
[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S99, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
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[7] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
[8] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: Y. T. Gagnon, K. J. Williams, and G. David Foley, NIOSH/DPSE.

FORMULA: $CH_3(C_2H_5)C\langle^{O-O}_{O-O}\rangle C(C_2H_5)CH_3$; $C_8H_{16}O_4$ — METHYL ETHYL KETONE PEROXIDE

METHOD: 3508

M.W.: 176.21 — ISSUED: 8/15/87

OSHA: no standard
NIOSH: no recommended standard
ACGIH: C 0.2 ppm
(1 ppm = 7.20 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.170 g/mL @ 20 °C;
flash point (open cup) 82 °C

SYNONYMS: 2-butanone peroxide; CAS #1338-23-4.

SAMPLING

SAMPLER: IMPINGER
(15 mL dimethyl phthalate)

FLOW RATE: 0.5 to 2 L/min

VOL-MIN: 52 L
-MAX: 520 L

SHIPMENT: transfer to silanized, foil-wrapped vials; ship in dry ice

SAMPLE STABILITY: 90% recovery after 21 days @ -4 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied for generated samples

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: diphenylcarbazide oxidation product

SAMPLE WORKUP: note liquid volume; remove 5 mL aliquot; add 5 mL diphenylcarbazide color reagent; heat at 85 ±5 °C for 15 min; cool in room temperature water bath exactly 5 min

ANALYSIS: color development; absorbance @ 565 nm

CALIBRATION: standard solutions of methyl ethyl ketone peroxide in dimethyl phthalate

RANGE: 75 to 750 µg per sample [1]

ESTIMATED LOD: 75 µg per sample [1]

PRECISION (s_r): 0.052 [3]

APPLICABILITY: The working range is 0.11 to 1.1 ppm (0.75 to 7.5 mg/m³) for a 100-L air sample [1]. This method has not been tested with aerosol generation or field samples. Special care must be taken in the conditioning of the glassware and in the storage of the samples.

INTERFERENCES: The diphenylcarbazide color reaction is relatively non-specific. Most ketones, except acetone, will exhibit positive interference at high levels. Other peroxides or any strong oxidant could also interfere with this procedure. Substances which catalyze the decomposition of peroxide may cause a significant decrease in the measurement; in particular, the presence of metal ions adsorbed on the glassware.

OTHER METHODS: This revises P&CAM 331 [1].

REAGENTS:

1. Acetic acid, glacial, reagent grade.
2. Dimethyl phthalate (DMP), reagent grade.
3. Water, distilled, deionized.
4. Toluene.
5. Methanol.
6. Isopropyl alcohol, reagent grade.
7. Sulfuric acid, conc.
8. Diphenylcarbazide (DPC) solution, 0.25% (w/v). Dissolve 0.25 g ± 0.01 g reagent grade DPC in DMP in an Al foil-covered, 100-mL volumetric flask. Agitate in ultrasonic bath to aid dissolution. Dilute to 100 mL.
   NOTE: This solution is light-sensitive. Prepare fresh immediately before using.
9. Color reagent. Mix 30 mL 0.25% DPC solution with 20 mL glacial acetic acid.
10. Methyl ethyl ketone peroxide (MEKP), 60%, technical grade, in dimethyl phthalate. Standardize as in APPENDIX.
11. Calibration stock solution.* Pipet ca. 10 µL of 60% MEKP into a 50-mL pre-weighed volumetric flask. Accurately weigh the flask plus MEKP; dilute to the mark with dimethyl phthalate. Wrap flask in Al foil. Prepare in duplicate.
12. Sodium thiosulfate solution, 0.1 N, standardized. Commercially available, or prepare as in APPENDIX.
13. Sodium iodide solution, 20% (w/v). Dissolve 20 g sodium iodide in 100 mL isopropyl alcohol.
14. Sodium bisulfite.
15. Nochromix.
16. Dichlorodimethylsilane, 5% (w/v), in toluene (Sylon CT, or equivalent).

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget impinger, 25-mL, silanized.*
2. Personal sampling pump, 0.5 to 2 L/min, with splashover protection (empty impinger placed between sampler and personal sampling pump) and flexible connecting tubing.
3. Vials, 20-mL, silanized, PTFE-lined screw caps.*
4. Aluminum foil.
5. Stopwatch.
6. Cold chest, insulated, dry-ice cooled.
7. Waterbath, 85 ± 5 °C.
8. Waterbath, 25 ± 5 °C.
9. Spectrophotometer, visible, 565 nm.
10. Cuvettes, matched glass, 1-cm pathlength.
11. Laboratory glassware, silanized:*
    a. pipets, TD, 10-µL; 1-, 5-, 10-, and 15-mL.
    b. volumetric flasks, 25-, 50-, and 100-mL; and 1-L, with glass stoppers.
    c. beakers, 150-mL and 1-L.
    d. burets, 50-mL.
    e. graduated cylinder, 50-mL;
    f. Erlenmeyer flasks or iodine flasks, 250-mL.
    g. test tubes, 18-mm x 150-mm, silanized, with glass stoppers and test tube rack.*
12. Ultrasonic bath.
13. Pipets, disposable, 2-mL.
14. Balance, readable to 0.1 mg.
15. Drying oven, 120 °C.
16. Stirrer, magnetic.

*It is extremely important to use glassware that has been thoroughly cleaned and silanized to remove heavy metal ions that catalyze peroxide decomposition.

For new glassware:

a. Wash in detergent, rinse with tap water, then deionized water.
b. Soak overnight in Nochromix solution (conc. sulfuric acid and a packet of Nochromix).
c. Rinse well with deionized water, dry in oven, then cool to room temperature.
d. Silanize by filling with 5% dichlorodimethyl-silane in toluene for 1 min. Rinse with toluene, then methanol, and dry.

After each use:

a. Rinse with methanol, wash in detergent, thoroughly rinse with tap water, then rinse four to five times with deionized water.
b. Rinse again with methanol. Dry overnight at 120 °C. Cool to room temperature.

SPECIAL PRECAUTIONS: MEKP is shock and heat sensitive. Store below 25 °C. MEKP solutions are extremely irritating and corrosive to the skin and eyes and may cause permanent eye injury. Use safety goggles. Dispose of waste MEKP solutions as follows:

a. Prepare 250 mL saturated aqueous sodium bisulfite in a 1-L beaker.
b. Store in a hood. Add all waste solutions containing MEKP to this beaker.
c. Allow to stand one week before disposing of the two-phase mixture.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Pipet 15 mL dimethyl phthalate into the impinger. Mark the level. Wrap with aluminum foil.
3. Sample at an accurately known flow rate between 0.5 and 2 L/min for a total sample size of 52 to 520 L.
4. Check liquid level in impinger and add dimethyl phthalate if necessary to bring level to 15.0 mL. Quantitatively transfer the contents of each impinger to a silanized, Al foil-wrapped vial and seal tightly. Quickly place in a cold chest.
5. Whenever possible, hand-deliver the samples packed in dry ice. Otherwise, ship samples in container with dry ice. Mark "FRAGILE" on the container.
6. Upon receipt in the laboratory, store vials in the freezer. Complete analysis as soon as possible.

SAMPLE PREPARATION:

7. Adjust sample volume to 15.0 mL if necessary. Transfer in duplicate exactly 5.0 mL (1/3) of each sample or field blank to silanized test tubes.
8. Pipet 5.0 mL color reagent into the test tubes. Stopper and invert several times to mix.
9. Loosen the stoppers and heat the test tubes in a waterbath at 85 ± 5 °C for 15 min.
10. Cool in a waterbath at 25 ± 5 °C for exactly 5 min.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least four working standards in duplicate.
    a. Pipet, e.g., 1.0, 2.0, 5.0, and 10.0 mL calibration stock solution to 25-mL silanized volumetric flasks, fitted with glass stoppers. Dilute to the mark with DMP. These working standards contain ca. 5, 10, 25, and 50 µg MEKP/mL (25, 50, 125, and 250 µg MEKP per 5-mL aliquot).
    b. Process the working standards together with samples, field blanks, media blanks, and reagent blanks (steps 7 through 10 and 12 and 13) during the same time period using the same batch of reagents.
    c. Prepare calibration graph (absorbance vs. µg MEKP). Extrapolate to zero concentration (y-intercept). Any sample whose absorbance is less than twice the "blank" should be reported as less than that level (about 25 µg MEKP per 5-mL aliquot). Perform a volumetric dilution to extend the range upward.

MEASUREMENT:

12. Set spectrophotometer according to manufacturer's instructions. Set zero with dimethyl phthalate vs. air.
13. Read sample absorbance at 565 nm vs. air when a stable value is obtained.
    NOTE: See SPECIAL PRECAUTIONS for procedure for disposal of waste MEKP solutions.

CALCULATIONS:

14. Determine the mass, µg, of MEKP in the 5-mL aliquot of sample, W, and the average media blank, B, from the calibration graph.
15. Calculate the concentration, C, of MEKP in the air volume sampled, V (L):

$$C = \frac{3 \cdot (W - B)}{V}, \text{ mg/m}^3.$$

NOTE: Correct for the average media blank, B, only if it exceeds twice the reagent blank (y-intercept).

EVALUATION OF METHOD:

This method is based on P&CAM 331 which was issued on August 29, 1980 [1] and was studied using technical grade MEKP containing 58.7% MEKP [2].

A two-level factorial experiment was run to study the effect of three different parameters on the color produced in the reaction between MEKP and DPC. A reaction bath temperature of 85 °C and reaction time of 15 min were determined to be optimum. Samples containing 204 µg MEKP per 5 mL stored in the freezer for 21 days showed 10% loss of MEKP. MEKP standard solutions were tested for interference with acetone, methyl ethyl ketone, cyclohexanone, and 3-methyl-2-butanone. All these ketones, except acetone, exhibited positive interference. Stability of MEKP solutions was tested using various substances which chould be likely co-contaminants. At freezer temperatures, samples containing styrene were stable for a week.

After 4 hrs at 1 L/min airflow through impingers containing MEKP standards in DMP, less than 10% of the MEKP carried over from the front to the backup bubbler.

The RSD of slopes of the calibration line determined from three levels close to 100, 170 and 210 µg/10 mL sample obtained over a six-month period was 9.8%. When the standards and samples were run on the same day, the RSD was 5.2%.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 6, P&CAM 331, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-125 (1980).
[2] Okenfuss, J. R. and J. C. Posner. Investigation of an Air Sampling and Analytical Method for Methyl Ethyl Ketone Peroxide, available as Order No. PB 81-167868 from NTIS, Springfield, VA 22161 (1980).

METHOD WRITTEN BY: Julie R. Okenfuss and Judd C. Posner, Ph.D., NIOSH/DPSE.

APPENDIX:

1. STANDARDIZATION OF 60% MEKP STOCK SOLUTION
   a. Weigh out to nearest mg 1 g 60% MEKP in a 100-mL volumetric flask. Dilute to the mark with isopropyl alcohol and cover flask with foil.
   b. Place ca. 25 mL isopropyl alcohol in a 250-mL iodine flask. Add 5 mL glacial acetic acid then add 10 mL 20% sodium iodide solution to the flask.
   c. Pipet exactly 10.0 mL MEKP-isopropyl alcohol solution (from step 1.a above) into the flask, cover and let stand in the dark for 15 min.
   d. Add 10 mL distilled water to the flask immediately before titrating.

e. Titrate with 0.1 N sodium thiosulfate from a yellow to colorless end point. Record the volume in mL used. Titrate a blank containing all reagents except MEKP in exactly the same way.

f. Calculate the weight % MEKP:

$$C_S = \frac{(V_S - V_b)4.405}{W}$$

where: C_S = percent MEKP as the cyclic dimer
V_S = volume of 0.1 N $Na_2S_2O_3$ used to titrate the sample (mL)
V_b = volume of 0.1 N $Na_2S_2O_3$ used to titrate the blank (mL)
W = weight of commercial MEKP used (g)
4.405 = constant containing the milliequivalent weight of MEKP (as the cyclic dimer) and various dilution factors.

2. STANDARDIZATION OF SODIUM THIOSULFATE, 0.1 N (or use commercially available standard)

a. Prepare the following solutions:

(1) Potassium dichromate, 0.1000 N. Dissolve 4.904 g anhydrous $K_2Cr_2O_7$, primary standard grade, in distilled water; dilute to 1 L.

(2) Starch indicator. Prepare a thin paste of 1 g soluble starch in a few mL distilled water. Bring 200 mL distilled water to a boil, remove from heat and stir in the starch paste. Prepare fresh before use.

(3) Sodium thiosulfate solution. Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ in freshly boiled, cooled distilled water; dilute to 1 L. Add 5 mL $CHCl_3$ as preservative. Age 2 weeks before standardizing.

b. Place 80 mL distilled, deionized water in 150-mL beaker, stirred with magnetic stirrer. Add 1 mL conc. H_2SO_4, 10.0 mL 0.1000 N $K_2Cr_2O_7$ and ca. 1 g KI. Allow to stand in dark for 6 min. Titrate with sodium thiosulfate solution. Upon approaching end point (brown changing to yellowish green), add 1 mL starch indicator solution and continue titrating to the end point (blue to light green). Calculate the normality, N, of the sodium thiosulfate solution:

$$N = \frac{1}{\text{mL } Na_2S_2O_3 \text{ used}}$$

FORMULA: CH_2Cl_2

M.W.: 84.94

METHYLENE CHLORIDE

METHOD: 1005
ISSUED: 2/15/84
REVISION #1: 8/15/87

OSHA: 500 ppm; C 1000 ppm; P 2000 ppm
NIOSH: lowest feasible; potential carcinogen [1]
ACGIH: 50 ppm; suspect carcinogen
(1 ppm = 3.47 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.323 g/mL @ 20 °C;
BP 40 °C; MP -95 °C;
VP 47 kPa (349 mm Hg; 46% v/v) @ 20 °C;
not flammable

SYNONYMS: dichloromethane; CAS #75-09-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 coconut shell charcoal tubes, 100 mg and 50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2.5 L

SHIPMENT: separate front and backup tubes

SAMPLE STABILITY: not determined

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 1700 to 7097 mg/m³ (1-L samples) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.073 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methylene chloride

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 to 225 °C
-DETECTOR: 250 °C
-COLUMN: 60 to 90 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: 3 m x 3 mm stainless steel, 10% SP-1000 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of CH_2Cl_2 in CS_2 with internal standard

RANGE: 0.3 to 10 mg per sample [3]

ESTIMATED LOD: 0.01 mg per sample [4,5]

PRECISION (s_r): 0.026 @ 1.3 to 5.3 mg per sample [2]

APPLICABILITY: The working range is 100 to 3000 ppm (350 to 10,400 mg/m³) for a 1-L air sample. The method is applicable to ceiling determinations.

INTERFERENCES: None identified. The method was validated using a 6 m x 3 mm stainless steel column packed with 10% FFAP on 100/120 mesh Supelcoport. Alternate chromatographic columns are 10% TCEP on 80/100 Chromosorb PAW, SP-2100, SP-2100 with 0.1% Carbowax 1500, or DB-1 fused silica capillary column.

OTHER METHODS: This revises Methods S329 [3], 1005 (dated 2/15/84), P&CAM 127 [4], and the criteria document method [6]. OSHA Method 59 uses larger (350-mg) sorbent sections and has been evaluated for 10-L air samples at 1 ppm methylene chloride [7].

REAGENTS:

1. Eluent: carbon disulfide*, chromatographic quality, containing 0.1% v/v decane, benzene or other suitable internal standard.
2. Methylene chloride.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: separate front and backup glass tubes with plastic caps, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg). A silylated glass wool plug is placed at each end of each tube. Pressure drop across the tubes at 1 L/min airflow must be less than 3.4 kPa.
   Note: Two commercially-available tubes, each containing 150 mg charcoal in two beds, may be used.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1005-1).
4. Vials, 2-mL, PTFE-lined septum crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Connect the two sorbent tubes with a short piece of flexible tubing. 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 of 0.5 to 2.5 L.
4. Separate the front and backup tubes and cap each tube to prevent migration of methylene chloride between tubes. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections (i.e., front and backup tubes) of the sampler 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.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 10 mg methylene chloride per sample.
   a. Add known amounts of methylene chloride to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg methylene chloride).
9. Determine desorption efficiency (DE) at least once for each lot 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 methylene chloride 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 methylene chloride 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 1005-1. 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.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of methylene chloride 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 methylene chloride 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:

Method S329 [3] was issued on June 6, 1975, and validated over the range 1700 to 7100 mg/m³ at 25 °C and 763 mm Hg using a 1-L sample [2]. Overall precision, s_r, was 0.073 with average recovery 95.3%, representing a non-significant bias. The concentration of methylene chloride was independently verified by calibrated syringe pump. Desorption efficiency was 0.97 in the range 1.3 mg to 5.3 mg methylene chloride per sample. Breakthrough (5% on back section) occurred at 18.5 min when sampling an atmosphere containing 6726 mg/m³ methylene chloride at 0.187 L/min at 0% RH.

REFERENCES:

[1] NIOSH Current Intelligence Bulletin 46. Methylene Chloride. U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (April 18, 1986).
[2] Documentation of the NIOSH Validation Tests, NIOSH, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S329, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[4] 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).
[5] User check, UBTL, NIOSH Sequence #3990-R (unpublished, November 3, 1983).
[6] Criteria for a Recommended Standard...Occupational Exposure to Methylene Chloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-138 (1976).

[7] OSHA Analytical Methods Manual (1985), available from ACGIH, 6500 Glenway Ave., Cincinnati, OH 45211.

METHOD REVISED BY: G. David Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; S329 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: C_nH_{2n+2} where $n \geq 16$

M.W.: not pertinent

MINERAL OIL MIST

METHOD: 5026
ISSUED: 8/15/87

OSHA: 5 mg/m³
NIOSH: no recommended standard [1]
ACGIH: 5 mg/m³ (as sampled by a method which does not collect vapor) [2]

PROPERTIES: liquid; d 0.8 to 0.9 g/mL @ 20 °C; BP 360 °C; vapor pressure negligible

SYNONYMS: airborne mist of white mineral oil or the following water-insoluble petroleum-based cutting oils: cable oil; cutting oil; drawing oil; engine oil; heat-treating oils; hydraulic oils; machine oil; transformer oil.

SAMPLING

SAMPLER: MEMBRANE FILTER (37-mm diameter, 0.8- or 5μ m-pore size, PVC or MCE, or glass fiber)

FLOW RATE: 1 to 2 L/min

VOL-MIN: 20 L @ 5 mg/m³
-MAX: 500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

BULK SAMPLE: required for quantitative data

ACCURACY

RANGE STUDIED: 2.5 to 11.7 mg/m³ [3] (100-L samples)

BIAS: not significant [3,4]

OVERALL PRECISION (s_r): 0.065 [3]

MEASUREMENT

TECHNIQUE: INFRARED SPECTROPHOTOMETRY

ANALYTE: mineral oil

EXTRACTION: 10 mL $C_2Cl_3F_3$

IR SCAN: 3200 to 2700 cm^{-1} vs. blank $C_2Cl_3F_3$

CALIBRATION: standard solutions of mineral oil in $C_2Cl_3F_3$

RANGE: 0.1 to 2.5 mg per sample

ESTIMATED LOD: 0.05 mg per sample [4]

PRECISION (s_r): 0.05 [4]

APPLICABILITY: The working range is 1 to 20 mg/m³ for a 100-L air sample. This method is applicable to all trichlorotrifluoroethane-soluble mineral oil mists, but not to (nor does OSHA's standard cover) semi-synthetic or synthetic cutting fluids.

INTERFERENCES: Any aerosol (e.g., tobacco smoke) which absorbs infrared radiation near 2950 cm-1 interferes.

OTHER METHODS: This revises P&CAM 283 [5]. P&CAM 159 [6] and S272 [7] use similar samplers with measurement by fluorescence spectrophotometry. These methods have not been revised because of limited applicability (i.e., not all mineral oils contain fluorescent components and other fluorescent compounds interfere). Infrared analysis overcomes both of these limitations.

REAGENTS:

1. Trichlorotrifluoroethane ($C_2Cl_3F_3$).
2. Stock mineral oil standard, 20 mg/mL. Weigh 1.0 g of the bulk mineral oil sample into a 50-mL volumetric flask. Dilute to volume with $C_2Cl_3F_3$. Prepare in duplicate.

   *See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: membrane filter, PVC or MCE, 37-mm, 0.8- or 5-µm pore size or glass fiber filter, 37-mm; two-piece filter cassette.
   NOTE 1: High concentrations of oil mist may plug membrane filters. Glass fiber filters have a higher capacity for oil mist than membrane filters.
   NOTE 2: Handle filters carefully with tweezers to avoid contamination by skin oil.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Infrared spectrophotometer, double beam, dispersive, with scanning capability in the 3200-2700 cm^{-1} region, and two 10-mm spectrophotometer cells, infrared quartz with PTFE stoppers mounted in demountable cell holders.
   NOTE: Standard glass cells may be used if infrared quartz cells are not available.
4. Vials, scintillation, 20-mL, with foil-lined or PTFE-lined caps.*
5. Volumetric flasks, 10-, 25-, and 50-mL.*
6. Volumetric pipet or reagent dispenser, 10-mL.*
7. Pipets, 2- to 250-µL.
8. Tweezers.

   *Rinse glassware with $C_2Cl_3F_3$. Air dry.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 2 L/min for a total sample size of 20 to 500 L.
   NOTE: High concentrations of oil mist may plug membrane filters creating unacceptably high pressure drops. If this occurs, terminate sampling.
3. Collect 5 to 10 mL of unused, undiluted mineral oil in a vial. Submit with samples for standard preparation.

SAMPLE PREPARATION:

4. Using tweezers, transfer each sample or blank filter to a vial. Add 10.0 mL $C_2Cl_3F_3$. Cap and shake vigorously.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least five working standards.
   a. Add known amounts of stock mineral oil standard to $C_2Cl_3F_3$ in 10-mL volumetric flasks and dilute to the mark to obtain mineral oil concentrations in the range 0.005 to 0.25 mg/mL.
   b. Analyze with samples and blanks (step 8).
   c. Prepare calibration graph (peak absorbance vs. mg mineral oil).

6. Determine recovery (R) at least once for each lot of filters used for sampling in the range of interest. Prepare three filters at each of five levels plus three media blanks.
   a. Deposit a known amount of stock mineral oil standard onto the filter. Allow solvent to evaporate.
   b. Store samples overnight in filter cassettes.
   c. Prepare and analyze with working standards.
   d. Prepare a graph of R vs. mg mineral oil recovered.
7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

8. Scan each standard solution and each blank or sample filter extract from 3200 to 2700 cm^{-1} in absorbance mode vs. $C_2Cl_3F_3$ in reference beam. Record absorbance at wavelength of largest absorbance near 2940 cm^{-1}.

CALCULATIONS:

9. Determine the mass, mg (corrected for R), of mineral oil found in the sample (W) and in the average media blank (B) from the calibration graph.
10. Calculate concentration, C, of mineral oil in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, \ mg/m^3.$$

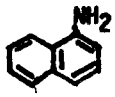
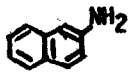
EVALUATION OF METHOD:

The sampling portion of this method was evaluated over the range 2.5 to 11.7 mg/m^3 at 22°C and 755 mm Hg using 100-L air samples of Gulf machine cutting oil with measurement by fluorescence spectrophotometry. Mixed cellulose ester filters, 0.8-µm pore size, were used for sampling [3,7]. The overall precision was 0.065 with an average recovery of 98%. The infrared measurement method was subsequently evaluated by NIOSH [4,5]. Precision and accuracy of the infrared and fluorescence spectrophotometric techniques are similar.

REFERENCES:

[1] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[2] Documentation of the Threshold Limit Values, 4th ed., ACGIH, 314 (1980).
[3] Documentation of the NIOSH Validation Tests, S272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as PB 274-248 from NTIS, Springfield, VA 22161.
[4] Bolyard, M. L. Infrared Quantitation of Mineral Oil Mist in Personal Air Samples, AIH Conference, Houston, TX (1980).
[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 283, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[6] Ibid., Vol. 1, P&CAM 159, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] Ibid., Vol. 3, S272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD WRITTEN BY: Michele Bolyard, NIOSH/DPSE.

FORMULA: (1):  (2): 

$C_{10}H_9N$

M.W.: 143.19

NAPHTHYLAMINES
METHOD: 5518
ISSUED: 8/15/87

OSHA: (2): carcinogen
NIOSH: no recommended standard
ACGIH: (1): no standard;
(2): recognized human carcinogen
(1 ppm = 5.85 mg/m³)

PROPERTIES: (1): solid; MP 92 to 94 °C;
VP 0.53 Pa (0.004 mm Hg;
31 mg/m³) @ 20 °C
(2): solid; MP 111 to 113 °C;
VP 0.48 Pa (0.0036 mm Hg; 27 mg/m³)
@ 20 °C

SYNONYMS: (1): 1-naphthylamine; alpha-naphthylamine; CAS #134-32-7.
(2): 2-naphthylamine; beta-naphthylamine; CAS #91-59-8.

SAMPLING

SAMPLER: FILTER + SOLID SORBENT
(glass fiber + silica gel,
100 mg/50 mg)

FLOW RATE: 0.2 to 0.8 L/min

VOL-MIN: 30 L @ 5 µg/m³
-MAX: 100 L

SHIPMENT: dry ice

SAMPLE STABILITY: 24 to 73% recovered after 8 days @ 23 °C [1]; 82 to 100% after 22 days @ -15 °C [1]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 4 to 90 µg/m³ [1]
(50-L samples)

BIAS: not determined [1]

OVERALL PRECISION (s_r): ≤0.10 [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1- and 2-naphthylamines

DESORPTION: 0.5 mL 0.05% (v/v) acetic acid in 2-propanol

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 190 °C
-DETECTOR: 165 °C
-COLUMN: 163 °C

CARRIER GAS: He, 24 mL/min

COLUMN: glass, 1.8 m x 2 mm ID, packed with 3% OV-225 on Chromosorb WHP

CALIBRATION: standard solutions of analytes in 0.05% (v/v) acetic acid in 2-propanol

RANGE: 0.15 to 3.5 µg per sample

ESTIMATED LOD: 0.01 µg per sample [2]

PRECISION (s_r): 0.08 @ 0.3 µg per sample [2]

APPLICABILITY: The working range is 0.003 to 0.07 mg/m³ (0.0005 to 0.01 ppm) for a 50-L air sample.

INTERFERENCES: The retention time of 1-nitronaphthalene is between those of the analytes and interferes with their determination. Column alternative: 10% Carbowax, 20 M, 4% KOH.

OTHER METHODS: This revises P&CAM 264 [2].

REAGENTS:

1. 1-Naphthylamine and 2-naphthylamine.*
2. 2-Propanol.
3. Acetic acid, glacial.
4. Eluent, 0.05% (v/v) acetic acid in 2-propanol.
5. Calibration stock solution, 500 µg/mL.* Weigh 5 mg of each analyte into a 10-mL volumetric flask. Dilute to volume with eluent. Prepare in duplicate. Stable one month if refrigerated.
6. Hydrogen, purified.
7. Helium, purified.
8. Air, compressed, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler (Fig. 1): high-efficiency glass fiber filter (Gelman Spectrograde or equivalent), 13-mm diameter, followed by 100 mg and 50 mg beds of 20/45 mesh silica gel (Coast Engineering Labs, Gardena, CA, grade 407).
   NOTE: Some other glass fiber filters contained an impurity with the same GC retention time as α-naphthylamine [1].
2. Personal sampling pump, 0.2 to 0.8 L/min, with flexible connecting tubing.
3. Insulated container, with dry ice.
4. Gas chromatograph, FID and column (page 5518-1).
5. Test tubes, 1-mL, with polyethylene stoppers.
6. Syringes, glass, 5- and 10-µL, readable to 0.1 µL.
7. Pipet, TD, 0.5-mL.
8. Volumetric flasks, low actinic, 10-mL.
9. Centrifuge.
10. Balance, analytical.
11. Test tube shaker, vortex type.

SPECIAL PRECAUTIONS: 2-Naphthylamine is a recognized human bladder carcinogen [3]. Avoid all contact with it. Use a glove box for preparation of standard solutions. Dispose of all unneeded solutions in accordance with accepted procedures for carcinogens.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 0.8 L/min for a total sample size of 30 to 100 L.
4. Cap the samplers. Pack securely for shipment in dry ice.

SAMPLE PREPARATION:

5. Bring samples to room temperature.
6. Place glass fiber filter and 100-mg section of silica gel in a test tube. Place the 50-mg section of silica gel in a separate test tube. Desorb PTFE rings and stainless steel screens with the appropriate stages. Discard sampler caps.
7. Add 0.5 mL eluent to each vial. Cap each test tube and mix with test tube shaker.
8. Allow to stand 60 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain analyte concentrations in the range 0.02 to 7 µg/mL.
   b. Analyze with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph (peak area vs. µg analyte).

10. Determine desorption efficiency (DE) at least once for each lot of filters and sorbent used for sampling in the range of interest. Prepare three samplers at each of five levels plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject separate known amounts (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, directly onto filter and front sorbent section with a microliter syringe.
    c. Cap the sampler. Allow to stand overnight.
    d. Desorb (steps 6 through 8) and analyze with working standards (steps 12 and 13).
    e. Prepare graphs for filter and sorbent (DE vs. µg analytes recovered).
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graphs and DE graphs are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5518-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: For the conditions given, t_r = 6 min for 1-naphthylamine and 7 min for 2-naphthylamine.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze and apply the appropriate dilution factor in calculations.
13. Measure peak area.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE) of analyte found on the sample filter (W_f) and sample sorbent (W_s) and on the media blank filter (B_f) and media blank silica gel (B_s) from the calibration graph.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

P&CAM 264 was issued on August 1, 1978 [2], and evaluated with generated atmospheres containing mixtures of the two analytes produced by controlled vapor diffusion [1]. Capacity of the 100-mg front sorbent section at breakthrough (effluent = 5% of test concentration) was approximately 5 µg 1-naphthylamine and 7.5 µg 2-naphthylamine at 80% RH with a sampling range of 0.8 L/min in atmospheres containing approximately 80 µg/m³ of the analytes. Breakthrough capacity was found to be strongly influenced by relative humidity, being reduced by 50% at 95% RH compared to the values found at 80% RH.

In storage tests, quantitative recovery was obtained for 0.5-µg masses of 1-naphthylamine on silica gel and filters if stored at -15 °C for up to seven days; recovery for samples stored 14 or 21 days at -15 °C was 81 to 82% for filters and 94% for silica gel. For 2-napthylamine under the same conditions, similar recoveries were observed, except that recovery from filters was quantitative at -15 °C when stored 14 or 21 days.

REFERENCES:
[1] Morales, R., S. M. Rappaport, R. W. Weeks, Jr., E. E. Campbell, and H. J. Ettinger, Development of Sampling and Analytical Methods for Carcinogens, Los Alamos Scientific Laboratory, Progress Report LA-7058-PR (January 1, 1976 to September 30, 1976), NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 264, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-185 (1978).
[3] Documentation of the Threshold Limit Values, 5th ed., ACGIH, Cincinnati, OH 45211 (1986).

METHOD REVISED BY: G. David Foley, NIOSH/DPSE.

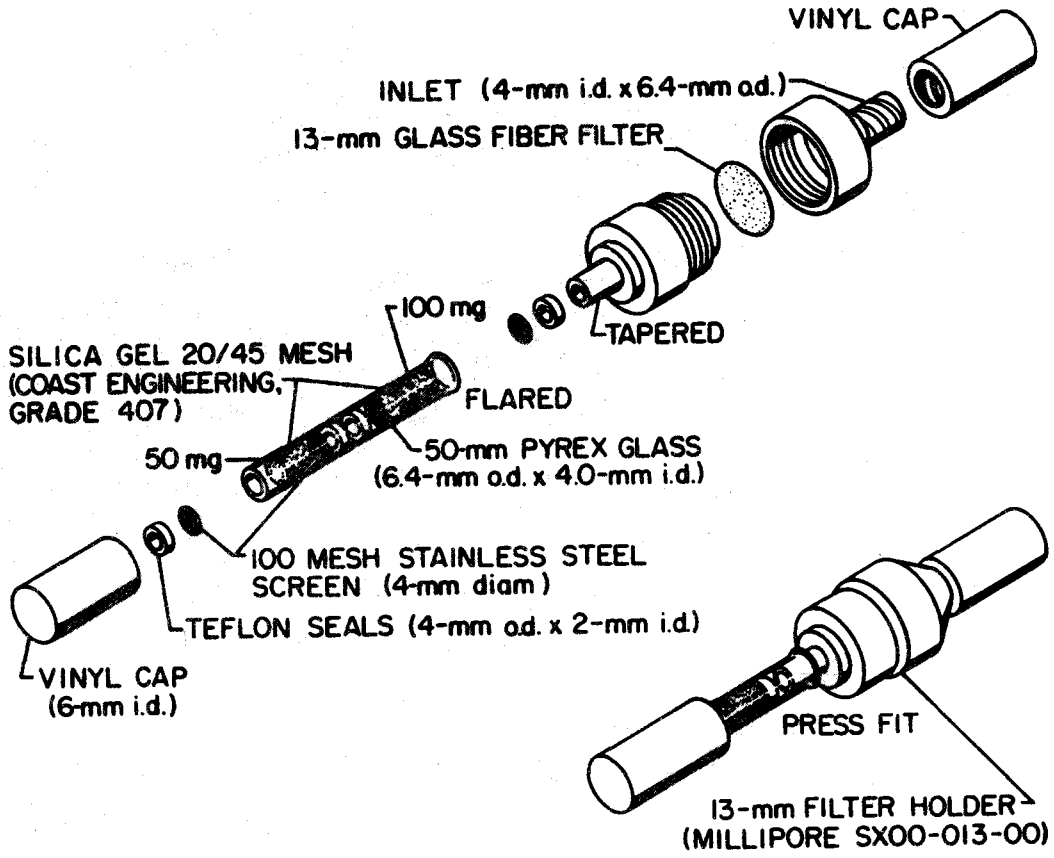


Figure 1. Sampler.

FORMULA: $Ni(CO)_4$

M.W.: 170.75

NICKEL CARBONYL

METHOD: 6007
ISSUED: 8/15/87

OSHA: 0.001 ppm
NIOSH: 0.001 ppm; carcinogen [1,2]
ACGIH: 0.05 ppm
(1 ppm = 6.98 mg/m³ @ NTP)

PROPERTIES [2]: liquid; d 1.318 g/mL @ 20 °C; BP 43 °C; MP -25 °C; VP 43 kPa (321 mm Hg; 42% v/v) @ 20 °C; lower explosive limit 2% (v/v) in air

SYNONYMS: CAS #13463-39-3.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(low-Ni charcoal, 120 mg/60 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 7 L @ 0.001 ppm
-MAX: 80 L

SHIPMENT: routine

SAMPLE STABILITY: 95% recovered after 17 days @ room temperature [3]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.0007 to 0.017 ppm [3]
(3- to 40-L air samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.099 [3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: nickel

DESORPTION: 1 mL 3% HNO_3; 30 min ultrasonic bath

INJECTION VOLUME: 20 µL

GRAPHITE FURNACE: 110 °C dry 30 sec;
800 °C char 15 sec;
≥2700 °C atomize 10 sec

WAVELENGTH: 232 nm, with background correction

CALIBRATION: standard solutions of Ni^{2+} in 3% (w/v) HNO_3

RANGE: 0.05 to 0.6 µg Ni per sample [3]

ESTIMATED LOD: 0.01 µg Ni per sample [3]

PRECISION (s_r): 0.028 @ 0.08 to 0.5 µg Ni per sample

APPLICABILITY: The working range is 0.0004 to 0.007 ppm (0.0025 to 0.05 mg/m³) nickel carbonyl for a 20-L air sample.

INTERFERENCES: Particulate nickel compounds will give a positive interference unless a prefilter is used during sampling.

OTHER METHODS: This revises P&CAM 344 [4]. A colorimetric method has also been recommended [1].

REAGENTS:

1. Water, double-distilled (or deionized).
2. Nitric acid, 70% (w/v) HNO_3, redistilled in glass.
3. Nitric acid, 3% (w/v) HNO_3. Add 31 mL 70% HNO_3 to distilled water. Dilute to 1 L.
4. Nickel stock solution, 1000 µg Ni/mL. Dissolve 1.000 pure Ni metal in minimum volume 70% HNO_3. Dilute to 1 L with 3% HNO_3. Commercially available.
5. Calibration stock solution, 50 µg Ni/mL. Dilute 0.500 mL nickel stock solution (1000 µg/mL) to 10 mL in a volumetric flask with 3% HNO_3. Store in a polyethylene bottle. Prepare fresh weekly.
6. Argon, high-purity purge gas in cylinder with a two-stage regulator.
   NOTE: Nitrogen cannot be used as purge gas because of the formation of UV-absorbing cyanogen.
7. Charcoal, acid-washed, activated. Acid-wash a sufficient quantity of coconut-based charcoal having an initial blank value of less than 0.02 µg Ni/200 mg, by soaking overnight in 3% nitric acid. Rinse several times with distilled water. Pour off excess water, cover with a watchglass, and activate by heating at 600 °C for 1.5 hrs in still air.

EQUIPMENT:

1. Sampler:
   a. Prefilter: 37-mm, 0.8-µm cellulose ester filter and cellulose backup pad in a plastic filter holder.
   b. Glass tube, 8 cm long, 6 mm OD, 4 mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh acid-washed activated (600 °C) coconut shell charcoal (front = 120 mg; back = 60 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.
   NOTE: The prefilter must be used when particulate nickel is present in the air to be sampled. Connect prefilter to sorbent tube with a short section of plastic tubing.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. File, triangular.
4. Atomic absorption spectrophotometer equippped with:
   a. Heated graphite atomizing rod, tube or furnace (either non-pyrolitic or pyrolitic; better sensitivity with pyrolitic).
   NOTE: Reproducible control of times and temperatures during dry, char, and atomize cycles is essential; minimum atomization temperature 2700 °C.
   b. Readout device (recorder or digital peak height or peak area analyzer).
   c. Pipetting system (automatic or manual, 5- to 50-µL, as appropriate to atomizer size).
   d. Background correction, e.g., D_2 or H_2 lamp or non-absorbing line (231.5 nm for the 232 nm Ni line).
   e. Hollow cathode lamp for nickel.
5. Vials, 2-mL, with plastic-lined screw caps.*
6. Pipet, TD, 1-mL.*
7. Ultrasonic water bath.
8. Volumetric flasks, 10-mL and 1-L.*
9. Bottles, polyethylene, 20-mL.
10. Syringe, 25-µL, readable to 0.1 µL.

*Soak new glassware 1 hr in hot, conc. nitric acid followed by thorough rinsing with distilled water. After each use, wash glassware with, in order, detergent solution, tap water, 3% nitric acid (soak ≥4 hrs) and distilled water.

SPECIAL PRECAUTIONS: None.

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 0.05 and 0.2 L/min for a total sample size of 7 to 80 L.
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 3% HNO_3 to each vial. Cap each vial.
7. Allow to stand 30 min in an ultrasonic water bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to 3% HNO_3 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain Ni^{2+} concentrations in the range 0.01 to 0.6 µg/mL. Store in polyethylene bottles and prepare fresh daily.
   b. Analyze with samples and blanks (steps 11 through 13).
   c. Prepare calibration graph (absorbance vs. µg Ni^{2+}).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, 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 with working standards (steps 11 through 13).
   e. Prepare a graph of DE vs. µg Ni^{2+} recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations, conditions given on page 6007-1, and the following:
    a. Inert gas flow: increased sensitivity if flow is interrupted during atomization.
    b. Wavelength: either 232 nm (more sensitive) or 341.5 nm.
    c. Dry cycle: 30 sec at 110 °C; longer time and ramp program may be needed for aliquots >20 µL.
    d. Ash (char) cycle: 15 sec at 800 °C.
    e. Atomize cycle: 10 sec at 2700 to 3000 °C; atomization is too slow for reproducible results below 2600 °C; "maximum power" feature will increase sensitivity.
12. Inject sample aliquot manually or with autosampler.

13. Measure peak height. Analyze a series of standards before and after each set of samples and analyze one mid-range standard after each ten samples. Analyze all solutions, including sorbent tube blanks and reagent blanks, in triplicate.
    NOTE 1: Peak occurs about 3 sec after start of atomize cycle.
    NOTE 2: If peak height is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with 3% HNO_3, reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE) of Ni 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 nickel carbonyl in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 2.91}{V}, \text{ mg/m}^3.$$

where: 2.91 = stoichiometric conversion factor from Ni to $Ni(CO)_4$.

EVALUATION OF METHOD:

Method P&CAM 344 was issued on August 31, 1981 [4], and evaluated with generated atmospheres of $Ni(CO)_4$ containing 6 to 300 ppm added carbon monoxide. Mean recovery was 93% (24 samples) in the range 5 to 121 µg/m³ (0.0007 to 0.017 ppm). Breakthrough (effluent = 5% of test concentration) did not occur after sampling for 240 min at 0.475 L/min from an atmosphere containing 34 µg/m³ (0.005 ppm) $Ni(CO)_4$ in air at 22 °C and 19% RH. Desorption efficiency for eighteen samples containing 0.08 to 0.5 µg Ni (nickel nitrate standard solution added to 120 mg charcoal) averaged 0.934 with $s_r = 0.029$. Nickel carbonyl was observed to pass quantitatively through 0.8-µm cellulose ester membrane filters in these experiments.

REFERENCES:

[1] Special Occupational Hazard Review and Control Recommendations for Nickel Carbonyl, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-184 (1977).
[2] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[3] Eller, P. M. "Determination of Nickel Carbonyl by Charcoal Tube Collection and Furnace Atomic Absorption," Appl. Ind. Hyg. 1:115-118 (1986).
[4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 344, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

METHOD WRITTEN BY: Peter M. Eller, Ph.D., NIOSH/DPSE.

FORMULA: $CH_3CH_2NO_2$; $C_2H_5NO_2$

M.W.: 75.07

NITROETHANE

METHOD: 2526
ISSUED: 8/15/87

OSHA: 100 ppm
NIOSH: no recommended standard [1]
ACGIH: 100 ppm
(1 ppm = 3.07 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.051 g/mL @ 20 °C;
BP 114 °C; MP -89.5 °C;
VP 2.8 kPa (21 mm Hg; 2.7% v/v) @ 25 °C;
lower explosive limit 3.4% (v/v) in air

SYNONYMS: CAS #79-24-3.

SAMPLING

SAMPLER: SOLID SORBENT TUBES
(XAD-2, 600 mg + 300 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1.5 L @ 100 ppm
-MAX: 3 L [2]

SHIPMENT: separate front and back sorbent tubes

SAMPLE STABILITY: stable 7 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 147 to 604 mg/m³
(3-L samples) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME IONIZATION DETECTOR

ANALYTE: nitroethane

DESORPTION: 2 mL ethyl acetate; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 160 °C
-DETECTOR: 200 °C
-COLUMN: 120 °C

CARRIER GAS: He or N_2, 30 mL/min

COLUMN: stainless steel, 6-m x 4-mm ID, packed with 10% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: standard solutions of nitroethane in ethyl acetate

RANGE: 0.5 to 2 mg per sample [2]

ESTIMATED LOD: not determined

PRECISION (s_r): 0.02 @ 0.47 to 1.9 mg per sample [2]

APPLICABILITY: The working range is 80 to 320 ppm (250 to 1000 mg/m³) for a 2-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S219 [3].

REAGENTS:

1. Eluent: Ethyl acetate, containing (optionally) 0.1% v/v 1-hexanol or other suitable internal standard.
2. Nitroethane, chromatographic quality.*
3. Methanol.
4. Methylene chloride.*
5. Calibration stock solution, 0.21 mg/µL. Add 2.1 g (2.0 mL) nitroethane to a 10-mL volumetric flask. Dilute to the mark with ethyl acetate.
6. Helium or nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two separate glass tubes, each 10 cm long, 10-mm OD, 8-mm ID, and packed with 20/50 mesh pre-extracted XAD-2 (front = 600 mg; back = 300 mg) (see APPENDIX). Connect the tubes with flexible tubing. The sorbent beds are held in place with plugs of silanized glass wool; the tubes are flame-sealed at both ends; with plastic caps.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Soxhlet extraction apparatus.
4. Gas chromatograph, FID, integrator and column (page 2526-1).
5. Vials, glass, 5-mL, PTFE-lined crimp caps.
6. Syringes, 2- to 20-µL, readable to 0.1 µL.
7. Volumetric flask, 10-mL.
8. Pipets, delivery-type, 1- and 2-mL; calibrated-type, 5-mL, readable to 0.01 mL.
9. File.

SPECIAL PRECAUTIONS: Contact with amines, strong acids, and alkalies may sensitize nitroethane so that it will readily explode [1]. Methylene chloride is a suspect carcinogen.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler tubes immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1.5 to 3 L.
   NOTE: High pressure drop across the sampler may occur at flow rates above 0.05 L/min, giving inaccurate sample volumes.
4. Immediately following sampling, separate and cap the two glass tubes. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool plugs.
6. Pipet 2.0 mL eluent into each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to eluent in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain nitroethane concentrations in the range 0.03 to 1 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of nitroethane to peak area of internal standard vs. mg nitroethane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
   a. Inject a known amount (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, directly onto front sorbent section (600 mg sorbent) with a microliter syringe.
   b. Cap the tube. Allow to stand overnight.
   c. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   d. Prepare a graph of DE vs. mg nitroethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2526-1. 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 an aliquot of the desorbed liquid with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of nitroethane by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of nitroethane 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 nitroethane 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:

Method S219 was issued on January 20, 1978 [3]. Synthetic atmospheres of the analyte in humidified air were generated dynamically at 22 °C and 777 torr over the range 143 to 614 mg/m³ by calibrated syringe pump delivery of the neat analyte into a humidified dilution airstream [2,4]. The concentrations were monitored by total hydrocarbon analyzer. A 600-mg bed of sorbent retained 2.8 mg analyte before 5% breakthrough occurred at 5 L when a challenge atmosphere of 585 mg/m³ analyte in humid air was sampled at 0.05 L/min. There were no statistically significant differences in the recoveries of 3-L samples collected from synthetic atmospheres containing 314 mg/m³ nitroethane in humid air and stored for one or seven days at ambient temperatures prior to analysis. It was found necessary to separate the front and back sorbent sections immediately after sampling due to analyte migration during storage. Desorption efficiency averaged 0.88 in the range 0.47 to 1.9 mg per sample. A previous study found nitroethane to be unstable on activated charcoal [5].

REFERENCES:
[1] 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.
[2] Backup Data Report for Nitroethane, NIOSH Contract #210-76-0123 (unpublished).
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, S219, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).
[5] Failure report, S219, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1976).

METHOD REVISED BY: Robert Glaser, NIOSH/DPSE; S219 originally validated under NIOSH Contract No. 210-76-0123.

APPENDIX: PREPARATION OF SAMPLER TUBES

1. Place up to 500g XAD-2 in a Soxhlet extractor.
2. Extract 24 hours each with water, methanol, and methylene chloride, in that order (2 mL solvent/g XAD-2).
3. After the last extraction, remove any remaining liquid solvent by filtration through a sintered filter fitted to a vacuum flask.
4. Place several grams of extracted sorbent into a wide-bore open glass tube (15 cm long x 10 mm ID) which is connected at one end to the injector port and at the other to the detector port of a gas chromatograph via Swagelok fittings and copper tubing (e.g., 6.4-mm OD or other convenient sizes). Retain the extracted sorbent bed in the wide-bore tube with silanized glass wool plugs at both ends of the bed.
5. Remove the solvent residue by purging the extracted sorbent with nitrogen for 2 hrs at 120 °C. Transfer the dried sorbent to a clean, dry, glass (not plastic) container.
6. Allow the extracted sorbent to cool in a clean dessicator.
7. Desorb 600 mg extracted sorbent with 2 mL ethyl acetate. Analyze this sample by gas chromatography for the presence of background interferences. If interfering peaks are observed in the chromatogram, Soxhlet-extract with ethyl acetate. Dry (steps 4 and 5 above), and reanalyze to assure the removal of the interferences.
8. Wash the glass sampling tubes with acetone to prevent the extracted sorbent from adhering to the walls. Allow the tubes to air dry.
9. Pack the sampler tubes, using silanized glass wool plugs to retain the extracted sorbent beds.

   NOTE 1: The pressure drop across the packed sampler must be less than 1.3 kPa (10 mm Hg) at 0.05 L/min.

   NOTE 2: Avoid excessive agitation of the extracted sorbent while handling. A static charge can be induced in the material which is not readily dissipated; the individual particles will agglomerate, making the tubes difficult to pack.

FORMULA: CH_3NO_2

M.W.: 61.04

NITROMETHANE

METHOD: 2527
ISSUED: 8/15/87

OSHA: 100 ppm
NIOSH: no recommended standard [1]
ACGIH: 100 ppm
(1 ppm = 2.50 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.138 g/mL @ 20 °C;
BP 101.2 °C; MP -29 °C;
VP 4.9 kPa (37 mm Hg; 4.8% v/v) @ 25 °C;
lower explosive limit 7.3% (v/v) in air

SYNONYMS: nitrocarbol, CAS #75-52-5.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Chromosorb 106, 600 mg/300 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1.2 L @ 100 ppm
-MAX: 3 L [2]

SHIPMENT: separate front and back sorbent sections

SAMPLE STABILITY: stable 7 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 123 to 501 mg/m³
(3-L samples) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.078 [2]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY,
! NITROGEN-SPECIFIC DETECTOR
!
!ANALYTE: nitromethane
!
!DESORPTION: 5 mL ethyl acetate; stand 30 min
!
!INJECTION VOLUME: 5.0 µL
!
!TEMPERATURE-INJECTOR: 225 °C
! -DETECTOR: 300 °C
! -COLUMN: 100 °C
!
!CARRIER GAS: He or N_2, 20 mL/min
!
!COLUMN: stainless steel, 2 m x 4 mm ID, packed
! with 10% SP 1000 on 80/100 mesh
! Chromosorb WHP
!
!CALIBRATION: standard solutions of nitromethane
! in ethyl acetate
!
!RANGE: 0.3 to 2 mg per sample [2]
!
!ESTIMATED LOD: not determined
!
!PRECISION (s_r): 0.042 @ 0.34 to 1.34 mg per
! sample [2]
!

APPLICABILITY: The working range is 60 to 360 ppm (150 to 900 mg/m³) for a 2-L air sample.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S220 [3].

REAGENTS:

1. Nitromethane, chromatographic quality.*
2. Ethyl acetate, chromatographic quality.
3. Acetone, chromatographic quality.
4. Calibration stock solution, 0.1138 mg/µL. Add 1.138 g (1.00 mL) nitromethane to a 10-mL volumetric flask Dilute to the mark with ethyl acetate.
5. Helium or nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10.0-cm long, 10-mm OD, 8-mm ID; two sections of 60/80 mesh pre-extracted Chromosorb 106 (front = 600 mg; back = 300 mg) (see APPENDIX) separated by a plug of silanized glass wool and held in place with plugs of silanized glass wool, flame-sealed at both ends; with plastic caps.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, nitrogen-phosphorus or alkali flame ionization detector, integrator and column (page 2527-1).
4. Vials, glass, 5-mL, PTFE-lined septum, screw-caps.
5. Syringes, 1- to 25-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipets, delivery, 1- and 5-mL.
8. File.

SPECIAL PRECAUTIONS: Nitromethane vapor forms highly explosive mixtures with air. When highly confined and heated, it can detonate [1].

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 0.05 L/min for a total sample size of 1.2 to 3 L.
   NOTE: High pressure drop across the sampler may occur at flow rates above 0.05 L/min, giving inaccurate sample volumes.
4. Immediately following sampling, remove the silanized glass wool from the end of the sampler nearer the pump and empty the 300-mg back sorbent section into a clean vial. Seal the vial with a PTFE-lined cap. Cap the tubes containing the front section. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front sorbent section of the sampler tube in a separate vial from that containing the back sorbent section. Discard the glass wool plugs.
6. Pipet 5.0 mL ethyl acetate into each vial. Immediately cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to ethyl acetate in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain nitromethane concentrations in the range 0.01 to 0.4 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg nitromethane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of 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 with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg nitromethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2527-1. 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 an aliquot of the desorbed liquid with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of nitromethane 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 nitromethane 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:

Method S220 was issued January 19, 1979 [3]. Synthetic atmospheres of the analyte in humidified air were generated dynamically at 20 to 24 °C and 767 to 774 torr over the range from 123 to 514 mg/m³ by calibrated syringe pump injection of the analyte into a dilution airstream [2,4]. The concentrations were monitored by total hydrocarbon analyzer. A 600-mg bed of the sorbent retained 2.6 mg of the analyte before 5% breakthrough occurred at 5.0 L, when a challenge atmosphere of 518 mg/m³ of analyte in humid air was sampled at 0.05 L/min. There were no statistically significant differences in the recoveries of 3-L samples collected from synthetic atmospheres containing 236 mg/m³ nitromethane in humid air and stored for one or seven days at ambient temperatures prior to analysis. Desorption efficiency averaged 0.971 in the range 0.34 to 1.34 mg per sample. A previous study showed that samples of nitromethane collected on activated charcoal were unstable [5].

REFERENCES:

[1] 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.
[2] Backup Data Report for Nitromethane, prepared under NIOSH Contract 210-76-0123 (unpublished, 1979).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6., S220, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).
[5] Failure report, S220, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1976).

METHOD REVISED BY: Robert Glaser, NIOSH/DPSE; S220 originally validated under NIOSH Contract No. 210-76-0123.

APPENDIX: PREPARATION OF SAMPLER TUBES:

1. Place ca. 50 g of Chromosorb 106 in a Soxhlet thimble and extract with 250 to 500 mL acetone for 2 hrs.
2. Remove the liquid acetone via filtration through a sintered filter fitted to a vacuum flask.
3. Place several grams of extracted sorbent into a wide-bore open glass tube (15 cm long x 10 mm ID), which is connected at one end to the injector port and at the other to the detector port of a gas chromatograph via Swagelok fittings and copper tubing (e.g., 6.4 mm OD or other convenient sizes). Retain the extracted sorbent bed in the wide-bore tube with silanized glass wool plugs at both ends of the bed.
4. Remove the solvent residue by purging the extracted sorbent with nitrogen for 2 hrs at 120 °C. Transfer the dried sorbent to a clean, dry glass (not plastic) container. Allow the extracted sorbent to cool in a clean dessicator.
5. Wash the glass sampling tubes with acetone in order to prevent the extracted sorbent from adhering to the walls. Allow the tubes to air dry.
6. Pack the sampler tubes, using silanized glass wool plugs to retain the extracted sorbent beds.

   NOTE 1: The pressure drops across the sampling tubes must be less than 1.3 kPa (10 mm Hg) at 0.05 L/min airflow.

   NOTE 2: Avoid excessive agitation of the sorbent while handling. A static charge can be induced in the material which is not readily dissipated; the individual particles will agglomerate, making the tubes difficult to pack.

FORMULA: $(CH_3)_2CHNO_2$; $C_3H_7NO_2$

M.W.: 89.09

2-NITROPROPANE

METHOD: 2528

ISSUED: 8/15/87

OSHA: 25 ppm
NIOSH: suspect carcinogen [1];
Group I Pesticide [2]
ACGIH: 10 ppm; suspect carcinogen
(1 ppm = 3.64 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.9821 g/mL @ 25 °C;
BP 120 °C; MP -91 °C;
VP 2.4 kPa (18 mm Hg; 2.4% v/v) @ 25 °C
lower explosive limit 2.6% (v/v) in air

SYNONYMS: dimethylnitromethane; CAS #79-46-9.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Chromosorb 106, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 25 ppm
-MAX: 2 L [3]

SHIPMENT: routine

SAMPLE STABILITY: 100% recovered after 7 days @ 25 °C + 21 days @ 0 °C [3]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 3.1 to 28.3 mg/m³
(3-L samples) [3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.05 [3]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FLAME IONIZATION DETECTOR

ANALYTE: 2-nitropropane

DESORPTION: 1 mL ethyl acetate; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 190 °C
-COLUMN: 90 °C

CARRIER GAS: He or N_2, 20 mL/min

COLUMN: stainless steel, 6-m x 4-mm ID, packed with 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of 2-nitropropane in ethyl acetate

RANGE: 0.01 to 0.15 mg per sample [3]

ESTIMATED LOD: 0.001 mg per sample [3]

PRECISION (s_r): 0.03 @ 0.01 to 0.1 mg per sample [3]

APPLICABILITY: The working range is 1.4 to 27 ppm (5 to 100 mg/m³) for a 2-L air sample.

INTERFERENCES: The method has been evaluated in epoxy spray paint operations with no apparent interference from methyl butyl ketone, heptane, 1-nitropropane, toluene and xylene [4].

OTHER METHODS: This revises P&CAM 272 [5].

REAGENTS:

1. 2-Nitropropane, chromatographic quality.*
2. Ethyl acetate, chromatographic quality.
3. Acetone, chromatographic quality.
4. Calibration stock solution, 9.82 mg/mL. Add 98.2 mg (100 µL) 2-nitropropane to a 10-mL volumetric flask. Dilute to the mark with ethyl acetate. Prepare in duplicate.
5. Helium or nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7.0-cm long, 6.0-mm OD, 4-mm ID; two sections of 60/80 mesh pre-extracted Chromosorb 106 (front = 100 mg; back = 50 mg) (see APPENDIX) separated by a 2-mm section of urethane foam and held in place with plugs of silanized glass wool, flame-sealed at both ends; with plastic caps.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2528-1).
4. Vials, glass, 2-mL, PTFE-lined septum crimp caps.
5. Syringes, 1- to 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, delivery, 1.0-mL.
8. File.

SPECIAL PRECAUTIONS: 2-Nitropropane is a suspected human carcinogen [1]. Perform all work with this chemical in a 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 0.05 L/min for a total sample size of 0.1 to 2 L.
   NOTE: High pressure drop across the sampler may occur at flow rates >0.05 L/min, giving inaccurate sample volumes.
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. Pipet 1.0 mL ethyl acetate into each vial. Cap each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to ethyl acetate in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain 2-nitropropane concentrations in the range 0.001 to 0.15 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg 2-nitropropane).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, 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 with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg 2-nitropropane recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2528-1. 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 an aliquot of the desorbed liquid with ethyl acetate, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.
NOTE: Retention time of 2-nitropropane is ca. 20 min under these conditions.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of 2-nitropropane 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 2-nitropropane 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:

Method P&CAM 272 was issued on August 1, 1978. Synthetic atmospheres of the analyte in humidified air were generated dynamically at 25 °C and 745 torr over the range 3.1 to 28.3 mg/m³ by the vapor pressure saturation/air dilution technique [3]. The concentrations were verified by total hydrocarbon analyzer. A 100-mg bed of sorbent retained 374 µg of analyte before 5% breakthrough occurred at 10.4 L when a challenge atmosphere of 36 mg/m³ analyte in humid air was sampled at 0.2 L/min. There were no statistically significant differences in the recoveries of 3-L samples collected from synthetic atmospheres containing 4.7 mg/m³ 2-nitropropane in humid air and stored for 1, 7, 14 or 28 days prior to analysis. The 14- and 28-day samples were stored at 0 °C after an initial seven-day storage at ambient temperature. A previous study showed 2-nitropropane to be unstable after collection on activated petroleum-based charcoal [6].

REFERENCES:

[1] NIOSH Current Intelligence Bulletin 17, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-127 (1978).
[2] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978), available as PB81-227001 from NTIS, Springfield, VA 22161.
[3] Glaser, R. and W. J. Woodfin. A Method for Sampling and Analysis of 2-Nitropropane in Air, Am. Ind. Hyg. Assoc. J., 42: 18-22 (1981).
[4] NIOSH Health Hazard Evaluation Report HHE-80-57-781 (1980).

[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 272, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[6] Failure report, S222, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1976).

METHOD WRITTEN BY: Robert Glaser, NIOSH/DPSE.

APPENDIX:

Preparation of Sampler Tubes:

1. Place ca. 50 g of Chromosorb 106 in a Soxhlet thimble and extract with 250 to 500 mL acetone for 2 hrs.
   NOTE: This is sufficient for ca. 300 samplers. Smaller lots may be processed.
2. Remove the liquid acetone via filtration through a sintered filter fitted to a vacuum flask.
3. Place several grams of extracted sorbent into a wide-bore open glass tube (15 cm long x 10 mm ID), which is connected at one end to the injector port and at the other to the detector port of a gas chromatograph via Swagelok fittings and copper tubing (e.g., 6.4 mm OD or other convenient sizes). Retain the extracted sorbent bed in the wide-bore tube with silanized glass wool plugs at both ends of the bed.
4. Remove the solvent residue by purging the extracted sorbent with nitrogen for 2 hrs at 120 °C. Allow the extracted sorbent to cool in a clean glass container in a clean dessicator.
5. Wash the glass sampling tubes with acetone in order to prevent the extracted sorbent from adhering to the walls. Allow the tubes to air dry.
6. Pack the sampler tubes, using silanized glass wool plugs to retain the extracted sorbent beds.
   NOTE 1: The pressure drops across the sampling tubes must be less than 1.3 kPa (10 mm Hg) at 0.05 L/min airflow.
   NOTE 2: Avoid excessive agitation of the sorbent while handling. A static charge can be induced in the material which is not readily dissipated; the individual particles will agglomerate, making the tubes difficult to pack.
   NOTE 3: Store any unused sorbent in a glass (not plastic) container.

FORMULA: Table 1

M.W.: Table 1

ORGANOTIN COMPOUNDS (as Sn)
METHOD: 5504
ISSUED: 8/15/87

OSHA: 0.1 mg/m^3
NIOSH: 0.1 mg/m^3 [1,?]
ACGIH: 0.1 mg/m^3 (except tricyclohexyltin hydroxide, 5.0 mg/m^3)

PROPERTIES: Table 1

COMPOUNDS: tetrabutyltin (TeBT); tributyltin chloride (TBTC); tricyclohexyltin hydroxide (TCHH); dibutyltin bis(isooctyl mercaptoacetate) (BuIOMA).

SYNONYMS: Table 1.

SAMPLING

SAMPLER: FILTER + SORBENT
(glass fiber + XAD-2, 80 mg/40 mg)

FLOW RATE: 1 to 1.5 L/min

VOL-MIN: 50 L
-MAX: 500 L

SHIPMENT: ship assembled sampler in dry ice

SAMPLE STABILITY: stable 7 days @ 0 °C [3]

FIELD BLANKS: 10% of samples

MEDIA BLANKS: 12 per sample

ACCURACY

RANGE STUDIED: 0.07 to 0.2 mg/m^3 [3]
(300-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.07 to 0.10 [3]

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: tin

DESORPTION: 10 mL 0.1% acetic acid/CH_3CN; ultrasonic

SEPARATION: HPLC (cation exchange)

GRAPHITE FURNACE: dry 30 sec @ 80 °C; atomize 5 sec @ 2750 °C (gas interrupt mode)

INJECTION VOLUME: 20 µL

WAVELENGTH: 286.3 nm, with background correction

CALIBRATION: standard solutions of organotin compounds in acetic acid/CH_3CN

RANGE: 5 to 50 µg Sn per sample

ESTIMATED LOD: 1 µg Sn per sample [3]

PRECISION (s_r): 0.07 to 0.08 [3]

APPLICABILITY: The working range is 0.015 to 1 mg/m^3 (as Sn) for a 300-L air sample. The method was validated using TeBT, TBTC, TCHH, and BuIOMA as surrogates for the most important classes of organotin compounds [3]. If speciation of organotin compounds is not required and if inorganic tin compounds are absent, the HPLC separation may be deleted. Use special care to avoid losses of TeBT and other volatile tetra-substituted organotin compounds.

INTERFERENCES: Organotin compounds not separated chromatographically will mutually interfere. Other compounds with similar retention times will not interfere unless they contain tin.

OTHER METHODS: This replaces the colorimetric criteria document method [1].

REAGENTS:

1. Zirconium acetate oxide.
2. Ammonium acetate.
3. Diammonium citrate.
4. Acetonitrile.
5. Deionized water.
6. Acetic acid.
7. Methanol.
8. Acetic acid, 0.1% (v/v) in acetonitrile.
9. Acetate buffer solution (v/v) 70% methanol, 27% deionized water, 3% aqueous 1 M ammonium acetate.
10. Citrate buffer solution (v/v) 70% methanol, 26.8% deionized water, 3% aqueous 1 M diammonium citrate in 0.2% (v/v) glacial acetic acid.
11. Organotin standard solutions, 1000 µg/mL (as Sn), prepared from pure organotin compounds in 0.1% (v/v) acetic acid in acetonitrile.
12. Calibration stock solution, 10 µg/mL (as Sn). Prepare a standard mixture of the organotin compounds of interest. Pipet 0.1 mL of each organotin standard solution into a 10-mL volumetric flask. Dilute to the mark with 0.1% (v/v) acetic acid in acetonitrile. Prepare fresh daily.

EQUIPMENT:

1. Sampler: glass fiber filter, 37-mm (Gelman Type A/E or equivalent) in cassette filter holder followed by XAD-2 sorbent tube, 80 mg front section/40 mg back section (SKC, Inc., Eighty-Four, PA 15330, Cat. No. 226-30).
2. Personal sampling pump, 1 to 1.5 L/min, with flexible connecting tubing.
3. Shipping container, refrigerated, with dry ice.
4. High performance liquid chromatograph (HPLC), interfaced with autoinjection system (Fig. 1), with binary solvent capability, solvent gradient capability and columns:
   a. non-tetraorganotin species: cation exchange column (Whatman, Inc., Partisil-10 Strong Cation Exchange Column and Solvecon Pre-Column Kit).
   b. tetraorganotin compounds: Lichrosorb column, C_{18} (Whatman, Inc.).
5. Atomic absorption spectrophotometer (AAS) having recorder output proportional to absorbance units, graphite furnace accessory (pyrolytic with Zr coating, coated L'vov platform may be required; see APPENDIX), sample autoinjection system with moving sample tube rack or carrousel (Fig. 1), automatic micropipettor for accurately injecting 20-µL sample aliquots into graphite furnace, background correction (e.g., D_2 or H_2 lamp) capability, and tin electrodeless discharge lamp or hollow cathode lamp.
6. Bath, ultrasonic.
7. Volumetric flasks, 10-mL.
8. Syringe, 20-µL, readable to 0.5 µL.
9. Beakers, Phillips, 125-mL.
10. Pipets, 5- and 10-mL; 10- and 100-µL.
11. Oven or muffle furnace, 200 °C.
12. Plastic film.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sorbent tube immediately before sampling and connect to the filter with a short piece of tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 1.5 L/min for a total sample size of 50 to 500 L.
4. Cap the samplers. Pack securely for shipment in dry ice.
   NOTE: The cassette and sorbent tube should remain connected for storage. Store samples at less than 0 °C. Analyze within seven days after collection.

SAMPLE PREPARATION:

5. Open the cassette filter holder. With tweezers, carefully transfer the filter to a 125-mL beaker.
6. Place the front sorbent section and the glass wool plug into a second beaker. Place the back sorbent section into a third beaker.
7. Pipet 10.0 mL acetonitrile and 10 µL acetic acid into each beaker. Cover with plastic film.
8. Agitate beakers in ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to 0.1% (v/v) acetic acid in acetonitrile in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain concentrations of each organotin compound in the range 0.1 to 5 µg/mL (as Sn).
   b. Analyze with samples and blanks (steps 12 through 15), alternating samples and standards with similar responses.
   c. Prepare calibration graph (peak height vs. µg Sn) for each organotin compound.
10. Determine recovery (R) in the range of interest. Prepare three samplers at each of three levels 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 organotin standard solution directly onto front sorbent section and a separate aliquot onto the filter, with a microliter syringe.
    c. Cap the sampler. Allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze with working standards (steps 12 through 15).
    e. Prepare a graph of R vs. µg Sn recovered for each organotin compound.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graphs and recovery graphs are in control.

MEASUREMENT:

12. Set the AAS and graphite furnace according to manufacturer's recommendations and to conditions on page 5504-1. Adjust the sample injection/dry/atomize cycle so that it occurs exactly once every 60 sec.
13. Operate the HPLC according to manufacturer's recommendations and the following conditions:
    a. For non-tetraorganotin compounds:
       (1) Column: strong cation exchange (EQUIPMENT, 4.a).
       (2) Flush column with 50 to 60 mL acetate buffer prior to sample injection.
       (3) Eluent: flowrate = 2 mL/min
       (4) Eluent Gradient:

Time (min)	% Acetate Buffer	% Citrate Buffer
0 - 15	100	0
15 - 18	100 - 0	0 - 100
18 - 40	0	100

       (5) After the chromatogram is complete, re-equilibrate the HPLC system to initial conditions by pumping acetate buffer through the column for 15 min.
       (6) Inject 100-µL sample aliquot.

b. For tetraorganotin compounds:
   (1) Column: Lichrosorb.
   (2) Flush column with 50 to 60 mL of 100% acetonitrile prior to sample injection.
   (3) Eluent: flowrate = 2 mL/min, isocratic, 100% acetonitrile.
   (4) Inject a 100-µL aliquot of sample solution.

14. Collect HPLC eluent at the rate of 1 fraction (2 mL) per minute in AAS autosampler (Fig. 1).
    NOTE: In this example system, the column effluent is fed directly into one of the sample cups. After 1 min, the sample holder rotates and the eluted sample is in a position to be sampled for AA measurement. The furnace injection device withdraws a portion of the sample and places it in the furnace while the next sample is being eluted and collected.
15. Measure total AAS peak area for each organotin compound.
    NOTE 1: The recorder output will consist of AA peaks which form a chromatographic peak for each organotin compound if a line is drawn connecting the highest points of the AA peaks. Determine total absorbance for a species by the sum of the absorbances of the corresponding AA peaks.
    NOTE 2: The characteristics of the graphite tube can influence the results drastically. Pay careful attention to the response of the standards and replace the graphite tube if erratic results and non-reproducible peak areas occur.

CALCULATIONS:

16. Read the mass, µg Sn (corrected for R), for each organotin compound found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blanks (filter (B) and front sorbent (B_f) and back sorbent (B_b) sections) from the calibration graphs.
17. Calculate concentration, C (mg Sn/m³), for each organotin compound in air as the sum of the particulate concentration and the vapor concentration in the air volume sampled, V (L):

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

NOTE: W_f and W_b include analyte originally collected on the filter as particulate, then volatilized during sampling or storage.

EVALUATION OF METHOD:

The method was validated with tetrabutyltin (TeBT), tributyltin chloride (TBTC), tricyclohexyltin hydroxide (TCHH), and dibutyltin bis(isooctylmercaptoacetate) (BuIOMA) [3]. The working ranges, validation ranges, and estimated linear working ranges (as tin) for 300-L air samples of these organotin species at an atmospheric temperature and pressure of 20 °C and 756 mm Hg, respectively, appear below:

Species	Validation Range (mg/m³)	Estimated Linear Working Range (mg/m³)	Estimated Linear Working Range (µg/mL)	Measurement Precision (% s_r)	Overall Precision (% s_r)
TeBT	0.027–0.112	0.02–0.17	0.05–5.0	8.1	10.0
TBTC	0.042–0.191	0.01–0.34	0.3–10	5.9	9.9
TCHH	0.071–0.218	0.01–0.34	0.3–10	6.9	7.1
BuIOMA	0.070–0.220	0.01–0.34	0.3–10	7.7	7.4

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Organotin Compounds, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157 (1976).
[2] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Tin, Organic Compounds (as Tin), U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[3] Gutknecht, W. F., P. M. Grohse, C. A. Homzak, C. Tronzo, M. H. Ranade, and A. Damle. Development of a Method for the Sampling and Analysis of Organotin Compounds, NIOSH Contract 210-80-0066, Research Triangle Institute, Research Triangle Park, NC 27709, available through NTIS, Springfield, VA 22161, as PB83-180737 (May, 1982).

METHOD REVISED BY: Thomas P. Carsey, Ph.D., NIOSH/DPSE.

APPENDIX:

PREPARATION OF Zr-COATED GRAPHITE FURNACE TUBE AND PLATFORM

1. Zirconium coating: soak pyrolytic graphite tubes and platforms overnight in 4.5% (w/v) zirconium acetate oxide solution; then dry in a muffle furnace for 2 hrs at 200 °C.
2. Pyrolytic zirconium-coated graphite furnace tubes are acceptable for measurements of all organotin compounds. However, a pyrolytic zirconium-coated graphite platform (e.g., L'vov platform) is recommended for better precision at low levels and improved atomization response for volatile species such as TeBT. Platforms may be purchased commercially or prepared from pyrolytic graphite tubes, as shown in Fig. 2. Special care must be exercised during placement of the platform in the tube (Fig. 3) and in optical alignment.

Table 1. Formulae and physical properties [3].

Compound	Formula	M.W.	% Sn	Synonyms
Dibutyltin bis(isooctyl mercaptoacetate)	$C_{28}H_{56}O_4S_2Sn$	639.57	18.6	BuIOMA; CAS #25168-24-5
Tetrabutyltin	$C_{16}H_{36}Sn$	347.16	34.2	Stannane, tetrabutyl-; TeBT; CAS #1461-25-2
Tributyltin chloride	$C_{12}H_{27}ClSn$	325.49	36.5	Stannane, chlorotributyl-; TBTC; CAS #1461-22-9
Tricyclohexyltin hydroxide	$C_{18}H_{34}OSn$	385.16	30.8	Stannane, tricyclohexylhydroxy-; TCHH; Plictran; Dowco-213; CAS #13121-70-5

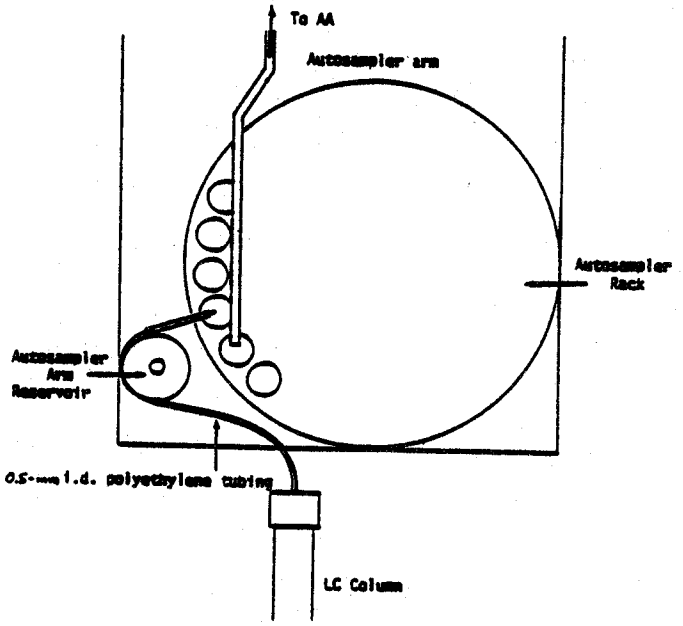


Figure 1. HPLC/AAS interface system.

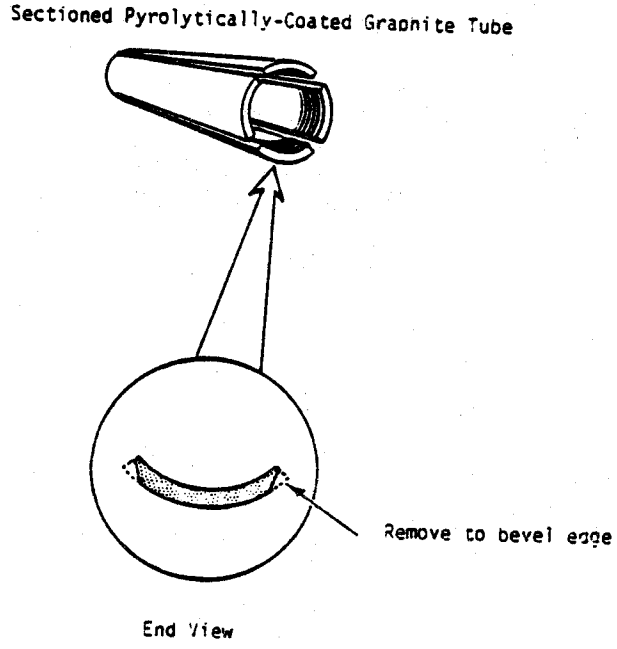


Figure 2. Construction of a laboratory-made platform.

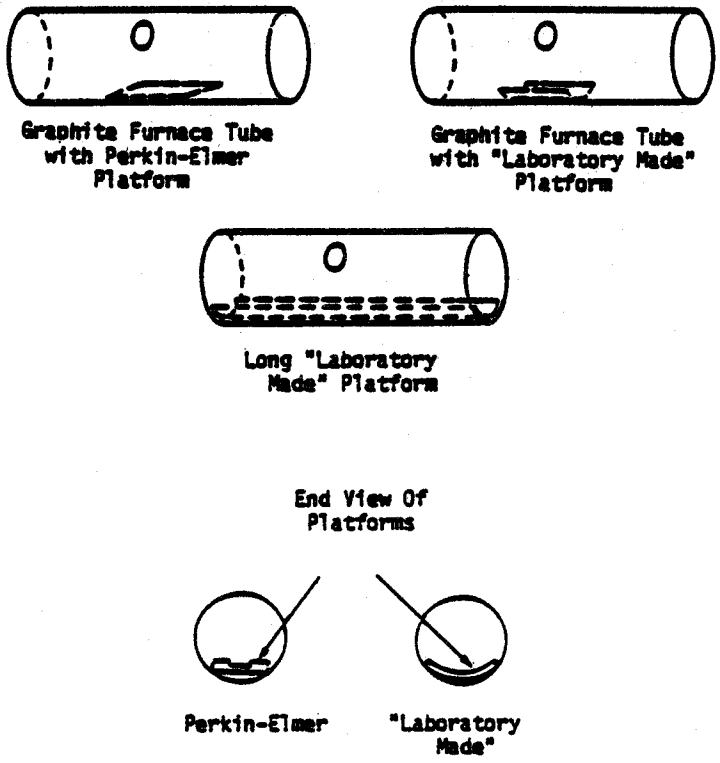


Figure 3. Placement of commercial and "laboratory-made" graphite L'vov platforms in furnace tubes.

FORMULA: P_4

M.W.: 123.90

PHOSPHORUS

METHOD: 7905
ISSUED: 8/15/87

OSHA: 0.1 mg/m³
NIOSH: no recommended standard [1];
Group I Pesticide [2]
ACGIH: 0.1 mg/m³
(1 ppm = 5.07 mg/m³ @ NTP)

PROPERTIES: solid; d 1.83 g/mL @ 20 °C;
MP 44 °C; BP 280 °C; sublimes;
VP 3.5 Pa (2.6×10^{-2} mm Hg;
172 mg/m³) @ 20 °C;
oxidizes spontaneously in air

SYNONYMS: white phosphorus; yellow phosphorus; CAS #7723-14-0.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Tenax GC, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 5 L @ 0.1 mg/m³
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 94% recovery after 7 days @ 25 °C [3]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.056 to 0.24 mg/m³ [3]
(12-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.090 [3]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, PHOSPHORUS FPD
!
!ANALYTE: phosphorus
!
!DESORPTION: 1 mL xylene; stand 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 200 °C
! -DETECTOR: 200 °C
! -COLUMN: 80 °C
!
!CARRIER GAS: He, 30 mL/min
!
!COLUMN: 1.8 m x 6 mm OD x 2 mm ID glass;
! 3% OV-101, 80/100 mesh Chromosorb WHP
!
!CALIBRATION: standard solutions of phosphorus
! in xylene
!
!RANGE: 0.5 to 5 µg per sample
!
!ESTIMATED LOD: 0.005 µg per sample [3]
!
!PRECISION (s_r): 0.024 @ 0.6 to 2.4 µg per
! sample [3]
!

APPLICABILITY: The working range is 0.04 to 0.8 mg/m³ (0.008 to 0.16 ppm) for a 12-L air sample. The method is applicable to vapor-phase phosphorus only. If particulate P_4 is expected in the air sample, use a filter in the sampling train.

INTERFERENCES: None identified.

OTHER METHODS: This combines and replaces S334 [4] and P&CAM 257 [5]. P&CAM 242, utilizing impinger sampler (xylene), has not been revised [6].

REAGENTS:

1. Phosphorus (white), purified, stored under distilled water.*
2. Xylene (mixed), reagent grade.
3. Acetone, purified.
4. Calibration stock solution, 0.20 mg/mL. Prepare under nitrogen or other inert gas. Dissolve a known mass (ca. 2 mg) of acetone-washed, dried white phosphorus in 10 mL xylene. Stir until dissolved. Prepare in duplicate.
5. Helium, prepurified.
6. Hydrogen, prepurified.
7. Air, compressed, filtered.
8. Nitrogen, purified.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: borosilicate glass tube, 7-cm long, 8-mm OD, 6-mm ID, flame-sealed ends with plastic caps, containing two sections of 35/60 mesh Tenax GC (front = 100 mg; back = 50 mg) separated and retained by 2-mm silylated glass wool plugs. Pressure drop across the sampler at 0.2 L/min airflow must be less than 3.3 kPa (25 mm Hg).
   NOTE: If the air sample is expected to contain particulate elemental phosphorus (P_4), precede the Texax tube with a 37-mm diameter, cellulose ester membrane filter.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame photometric detector (phosphorus mode), integrator and column (page 7905-1).
4. Vials, 20-mL, PTFE-lined septum caps.
5. Syringes, 5-, 10- and 25-µL, for making standards and GC injections.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.
8. Balance, analytical, readable to 0.01 mg.

SPECIAL PRECAUTIONS: White phosphorus may be fatal if ingested, even in small quantities [7]. Phosphorus vapor is toxic; work in a contained atmosphere with adequate care.

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 of 5 to 100 L.
4. Cap the samplers 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 plugs.
6. Pipet 1.0 mL xylene into each vial. Cap each vial.
   NOTE: Use 5.0 mL xylene for filters, if applicable.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution, or a serial dilution thereof, to xylene in 10-mL volumetric flasks and dilute to the mark to produce phosphorus concentrations in the range 0.01 to 5 µg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. µg phosphorus).

9. Determine desorption efficiency (DE) at least once for each batch of Tenax-GC used for sampling in the range of interest. 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 (2 to 20 µL) of 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 phosphorus recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 7905-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the range of the working standards, dilute with xylene, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of phosphorus 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 phosphorus in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S334 was issued on November 25, 1977 [4], and validated with generated atmospheres using a solution (11 mg/mL) of phosphorus in tetralin in a calibrated syringe drive, verified by independent collection in xylene [3]. Average recovery was 106% with s_r = 7.4% (18 samples) in the range 0.056 to 0.24 mg/m³ for 12-L samples. In an experiment in which 25-L samples of an atmosphere containing 0.35 mg/m³ phosphorus vapor were analyzed, the same phosphorus concentration was found in xylene-filled impingers with or without cellulose ester membrane prefilters. Breakthrough (effluent = 5% of test concentration) did not occur after sampling for 240 min at 0.2 L/min from an atmosphere containing 0.311 mg/m³ at 85% RH. Desorption efficiency for 18 samples in the range 0.6 to 2.4 µg per sample averaged 98% with s_r = 2.6%.

REFERENCES:

[1] 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.
[2] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978), available as PB81-227001 from NTIS, Springfield, VA 22161.
[3] Backup Data Report, S334, (November 25, 1977), available as "Ten NIOSH Analytical Methods, Set 5," order No. PB 287-499, from NTIS, Springfield, VA 22161.

[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S334, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[5] Ibid., Vol. 1, P&CAM 257, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[6] Ibid., P&CAM 242.
[7] Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).

METHOD REVISED BY: Gangadhar Choudhary, Ph.D., and Peter M. Eller, Ph.D., NIOSH/DPSE: S334 originally validated under NIOSH Contract CDC-210-75-0047.

	(1)	(2)	(3)	
FORMULA:	$C_6H_3Cl_3$	$C_6H_2Cl_4$	C_6HCl_5	POLYCHLOROBENZENES
				METHOD: 5517
M.W.: 181.45 (1); 215.89 (2); 250.34 (3)				ISSUED: 8/15/87

OSHA: no recommended standards
NIOSH: no recommended standards
ACGIH: C 40 mg/m³ [(1) only]

PROPERTIES: Table 1

SYNONYMS: (1) 1,2,4-trichlorobenzene, CAS #120-82-1;
(2) 1,2,4,5-tetrachlorobenzene, CAS #95-94-3;
(3) pentachlorobenzene, CAS #608-93-5.

SAMPLING

SAMPLER: FILTER AND SOLID SORBENT TUBE
(PTFE fiber mat + Amberlite XAD-2,
100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L
-MAX: 12 L

SHIPMENT: separate filter and sorbent tube

SAMPLE STABILITY: no significant losses after 13 d @ room temperature [1]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED [1]: (1) 0.002 to 100 mg/m³;
(2) 0.003 to 31 mg/m³;
(3) 0.008 to 22 mg/m³
(10-L samples)

BIAS: not significant [1]

OVERALL PRECISION (s_r) [1]: (1) 0.093;
(2) 0.097;
(3) 0.098

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ^{63}Ni ECD

ANALYTES: compounds above

DESORPTION: 2 mL hexane; 30 min ultrasonic agitation

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 220 °C
-DETECTOR: 300 °C
-COLUMN: 160 °C

GASES-CARRIER: nitrogen, 30 mL/min
-PURGE: nitrogen, 90 mL/min

COLUMN: 2.0 m x 2 mm ID nickel, 10% Carbowax 20M-TPA on 80/100-mesh Chromosorb W AW

CALIBRATION: standard solutions of analytes in hexane

RANGE: 0.02 to 500 µg per sample [1]

ESTIMATED LOD: 0.001 µg/mL in hexane [1]

PRECISION (s_r) [1]: (1) 0.044;
(2) 0.042;
(3) 0.057

APPLICABILITY: The working range is 0.002 to greater than 30 mg/m³ for each analyte for a 10-L air sample. Linear range of the detector is limited but samples are diluted prior to measurement.

INTERFERENCES: Using chromatographic conditions given above, 1,2,3,5-tetrachlorobenzene coelutes with 1,2,4,5-tetrachlorobenzene.

OTHER METHODS: This revises P&CAM 343 [2].

REAGENTS:

1. Hexane, distilled in glass.*
2. Pentachlorobenzene, 98%.*
3. 1,2,4,5-Tetrachlorobenzene, 98%.*
4. 1,2,4-Trichlorobenzene, 99%.*
5. Calibration stock solution, 100 mg/mL. Dilute accurately weighed 500-mg portions of each analyte to 5 mL with hexane. Store in airtight container. Stock solution is stable indefinitely.
6. Amberlite, XAD-2, 20/50 mesh. Cleanse by Soxhlet extraction for 4 hrs with 4:1 (v/v) acetone/methanol, 4 hrs with hexane, and drying overnight at 70 to 100 °C under vacuum.
   NOTE: During method evaluation, the capacity of cleansed bulk Amberlite XAD-2 was much higher than that of Amberlite XAD-2 obtained from some commercially available sorbent tubes.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Two-stage sampler (Fig. 1):
   a. Filter: 13-mm PTFE fiber mat (Millipore Cat. No. LSWP01300, or equivalent) in stainless steel holder (Millipore Swinny, Cat. No. XX3001200, or equivalent).
   b. Sorbent tube: glass, 7 cm long, 6.4 mm OD, 4 mm ID, containing two sections of cleansed Amberlite XAD-2 (front = 100 mg; back = 50 mg), separated and held in place by 4-mg silanized glass wool plugs. Couple filter holder to sorbent tube by bored-through 6.4-mm nylon union (Crawford Catalog No. NY-400-6, or equivalent). A 6.4-mm x 3.2-mm PTFE reducing ferrule (Alltech Catalog No. RF-400/200-T, or equivalent), bored out to 4 mm, receives Luer tip of filter holder. Attach sorbent tube with PTFE ferrules (Crawford Catalog Nos. T-404-1 and T-403-1, or equivalent) and position so that front end butts against reducing ferrule. After assembly, seal inlet of filter holder and outlet of sorbent tube with PTFE tape and plastic caps. Include extra caps and tape for sealing separated filter holder and sorbent tube. Typical pressure drop across assembled sampler is 1 kPa at 0.2 L/min airflow.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, ^{63}Ni electron capture detector, integrator, and column (see page 5517-1).
4. Vials, 5-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 5-mL, and convenient sizes for making dilutions.
7. Pipets, 2-mL, and convenient sizes for making dilutions.
8. Ultrasonic bath.
9. Balance, readable to 1 mg.

SPECIAL PRECAUTIONS: Hexane (flash point = -22 °C) is highly flammable. Prepare samples and standards in well-ventilated hood.

Chlorinated benzenes may irritate skin, eyes, and mucous membranes. Avoid inhalation and contact.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: The filter stage permits measurement of exposures to polychlorobenzene aerosols. If it is known that such exposure is not likely, the filter may be omitted.
2. Remove caps from 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 total sample size of 3 to 12 L.
4. Separate filter from sorbent tube and seal both with PTFE tape and caps. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place filter in one vial, front glass wool plug and sorbent section in another vial, and rear sorbent section and enclosing glass wool plugs in third vial.
6. Add 2.0 mL hexane to each vial. Cap each vial.
7. Allow to stand 30 min with ultrasonic agitation.
8. Wash inside surfaces of filter holder with 2 to 3 mL hexane. Transfer washings to 5-mL volumetric flask and dilute to mark with hexane.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the linear range of the detector.
   a. Prepare working standards by serial dilution of the calibration stock solution.
   b. Analyze together with samples and blanks (steps 12 and 13).
   c. Prepare calibration graph for each analyte (peak height or area vs. µg/mL analyte).
10. Determine desorption efficiency (DE) over range of interest at least once for each lot of filters and sorbent used. Prepare three samplers at each of five levels plus three media blanks.
    a. Prepare known concentrations of the analytes in hexane.
    b. Inject a 5-µL aliquot directly onto the filter of an assembled sampler with a microliter syringe while drawing 12 L of analyte-free air through the sampler at 0.2 L/min.
    c. Separate filter holder and sorbent tube, seal, and allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 12 and 13).
    NOTE: Significant amounts should be found on the filters and holders only at the higher loadings. See EVALUATION OF METHOD.
    e. Prepare graph of DE vs. µg of each analyte recovered. DE is the sum of amounts recovered from filter, holder, and sorbent sections divided by the amount taken.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5517-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Under these conditions, approximate t_rs are: 1,2,4-trichlorobenzene, 2.0 min; 1,2,4,5-tetrachlorobenzene, 3.3 min; pentachlorobenzene, 7.5 min.
    NOTE 2: If peak area is above range of working standards, dilute with hexane, reanalyze and apply appropriate dilution factor in calculations.
13. Measure peak height or area.

CALCULATIONS:

14. Determine the concentration, µg/mL, for each sample, and multiply by the desorption volume, mL, and the dilution factor, if any, to calculate the mass, µg, recovered.
15. Add the amounts recovered from filter, filter holder, sorbent front (W_f), and sorbent back (W_b) sections to determine the mass found in a field sample (W) or the average sampler blank (B), and correct for DE.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.

16. Calculate concentration, C, of each analyte in air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

P&CAM 343 was issued on August 31, 1981 [2]. The two-stage sampler was tested using 10- to 12-L samples at 28 to 30 °C and >80% RH over the ranges 0.002 to 100 mg/m³ for 1,2,4-trichlorobenzene, 0.003 to 31 mg/m³ for 1,2,4,5-tetrachlorobenzene, and 0.008 to 22 mg/m³ for pentachlorobenzene [1,2]. The average recoveries were 0.957 for 1,2,4-trichlorobenzene, 1.014 for 1,2,4,5-tetrachlorobenzene, and 0.968 for pentachlorobenzene, with concentrations independently verified by collection in impingers. These biases were insignificant at a 0.05 significance level. For levels of 0.02, 0.1, 0.4, 0.5, 25, and 500 µg per sample, the average desorption efficiencies were 0.908 for 1,2,4-trichlorobenzene, 0.901 for 1,2,4,5-tetrachlorobenzene, and 0.917 for pentachlorobenzene. At 25 µg, only pentachlorobenzene was observed in significant amounts on the filter and holder (4.7% of the total amount recovered). However, at 500 µg, the average contribution from the filter and holder to the totals were 7.2% for 1,2,4-trichlorobenzene, 55.2% for 1,2,4,5-tetrachlorobenzene, and 67.9% for pentachlorobenzene. The use of polypropylene filter holders was rejected because even at the 500-ng level, polypropylene filter holders retained 14% of the 1,2,4-trichlorobenzene, 34% of the 1,2,4,5-tetrachlorobenzene, and 45% of the pentachlorobenzene. After storage for several days, this might not be recoverable. Polystyrene holders did not appear to retain chlorobenzenes, but were not available in the 13-mm size.

The capacity of the 100-mg sorbent section for 1,2,4-trichlorobenzene, the most volatile of the analytes, was 24 L for a concentration of 45 mg/m³ at 40 °C and >80% RH. The test atmosphere also contained 1,2,4,5-tetrachlorobenzene at 22 mg/m³ and pentachlorobenzene at 15 mg/m³. Capacities for the latter two analytes were not specifically determined, but were greater than 24 L. A storage stability study found no significant losses after 13-day storage in the dark at room temperature for 2.5-L samples containing 35 ng 1,2,4-trichlorobenzene, 63 ng 1,2,4,5-tetrachlorobenzene, and 43 ng pentachlorobenzene.

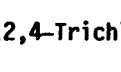
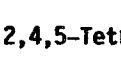
REFERENCES:

[1] Dillon, H. K., and M. L. Bryant. Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene; and Polychlorinated Terphenyls: Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene, NIOSH Contract No. 210-79-0102, Southern Research Institute, Birmingham, AL (1981).

[2] NIOSH Manual of Analytical Methods, 2nd ed., V. 7, P&CAM 343, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1982).

METHOD REVISED BY: R. Alan Lunsford, Ph.D., NIOSH/DPSE; data obtained under NIOSH Contract 210-79-0102.

Table 1. Properties.

Name	Structure	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	Vapor Pressure @ 25 °C (kPa)	Density @ 20 °C (g/mL)	mg/m³ per ppm @ NTP
1,2,4-Trichlorobenzene		16.95	213.5	0.291	0.039	1.454	7.42
1,2,4,5-Tetrachlorobenzene		139.5–140.5	243–246			1.858[a]	8.83
Pentachlorobenzene		86	277			1.834[b]	10.23

[a]Solid @ 22 °C.
[b]Solid @ 16.5 °C.

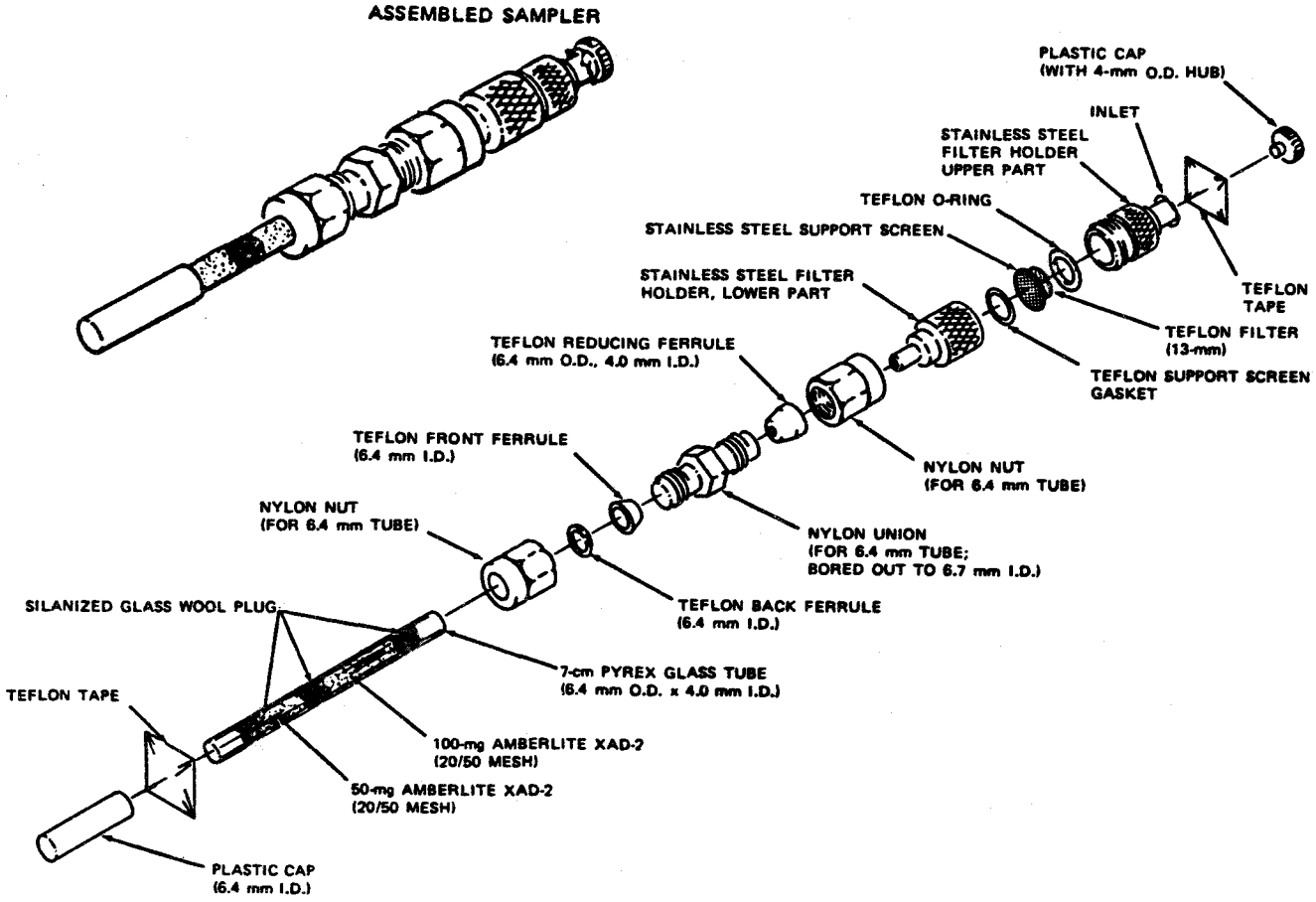


Figure 1. Two-stage sampler for polychlorobenzenes.

FORMULA: mixture: $C_{12}H_{10-x}Cl_x$
[where x = 1 to 10]
M.W.: ca. 258 (42% Cl ; $C_{12}H_7Cl_2$);
ca. 326 (54% Cl ; $C_{12}H_5Cl_5$)

POLYCHLOROBIPHENYLS
METHOD: 5503
ISSUED: 2/15/84
REVISION #1: 8/15/87

OSHA: 1 mg/m³ (42% Cl);
0.5 mg/m³ (54% Cl)
NIOSH: 0.001 mg/m³ [1,2]
ACGIH: 1 mg/m³ (42% Cl); STEL 2 mg/m³
0.5 mg/m³ (54% Cl); STEL 1 mg/m³
(skin)

PROPERTIES: 42% Cl: BP 325 to 366 °C; MP -19 °C;
d 1.38 g/mL @ 25 °C;
VP 0.01 Pa (8 x 10^{-5} mm Hg;
1 mg/m³) @ 20 °C [3]
54% Cl: BP 365 to 390 °C; MP 10 °C;
d 1.54 g/mL @ 25 °C;
VP 0.0004 Pa (3 x 10^{-6} mm Hg;
0.05 mg/m³) @ 20 °C [3,4]

SYNONYMS: PCB; CAS #1336-36-3; 1,1'-biphenyl chloro (CAS #27323-18-8); chlorodiphenyl, 42% Cl (Aroclor 1242; CAS #53469-21-9), and 54% Cl (Aroclor 1254; CAS #11097-69-1)

SAMPLING

SAMPLER: FILTER + SOLID SORBENT
(13-mm glass fiber + Florisil,
100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min or less

VOL-MIN: 1 L @ 0.5 mg/m³
-MAX: 50 L

SHIPMENT: transfer filters to
glass vials after sampling

SAMPLE STABILITY: unknown for filters;
2 months for Florisil
tubes [5]

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

OVERALL PRECISION (s_r): not evaluated

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD (^{63}Ni)

ANALYTE: polychlorobiphenyls

DESORPTION: filter + front section, 5 mL hexane;
back section, 2 mL hexane

INJECTION VOLUME: 4 µL with 1-µL backflush

TEMPERATURE-INJECTION: 250 - 300 °C
-DETECTOR: 300 - 325 °C
-COLUMN: 180 °C

CARRIER GAS: N_2, 40 mL/min

COLUMN: glass, 1.8 m x 2 mm ID, 1.5% OV-17/1.95%
QF-1 on 80/100 mesh Chromosorb WHP

CALIBRATION: standard PCB mixture in hexane

RANGE: 0.4 to 4 µg per sample [6]

ESTIMATED LOD: 0.03 µg per sample [6]

PRECISION (s_r): 0.044 [5]

APPLICABILITY: The working range is 0.01 to 10 mg/m³ for a 40-L air sample [5]. With modifications, surface wipe samples may be analyzed [7,8].

INTERFERENCES: Chlorinated pesticides, such as DDT and DDE, may interfere with quantitation of PCB. Sulfur-containing compounds in petroleum products also interfere [9].

OTHER METHODS: This method revises Methods S120 [10], 5503 (dated 2/15/84), and P&CAM 244 [5]. Methods S121 [11] and P&CAM 253 [12] for PCB have not been revised.

REAGENTS:

1. Hexane, pesticide quality.
2. Florisil, 30/48 mesh sieved from 30/60 mesh. After sieving, dry at 105 °C for 45 min. Mix the cooled Florisil with 3% (w/w) distilled water.
3. Nitrogen, purified.
4. Stock standard solution of the PCB in methanol or isooctane (commercially available).*

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 13-mm glass fiber filter without binders in a Swinnex cassette (Cat. No. SX 0001300, Millipore Corp.) followed by a glass tube, 7 cm long, 6 mm OD, 4 mm ID containing two sections of 30/48 mesh deactivated Florisil. The front section is preceded by glass wool and contains 100 mg and the backup section contains 50 mg; urethane foam between sections and behind the backup section. Join the cassette and Florisil tube with PVC tubing, 3/8" L x 9/32" OD x 5/32" ID, on the outlet of the cassette and with another piece of PVC tubing, 3/4" L x 5/16" OD x 3/16" ID, complete the union.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Tweezers.
4. Vials, glass, 4- and 7-mL, with aluminum or PTFE-lined caps.
5. Gas chromatograph, electron capture detection (^{63}Ni), integrator and column (page 5503-1).
6. Volumetric flasks, 10-mL and other convenient sizes for preparing standards.
7. Syringe, 10-µL.

SPECIAL PRECAUTIONS: Avoid prolonged or repeated contact of skin with PCB and prolonged or repeated breathing of the vapor [1,2,13].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the Florisil tube immediately before sampling. Connect Florisil tube to Swinnex cassette and attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.2 L/min for a total sample size of 1 to 50 L.
   NOTE: At low PCB concentrations, the sampler was found to be efficient when operated at flow rates up to 1 L/min, for 24 hours [8]. Under these conditions, the limit of detection was 0.02 µg/m^3.
4. Transfer the glass fiber filters to 7-mL vials. Cap the Florisil tubes with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the glass wool and 100-ml Florisil bed in the same 7-mL vial in which the filter was stored. Add 5.0 mL hexane.
   NOTE: For surface wipe samples, extract each gauze pad with 25 mL hexane [7].
6. In a 4 mL vial, place the 50-mg Florisil bed including the two urethane plugs. Add 2.0 mL hexane.
7. Allow to stand 20 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 10 to 500 ng PCB/mL.
   a. Add known amounts of stock standard solution to hexane in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (sum of areas of selected peaks vs. ng PCB/mL).
9. Determine desorption efficiency (DE) at least once for each lot of glass fiber filters and Florisil 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 Florisil tube.
   b. Inject known amounts of stock standard solution directly onto front sorbent section and onto a media blank filter 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 PCB recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 5503-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Where individual identification of PCB is needed, a procedure using a capillary column may be used [14].
    NOTE 2: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze and apply the appropriate dilution factor in calculations.
12. Sum the areas for five or more selected peaks.

CALCULATIONS:

13. Determine the mass, ng (corrected for DE) of PCB found on the glass fiber filter (w) and in the Florisil front (W_f) and back (W_b) sorbent sections, and in the average media blank filter (B) and 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 PCB in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method uses 13-mm glass fiber filters which have not been evaluated for collecting PCB. In Method S120, however, Aroclor 1242 was completely recovered from 37-mm glass fiber filters using 15 mL isooctane [12,15,16]. With 5 mL of hexane, Aroclor 1016 was also completely recovered from 100-mg Florisil beds after one-day storage [5]. Thus, with no adsorption effect likely on glass fiber filters for PCB, 5 mL hexane should be adequate to completely extract PCB from combined filters and front sorbent sections. Sample stability on glass fiber filters has not been investigated. Breakthrough volume was >48 L for the Florisil tube at 75% RH in an atmosphere containing 10 mg/m³ Aroclor 1016 [5].

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METHOD REVISED BY: James E. Arnold, NIOSH/DPSE; S120 originally validated under NIOSH Contract 210-76-0123.

Table 1. Composition of some Aroclors [3].

Major Components	Aroclor 1016	Aroclor 1242	Aroclor 1254
Biphenyl	0.1%	<0.1%	<0.1%
Monochlorobiphenyls	1	1	<0.1
Dichlorobiphenyls	20	16	0.5
Trichlorobiphenyls	57	49	1
Tetrachlorobiphenyls	21	25	21
Pentachlorobiphenyls	1	8	48
Hexachlorobiphenyls	<0.1	1	23
Heptachlorobiphenyls	none detected	<0.1	6
Octachlorobiphenyls	none detected	none detected	none detected

FORMULA:  ; C_5H_5N

M.W.: 79.10

PYRIDINE

METHOD: 1613
ISSUED: 8/15/87

OSHA: 5 ppm
NIOSH: no recommended standard [1]
ACGIH: 5 ppm
(1 ppm = 3.23 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.98 g/mL @ 20 °C;
BP 115 °C; MP -42 °C;
VP 2.4 kPa (18 mm Hg; 2.4% v/v) @ 20 °C;
explosive limits 1.8 to 12.4% v/v in air

SYNONYMS: CAS #110-86-1.

SAMPLING

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

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 18 L
-MAX: 150 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 7.6 to 30 mg/m³ [2]
(100-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.059 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: pyridine

DESORPTION: 1 mL methylene chloride;
stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 260 °C
-DETECTOR: 285 °C
-COLUMN: 140 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 3 mm OD stainless steel packed with 5% Carbowax 20M on 80/100 mesh acid-washed DMCS Chromosorb W

CALIBRATION: standard solutions of pyridine in methylene chloride

RANGE: 0.3 to 4.5 mg per sample

ESTIMATED LOD: 0.02 mg per sample [3]

PRECISION (s_r): 0.014 @ 0.8 to 3.1 mg per sample [2]

APPLICABILITY: The working range is 1 to 14 ppm (3 to 45 mg/m³) for a 100-L air sample.

INTERFERENCES: None detected. The chromatographic column or separation may be changed to circumvent interference problems (e.g., 30 m x 0.32 mm capillary column with 1 µm DB-5 at 50 °C [3]).

OTHER METHODS: This revises Method S161 [4].

REAGENTS:

1. Methylene chloride (CH_2Cl_2), chromatographic quality.
2. Pyridine, reagent grade.*
3. Hexane, chromatographic quality.
4. DE stock solution, 300 mg/mL. Weigh 3 g pyridine (ca. 3.1 mL) into a 10-mL volumetric flask. Dilute to volume with hexane. Prepare in duplicate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

*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 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 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1613-1).
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.
8. Balance, analytical.

SPECIAL PRECAUTIONS: Pyridine can cause liver and kidney damage, and CNS depression if it is inhaled or contacts the eyes or skin [1,5]. Methylene chloride is a suspect carcinogen [6].

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 1 L/min for a total sample size of 18 to 150 L.
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. Pipet 1.0 mL CH_2Cl_2 into each vial. Cap each vial.
   NOTE: A suitable internal standard, such as toluene, may be added at this step [3].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of pyridine to CH_2Cl_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain pyridine concentrations in the range 0.02 to 4.5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg pyridine).
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 (2 to 20 µL) of DE stock solution, or a serial dilution thereof, 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 pyridine recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1613-1. 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 CH_2Cl_2, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of pyridine 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 pyridine 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:

Method S161 was issued on August 1, 1975 [4], and validated with atmospheres generated by calibrated syringe pump and confirmed using a total hydrocarbon analyzer [2]. Average recovery was 109% ± 3.6% (18 samples) in the range 7.6 to 30.4 mg/m³ for 100-L samples. Breakthrough (effluent concentration = 5% of test concentration) was not observed after sampling for 240 min at 0.93 L/min from an atmosphere containing 30.4 mg/m³ pyridine in dry air. Carbon disulfide and methanol were tested and rejected as possible desorbing solvents. Carbon disulfide gave an average DE of 0.734; methanol, 0.201. Desorption efficiency using methylene chloride for 18 spiked samples in the range 0.8 to 3.1 mg pyridine per sample averaged 0.81 with $s_r = 0.013$.

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METHOD REVISED BY: G. David Foley, NIOSH/DPSE.

FORMULA: SbH_3 — STIBINE

METHOD: 6008

M.W.: 124.77 — ISSUED: 8/15/87

OSHA: 0.1 ppm
NIOSH: no recommended standard [1]
ACGIH: 0.1 ppm
(1 ppm = 5.10 mg/m³ @ NTP)

PROPERTIES: gas; BP -17 °C; MP -88 °C; VP >1 atm

SYNONYMS: antimony trihydride; CAS #7803-52-3.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
($HgCl_2$-coated silica gel, 1 g/0.5g)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 4 L
-MAX: 50 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days at 25 °C [2]

FIELD BLANKS: 10% of samples)

ACCURACY

RANGE STUDIED: 0.12 to 1 mg/m³ [3]
(20-L samples)

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.087 [3]

MEASUREMENT

TECHNIQUE: COLORIMETRIC

ANALYTE: antimony

EXTRACTION: 15 mL conc. HCl; 30 min

WAVELENGTH: 552 nm

CALIBRATION: standard solutions of Sb(III) in conc. HCl

RANGE: 2 to 20 µg Sb per sample [2]

ESTIMATED LOD: 0.4 µg SbH_3 per sample [2]

PRECISION (s_r): not defined

APPLICABILITY: The working range is 0.1 to 3.5 mg/m³ (0.02 to 0.7 ppm) for a 20-L air sample.

INTERFERENCES: Colorimetric determination of Sb is subject to interference by elements which form a Rhodamine B complex extractable into isopropyl ether. Am(III) (>250 µg); Au (>1000 µg); Fe(III) (>30,000 µg); Tl(I) (>1000 µg); and Sn(II) (>1000 µg) interfere [4]. If the possibility of an interference exists, an alternate measurement procedure should be used (e.g., ICP or AAS).

OTHER METHODS: This revises Method S243 [3].

REAGENTS:

1. Water, distilled or deionized.
2. Hydrochloric acid (HCl), conc.*
3. Antimony stock solution, 1000 µg Sb(III)/mL.
4. Ceric sulfate, $Ce(SO_4)_2$, solid.
5. Isopropyl ether.
6. Rhodamine B stock solution, 0.2% in water. Dissolve 0.5 g Rhodamine B in 250 mL water. Prepare in duplicate.
7. Working Rhodamine B solution, 0.01% in 0.5 M HCl. Dilute 25 mL Rhodamine B stock solution and 24 mL conc. HCl to 500 mL. Prepare fresh daily.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, with plastic caps, containing two sections of $HgCl_2$-coated silica gel (front = 1.0 g; back = 0.5 g) separated and contained by silylated glass wool. 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. Visible spectrophotometer capable of measuring absorbance at 552 nm, with two matched 1-cm silica. absorption cells with tight-fitting PTFE caps.*
4. Separatory funnels, 125-mL.*
5. Beakers, Griffin, 50-mL.*
6. Volumetric flasks, 25-, 50-, 250-, and 500-mL.*
7. Pipets, 4-, 15-, and 20-mL.*
8. Graduated cylinders, 10- and 25-mL.*
9. Centrifuge, with centrifuge tubes, 15-mL, with plastic caps.*

*Clean all glassware with conc. HCl and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all concentrated acid-handling in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove sampler caps immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
   NOTE: Use a cellulose ester membrane prefilter if particulate antimony compounds may be present.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 4 to 50 L.
4. Cap the sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place front and back sorbent sections of the sampler tube in separate 50-mL beakers. Discard the glass wool.
6. Add 15.0 mL conc. HCl to each beaker.
7. Mildly agitate (swirl) the beaker contents every 10 min for a total desorption time of 30 min. Pour the solution into a 25-mL volumetric flask.
8. Add 4.0 mL conc. HCl to the sorbent in the beaker. Swirl and decant into the volumetric flask from step 7.
9. Repeat step 8. Dilute to volume with conc. HCl and swirl to mix.
   NOTE: Perform steps 10 through 15 within a 15-min period.
10. Pipet 15.0 mL of the sample extract into a separatory funnel.
11. Add 15 ± 5 mg ceric sulfate, swirl to dissolve and let stand unstoppered 60 sec.

12. Add 15.0 mL isopropyl ether to the funnel, stopper, and shake 30 sec, releasing pressure only at the beginning and end of that period.
13. Add 7.0 mL water. Shake 60 sec. Wait 60 sec to allow for separation. Remove and discard the aqueous layer. Be careful to remove all of the aqueous layer.
14. Add 20.0 mL working Rhodamine B solution, shake 60 sec, releasing pressure only at the beginning and end of that period. Allow 60 sec for the phases to separate. Remove and discard aqueous (lower) layer. Drain ca. 10 mL of the remaining solution into a 15-mL centrifuge tube and cap tightly.
15. Centrifuge 120 sec at 2000 rpm. Transfer ca. 3 mL of the supernatant liquid to an absorption cell and cap. Proceed immediately to step 18.

CALIBRATION AND QUALITY CONTROL:

16. Calibrate daily with at least six working standards over the range 2 to 20 µg antimony per sample.
    a. Add known amounts of antimony stock solution and conc. HCl to cover the antimony concentration of 2 to 20 µg Sb per 15 mL and a reagent blank.
    b. Proceed as in steps 10 through 15 and 18 and 19.
    c. Prepare a calibration graph (absorbance vs. µg antimony/15 mL).
17. Analyze three quality control spikes to ensure that the calibration graph is in control.

MEASUREMENT:

18. Set the spectrophotometer to manufacturer's recommendations and to conditions given on page 6008-1.
19. Measure the absorbance using isopropyl ether as a blank.

CALCULATIONS:

20. Determine the mass, µg, of stibine found in the sample front (W_f) and back (W_b) sorbent sections, and in the average blank front (B_f) and back (B_b) sorbent sections by multiplying the mass of antimony/15 mL found for each of these sections by 1.708.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
21. Calculate concentration, C, of stibine in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S243 was evaluated over the range 0.119 to 1.01 mg/m³ using 20-L air samples [2]. Recovery averaged 98.6% in the range 0.12 to 1.0 µg SbH_3 per sample. The capacity of the sampling tubes (at a flow rate of 0.22 L/min, a concentration of 1.326 mg SbH_3/m^3, and a relative humidity of 85%) was shown to be greater than 70 µg (as SbH_3). Previously, activated charcoal tubes were tried as a collection medium for stibine but were rejected because of poor collection efficiency [5].

REFERENCES:

[1] 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.
[2] S243, Backup Data Report for Stibine, prepared under NIOSH Contract No. 210-76-0123 (March 18, 1977), available as "Ten NIOSH Analytical Methods, Set 2," Order #PB271-464 from NTIS, Springfield, VA 22161.

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S243, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] Ward, F. N., and H. W. Lakin. Anal. Chem., 26, 1168 (1954).
[5] Failure Report S243, Stibine, prepared under NIOSH Contract CDC-99-74-45 (unpublished, 1977).

METHOD REVISED BY: R. DeLon Hull, NIOSH/DBBS.

FORMULA: SO_2

M.W.: 64.06

SULFUR DIOXIDE

METHOD: 6004
ISSUED: 8/15/87

OSHA: 5 ppm
NIOSH: 0.5 ppm [1,2]; Group I Pesticide [3]
ACGIH: 2 ppm
(1 ppm = 2.62 mg/m³ @ NTP)

PROPERTIES: gas; vapor density 2.26 (air = 1); BP -10 °C; MP -75.5 °C; nonflammable

SYNONYMS: CAS #7446-09-5.

SAMPLING

SAMPLER: FILTER
(cellulose + KOH; preceded by 0.8-µm cellulose ester membrane)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 15 L @ 0.5 ppm
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY

ANALYTE: sulfite and sulfate ions

DESORPTION: 10 mL 3 mM $NaHCO_3$/2.4 mM Na_2CO_3

INJECTION LOOP VOLUME: 100 µL

ELUENT: 3 mM $NaHCO_3$/2.4 mM Na_2CO_3, 2 to 3 mL/min @ ambient temperature

COLUMNS: anion precolumn, fast run, anion separator, fast run; anion suppressor

CONDUCTIVITY SETTING: 10 µS full scale

CALIBRATION: standard solutions of $SO_3^=$ and $SO_4^=$ in eluent

RANGE: 0.02 to 0.2 mg SO_2 per sample

ESTIMATED LOD: 0.01 mg SO_2 per sample [4]

PRECISION (s_r): 0.05 @ 0.05 to 1 mg SO_2 per sample [5]

APPLICABILITY: The working range is 0.07 to 1.9 ppm (0.2 to 5 mg/m³) for a 100-L air sample. SO_2 is collected on the back (treated) filter. Sulfuric acid, sulfate salts, and sulfite salts are collected on the front filter and may be quantitated as total particulate sulfate and sulfite.

INTERFERENCES: Bromide has the same retention time as sulfite on these columns. Sulfur trioxide gas, if present in dry atmospheres, may give a positive interference in SO_2 determinations.

OTHER METHODS: This revises P&CAM 268 [5]. P&CAM 146 [6], P&CAM 163 [7], and S308 [8] use 0.3 N H_2O for sampling and titration with NaOH or barium perchlorate. P&CAM 160 [9] uses tetrachloromercurate solution and visible spectrophotometry. P&CAM 204 [10] uses a solid sorbent (molecular sieve 5A), thermal desorption, and mass spectrometry.

REAGENTS:

1. Water, deionized, filtered, specific conductance ≤10 µS/cm.
2. Filter-impregnating solution. Dissolve 20 g KOH in about 50 mL deionized water. Add 10 mL glycerol and dilute with deionized water to 100 mL.
3. Eluent: 3 mM $NaHCO_3$/2.4 mM Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in 4 L filtered deionized water.
4. Formaldehyde, 0.5% (w/v) in deionized, filtered water.
5. Calibration stock solutions, 1 mg/mL (as the anion). Prepare in duplicate.
   a. Sulfite: dissolve 0.1575 g Na_2SO_3 in 0.5% (w/v) formaldehyde in water. Dilute to 100 mL.
   b. Sulfate: dissolve 0.1479 g Na_2SO_4 in deionized water; Dilute to 100 mL.
6. Hydrogen peroxide (H_2O_2), 30% (w/v).*

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: two 37-mm diameter cassette filter holders (connected in series by a M-M Luer adapter, e.g., Millipore XX1102503, or a short piece of plastic tubing) containing:
   a. (Front cassette) cellulose ester membrane cellulose filter, 0.8-µm pore size, supported by a backup pad.
   b. (Back cassette) cellulose filter (e.g., Whatman 40) which has been saturated with filter-impregnating solution and dried 20 to 30 min at 100 °C, supported by a cellulose backup pad.
2. Personal sampling pump, 0.5 to 1.5 L/min, with flexible connecting tubing.
3. Vials, glass, 20-mL, screw-cap, such as scintillation vials.*
4. Ion chromatograph, fast run anion separator and precolumn, anion suppressor column, conductivity detector, and strip chart recorder. (Optional: integrator.)
5. Syringes, 10-mL, polyethylene, with luer tip.*
6. Filters, luer tip holder with membrane filter, 13- or 25-mm, 0.45-µm pore size.
7. Micropipets, 50- to 1000-µL, with disposable tips.*
8. Volumetric flasks, 50- and 100-mL.*
9. Pipet, 10-mL.*
10. Polyethylene bottles, 250-mL.*

*Clean by rinsing thoroughly with deionized water.

SPECIAL PRECAUTIONS: H_2O_2 is a strong oxidizer and can be explosive. Avoid contact with skin. Should contact occur, flush immediately with water.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove end caps of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1.5 L/min for a total sample size of 15 to 400 L. Do not exceed a total particulate loading of 2 mg on the front filter.
4. Seal the sampler and pack securely for shipment.

NOTE 1: If determination of sulfuric acid is required, transfer the front (membrane) filter to a clean vial within 4 hrs to avoid low recovery of sulfate. Handle the filter with tweezers to avoid contamination.

NOTE 2: If particulate sulfite analysis is desired or if particulate sulfite is present and its interference with particulate sulfate is to be prevented, transfer the front (membrane) filter to a vial containing 10.0 mL 0.5% formaldehyde solution.

SAMPLE PREPARATION:

6. Put the two filters from the sampler into separate, clean vials. Discard the backup pads. Add 10.0 mL eluent to each vial and let stand, with occasional vigorous shaking, for 30 min.
7. Add one drop of 30% H_2O_2 to oxidize sulfite to sulfate.
   NOTE 1: Do not add H_2O_2 to the front filter if particulate sulfite is to be determined.
   NOTE 2: The SO_2 collected on the treated (back) filter is present as sulfite, which oxidizes in air slowly (over several weeks) to sulfate. This H_2O_2 oxidation step may be omitted for the back filter, in which case the contributions of sulfite and sulfate found on the back filter must be summed, with appropriate stoichiometric factors applied, to give the SO_2 concentration.
8. Pour each sample into a syringe fitted with an in-line filter.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards.
   a. Add known aliguots of sulfate calibration stock solution to eluent in 50-mL volumetric flasks and dilute to the mark to produce solutions containing 0.001 to 0.02 mg/mL $SO_4^=$. Prepare sulfite standards in the same range in 0.5% formaldehyde solution [11].
   b. Store working standards in tightly-capped polyethylene bottles. Prepare fresh working standards weekly.
   c. Analyze working standards with samples and blanks.
   d. Prepare a calibration graph for each anion [peak height (mm or μS) vs. mg sulfite or sulfate].
      NOTE: If any samples have been treated with 0.5% formaldehyde solution, prepare two or three sulfate standards in this solution to verify that this matrix does not affect detector response. If an effect is noted, prepare a calibration graph in this matrix.

MEASUREMENT:

10. Set ion chromatograph to conditions given on page 6004-1, according to manufacturer's instructions.
11. Inject sample aliquot. For manual operation, inject 2 mL of sample from syringe to ensure complete rinse of sample loop.
    NOTE: All samples, eluents, and water flowing through the ion chromatograph must be filtered to avoid plugging system valves or columns.
12. Measure peak height.
    NOTE: If peak height exceeds linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

13. Determine the mass, mg, of sulfate found on the front (W_f) and back (W_b) filters and in the corresponding average media blanks (B_f and B_b).
14. Calculate the concentration, C_1, of sulfur dioxide:

$$C_1 = \frac{(W_b - B_b)}{V} \cdot 667, \text{ mg/m}^3$$

15. Calculate the concentration, C_2, of particulate sulfate in the air volume sampled, V (L):

$$C_2 = \frac{(W_f - B_f) \cdot 10^3}{V}, \text{ mg/m}^3$$

16. If step 7 was omitted for the front filter, determine the mass, mg, of sulfite on the front filter (S_f) and in the average media blank (B_s). Calculate the concentrations, C_3, of particulate sulfite:

$$C_3 = \frac{(S_f - B_b) \cdot 10^3}{V}, mg/m^3$$

NOTE: Under the ion chromatographic conditions, $SO_3^=$ and Br^- coelute. Therefore, the presence of $SO_3^=$ cannot be confirmed unless it is also determined under conditions where it does not coelute with Br^-.

EVALUATION OF METHOD:
The sampler was adapted from that of Pate, et al. [12]. In experiments in which SO_2 was generated by permeation tube and collected in impingers containing H_2O_2, untreated 0.8-µm cellulose ester membrane filters were shown to allow complete passage of SO_2 [13]. In subsequent sampling of an atmosphere containing ca. 10 ppm SO_2 at 1 L/min for 30 min, two treated filters were placed in series following a cellulose ester membrane filter. Recoveries were: 0.667 mg SO_2 from the first treated filter, 0.02 mg SO_2 from the second treated filter, and less than 0.003 mg SO_2 in the backup impinger containing 0.3 N H_2O_2 [14].

Three 0.8-µm pore size mixed cellulose ester filters were spiked with 0.2 mg H_2SO_4 and gave the following recoveries: 83.5% using H_2O extraction, 98.5% using hot H_2O extraction, and 82.5% using 0.01 M HCl for extraction. One filter was spiked with 0.2 mg sulfate from K_2SO_4 and gave 109.5% recovery with water extraction. Two filters were spiked with 0.1 mg sulfate from $(NH_4)_2SO_4$ and $CuSO_4$ solutions and gave recoveries of 109 and 110%, respectively, when extracted with water.

REFERENCES:
[1] Criteria for a Recommended Standard...Occupational Exposure to Sulfur Dioxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 74-111 (1974); revised by Baier, E., Testimony before the U.S. Department of Labor (May, 1977).
[2] 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.
[3] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978), available as PB81-227001 from NTIS, Springfield, VA 22161.
[4] UBTL, Inc., NIOSH Sequence #4205-J (unpublished, February 23, 1984).
[5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 268, U.S. Department of Health and Human Services, Publ. (NIOSH) 79-141 (1979).
[6] Ibid., 2nd ed., Vol. 1, P&CAM 146, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[7] Ibid., 2nd ed., Vol. 1, P&CAM 163, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[8] Ibid., 2nd ed., Vol. 4, S308, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[9] Ibid., 2nd ed., Vol. 1, P&CAM 160, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[10] Ibid., 2nd ed., Vol. 1, P&CAM 204, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[11] Bolyard, M. L. (NIOSH, personal communication, 1985).
[12] Pate, J. B., J. P. Lodge, Jr., and M. P. Neary. The Use of Impregnated Filters to Collect Traces of Gases in the Atmosphere, Anal. Chim. Acta, 28:341 (1963).
[13] Grote, A. A. (NIOSH, unpublished results, 1973).
[14] Eller, P. M. and M. A. Kraus. Methods for the Determination of Oxidized Sulfur and Nitrogen Species in Air, Internal report (July 29, 1977).

METHOD REVISED BY: Peter M. Eller, Ph.D, CIH, NIOSH/DPSE.

FORMULA: (1): CCl_3CClF_2; $C_2Cl_4F_2$
(2): CCl_2FCCl_2F; $C_2Cl_4F_2$
M.W.: 203.83

(1) 1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and
(2) 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE

METHOD: 1016
ISSUED: 8/15/87

OSHA: 500 ppm
NIOSH: no recommended standard [1]
ACGIH: 500 ppm
(1 ppm = 8.33 mg/m³ @ NTP)

PROPERTIES: solids; MP (1) 40.6 °C, (2) 26 °C;
BP (1) 91.5 °C, (2) 93 °C;
VP 5.3 kPa (40 mm Hg; 5.2% v/v) @ 20 °C;
not combustible

SYNONYMS: (1): Refrigerant 112a; CAS #76-11-9.
(2): Refrigerant 112; CAS #76-12-0.

SAMPLING

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

FLOW RATE: 0.01 to 0.035 L/min

VOL-MIN: 0.5 L
-MAX: 2 L

SHIPMENT: routine

SAMPLE STABILITY: not tested

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: (1): 2160 to 9020 mg/m³ [2]
(2): 1880 to 8060 mg/m³ [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): (1): 0.069;
(2): 0.054 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,1,2-tetrachloro-2,2-difluoroethane;
1,1,2,2-tetrachloro-1,2-difluoroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

	(1)	(2)
TEMPERATURE-INJECTION:	185 °C	50 °C
-DETECTOR:	250 °C	240 °C
-COLUMN:	50 °C	50 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 3 m x 3 mm OD stainless steel packed
with 10% FFAP on 80/100 mesh
Chromosorb WHP

CALIBRATION: standard solutions in CS_2

RANGE: 2 to 20 mg per sample

ESTIMATED LOD: 0.3 mg per sample

PRECISION (s_r): (1): 0.027 @ 4 to 17 mg per sample [2]; (2): 0.005 @ 4 to 17 mg per sample [2]

APPLICABILITY: The working range for either analyte is 120 to 1600 ppm (1000 to 13,000 mg/m³) for a 2-L air sample. These compounds are used as degreasing solvents, refrigerants, foaming agents and corrosion inhibitors.

INTERFERENCES: None reported.

OTHER METHODS: This combines and revises Methods S131 and S132 [1].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,1,2-Tetrachloro-2,2-difluoroethane and 1,1,2,2-tetrachloro-1,2-difluoroethane, reagent grade.*
3. Hexane, chromatographic quality.
4. Calibration stock solution, 0.2 mg/µL. Dissolve 2 g analyte in CS_2 to prepare 10 mL solution. Prepare in duplicate.
5. DE stock solution, 1 mg/µL. Dissolve 10 g analyte in hexane to prepare 10 mL solution. Prepare in duplicate.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered, compressed.

*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 0.035 L/min, with flexible connecting tubing.
3. File, triangular.
4. Gas chromatograph, flame ionization detector, integrator and column (page 1016-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10-µL, readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Pipets, TD, 10- to 1000-µL.

SPECIAL PRECAUTIONS [3]: Tetrachloro-1,2-difluoroethane has been determined to be a carcinogen [1]. Both analytes react with chemically-active metals such as sodium, potassium and beryllium or with powdered magnesium, aluminum and zinc.

Hazardous products such as hydrogen chloride, hydrogen fluoride and carbon monoxide may be released when either analyte decomposes. Both analytes will attack some forms of plastics, rubber and coatings.

Carbon disulfide is toxic and flammable; work with it only in a 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 0.035 L/min for a total sample size of 0.5 to 2 L.
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.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain analyte concentrations in the range 0.3 to 20 mg/mL.

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 sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of DE stock solution, or a serial dilution thereof, 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 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 ensure 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 1016-1. 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 an aliquot of the desorbed liquid 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):

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

EVALUATION OF METHOD:

1,1,1,2-Tetrachloro-2,2-difluoroethane: Method S131 was issued on May 9, 1975 [3], and was validated at 2.08, 4.17 and 8.35 mg/m³ [2]. The generated concentrations were confirmed by gas chromatographic analysis and comparison to bag standards. The average desorption efficiency was 103.6% over the range 4 to 17 mg per sample. The breakthrough volume was 2.7 L when sampling 14,300 mg/m³ at 0.035 L/min.

1,1,2,2-Tetrachloro-1,2-difluoroethane: Method S132 was issued on May 9, 1975 [3], and was validated at 20.05, 4.15 and 8.35 mg/m³ [2]. The generated concentrations were confirmed by gas chromatographic analysis and comparison to bag standards. The average desorption efficiency was 102% over the range 4 to 17 mg per sample. Breakthrough had not occurred after 3 hrs sampling 6990 mg/m³ at 0.041 L/min. The test was stopped after 3 hrs.

REFERENCES:
[1] 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.
[2] Documentation of the NIOSH Validation Tests, S131 and S132, 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.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S131 and S132, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY: Y. T. Gagnon, NIOSH/DPSE.

FORMULA: $Cl_2CHCHCl_2$; $C_2H_2Cl_4$

M.W.: 167.85

1,1,2,2-TETRACHLOROETHANE

METHOD: 1019
ISSUED: 8/15/87

OSHA: 5 ppm (skin)
NIOSH: 1 ppm [1]; suspect carcinogen [2]; Group I Pesticide [3]
ACGIH: 1 ppm (skin)
(1 ppm = 6.86 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.5866 g/mL @ 25 °C; BP 146.5 °C; MP -44 °C; VP 0.8 kPa (6 mm Hg; 0.8% v/v) @ 25 °C; nonflammable

SYNONYMS: acetylene tetrachloride; CAS #79-34-5.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 3 L @ 5 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 18 to 74 mg/m³ [4]
(10-L samples)

BIAS: not significant [4]

OVERALL PRECISION (s_r): 0.057 [4]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,2,2-tetrachloroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 230 °C
-COLUMN: 160 °C

CARRIER GAS: N_2, 25 mL/min

COLUMN: stainless steel, 3 m x 3 mm OD, packed with 10% FFAP on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 0.1 to 1 mg per sample

ESTIMATED LOD: 0.01 mg per sample [5]

PRECISION (s_r): 0.016 @ 0.16 to 0.64 mg per sample [4]

APPLICABILITY: The working range is 1.5 to 15 ppm (10 to 100 mg/m³) for a 10-L air sample.

INTERFERENCES: None known.

OTHER METHODS: This revises Method S124 [6] and the method which appears in the criteria document [1].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,2,2-Tetrachloroethane, reagent grade.*
3. Hexane, chromatographic quality.*
4. DE stock solution, 50 mg/mL. Dilute 0.5 g 1,1,2,2-tetrachloroethane to 10 mL with hexane. Prepare in duplicate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

*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 petroleum-based 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 (SKC Lot 104, #ST 226-38, or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1019-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.

SPECIAL PRECAUTIONS: 1,1,2,2-Tetrachloroethane is a powerful narcotic, liver poison, and suspected carcinogen, and can be absorbed through the skin [1,2,7]. Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Hexane is a dangerous fire hazard (flash point = -26 °C). Work with these substances only in a 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 of 3 to 30 L.
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.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of 1,1,2,2-tetrachloroethane to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain 1,1,2,2-tetrachloroethane concentrations in the range 0.01 to 1 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg 1,1,2,2-tetrachloroethane).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of DE stock solution, or a serial dilution thereof, 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 with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg 1,1,2,2-tetrachloroethane recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1019-1. 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 an aliquot of the desorbed liquid 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 1,1,2,2-tetrachloroethane 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 1,1,2,2-tetrachloroethane 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:

Method S124 was issued on May 9, 1975 [6], and validated with generated atmospheres which were calibrated by gas chromatography [4]. Average recovery was 106% at 5 ppm. Breakthrough did not occur after sampling 4 hrs at 0.185 L/min from an atmosphere containing 101 mg/m³ in dry air. Desorption efficiency for SKC Lot 104 petroleum-based charcoal was 0.83, 0.87, and 0.88 at 0.16, 0.32, and 0.64 mg 1,1,2,2-tetrachloroethane per sample, respectively. Lower recoveries were observed for coconut shell charcoal (SKC Lot 105). In subsequent work, 1,1,2,2-tetrachloroethane was observed to degrade rapidly into trichloroethylene during storage on Pittsburgh activated carbon; 19% converted during one day and 63% converted during eight days at ambient conditions [8]. Therefore, the analyte is sensitive to the sorbent type; only the recommended sorbent should be used.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to 1,1,2,2-Tetrachloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-121 (1976), available as PB 273-802 from NTIS, Springfield, VA 22161.

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

[3] Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978), available as PB81-227001 from NTIS, Springfield, VA 22161.
[4] Documentation of the NIOSH Validation Tests, S124, 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.
[5] UBTL Report for Sequence 1977 (NIOSH, unpublished, September 7, 1979).
[6] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S124, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[7] 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.
[8] Arnold, J. Internal memo (NIOSH, unpublished, May 8, 1984).

METHOD WRITTEN BY: G. David Foley, NIOSH/DPSE.

FORMULA: $Pb(C_2H_5)_4$

M.W.: 323.44

TETRAETHYL LEAD (as Pb)

METHOD: 2533
ISSUED: 8/15/87

OSHA: 0.075 mg/m³ (as Pb; skin)
NIOSH: no recommended standard [1]
ACGIH: 0.1 mg/m³ (as Pb; skin)

PROPERTIES: liquid; d = 1.653 g/mL @ 20 °C; BP 100 °C (dec.); MP -130 to -138 °C; VP 27 Pa (0.2 mm Hg; 2.2 g/m³) @ 20 °C

SYNONYMS: TEL; lead tetraethyl; CAS #78-00-2.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(XAD-2 resin, 100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 30 L
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: 100% recovery after 1 week @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.045 to 0.20 mg/m³ (as Pb) (120-L samples) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.087 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOTOIONIZATION DETECTOR

ANALYTE: tetraethyl lead

DESORPTION: 1 mL pentane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 185 °C
-MANIFOLD: 200 °C
-PID: 210 °C
-COLUMN: 75 °C

CARRIER GAS: N_2, 20 mL/min

COLUMN: 3 m x 3 mm OD stainless steel packed with 5% Carbowax 20M on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of tetraethyl lead in pentane

RANGE: 2 to 30 µg (as Pb) per sample

ESTIMATED LOD: 0.1 µg (as Pb) per sample [2]

PRECISION (s_r): 0.067 @ 4.3 to 17 µg (as Pb) per sample

APPLICABILITY: The working range is 0.017 to 0.23 mg/m³ (as Pb) for a 120-L air sample.

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

OTHER METHODS: This revises Method S383 [3].

REAGENTS:

1. Pentane (reagent grade).
2. Tetraethyl lead.*
3. XAD-2 resin (Rohm & Haas Co.). Extract, in order, for 24 hrs each in Soxhlet or Giant extractor with: water, methanol, diethylether, and n-pentane. Dry 24 hrs under vacuum (0.1 to 1 kPa) at low heat.
4. Calibration stock solution, 2 mg/mL (as Pb). Dissolve 31.2 mg tetraethyl lead (ca. 19 µL) in pentane to make 10 mL solution. Prepare in duplicate.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tubes, 10-cm long, 6-mm OD, and 4-mm ID with plastic caps, containing two sections of 20/50 mesh XAD-2 resin (front = 100 mg, back = 50 mg), separated and contained by silylated glass wool plugs. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1.0 L/min, with flexible connecting tubing.
3. Gas chromatograph, with photoionization detector, integrator, and column.
4. Vials, 2-mL, glass, with PTFE-lined caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-µL, readable to 0.1 mL.
7. Pipet, 1 mL, with bulb.

SPECIAL PRECAUTIONS: Tetraethyl lead is extremely poisonous. Acute or chronic poisoning may occur if inhaled or absorbed through skin [1].

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 1 L/min for a total sample size of 30 to 200 L.
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 plugs.
6. Add 1.0 mL pentane to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as 0.1% (v/v) dodecane, may be added to samples, blanks, and working standards at this step [3].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to pentane in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain tetraethyl lead (as Pb) concentrations in the range 0.1 to 30 µg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph [peak area vs. µg tetraethyl lead (as Pb)].
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of 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 with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. µg tetraethyl lead (as Pb) recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2533-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE 1: Under these conditions, t_r = 4.5 min for tetraethyl lead; dodecane elutes later.
NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with pentane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of tetraethyl lead (as Pb) 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 tetraethyl lead (as Pb) in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S383 was issued on March 18, 1977 [3], and validated with generated atmospheres in the range 0.045 to 0.2 mg/m³ for eighteen 120-L samples [2,4]. Partial breakthrough (effluent = 2.5% of test concentration) occurred after sampling for 240 min at 1.0 L/min from an atmosphere containing 0.156 mg/m³ tetraethyl lead (as Pb) at 90% RH. Desorption efficiency for eighteen spiked samples in the range 4.3 to 17 µg tetraethyl lead (as Pb) averaged 1.05 with s_r = 0.04.

REFERENCES:

[1] 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.
[2] A. D. Little, Inc., Backup Data Report S383 prepared under NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB-275-834 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S383, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: G. David Foley, NIOSH/DPSE.

FORMULA: $Pb(CH_3)_4$

M.W.: 267.33

TETRAMETHYL LEAD (as Pb)

METHOD: 2534
ISSUED: 8/15/87

OSHA: 0.075 mg/m³ (as Pb; skin)
NIOSH: no recommended standard [1]
ACGIH: 0.15 mg/m³ (as Pb; skin)

PROPERTIES: liquid; d 1.99 g/mL @ 20 °C;
BP 110 °C; MP -30 °C;
VP 2.9 kPa (22 mm Hg; 268 g/m³ as Pb) @ 20 °C;
lower explosive limit 1.8% v/v in air

SYNONYMS: TML; lead tetramethyl; CAS #75-74-1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(XAD-2 resin, 400 mg/200 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 15 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 98% recovered after 7 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.04 to 0.18 mg/m³ (as Pb) (24-L samples) [2]

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.087 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOTOIONIZATION DETECTOR

ANALYTE: tetramethyl lead

DESORPTION: 2 mL pentane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 185 °C
-MANIFOLD: 200 °C
-PID: 210 °C
-COLUMN: 75 °C

CARRIER GAS: N_2, 17 mL/min

COLUMN: 6 m x 3 mm OD stainless steel packed with 10% Carbowax 20M on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of tetramethyl lead in pentane

RANGE: 1 to 10 µg (as Pb) per sample

ESTIMATED LOD: 0.4 µg (as Pb) per sample [3]

PRECISION (s_r): 0.091 @ 0.9 to 3.6 µg (as Pb) per sample [2]

APPLICABILITY: The working range is 0.04 to 0.4 mg/m³ (as Pb) for a 24-L air sample.

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

OTHER METHODS: This revises Method S384 [3].

REAGENTS:

1. Pentane (reagent grade).
2. Tetramethyl lead.*
3. XAD-2 resin (Rohm & Haas Co.). Extract, in order, for 24 hrs each in Soxhlet or Giant extractor with: water, methanol, diethylether, and n-pentane. Dry 24 hrs under vacuum (0.1 to 1 kPa) at 70 °C.
4. Calibration stock solution, 0.4 mg/mL (as Pb). Dissolve 5.16 mg tetramethyl lead (ca. 2.6 µL) in pentane to make 10 mL solution. Prepare in duplicate.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10-cm long, 8-mm OD and 6-mm ID, with plastic caps, containing two sections of 20/50 mesh XAD-2 resin (front = 400 mg, back = 200 mg), separated and contained by silylated glass wool plugs. Pressure drop <3.4 kPa @ 1 L/min airflow. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph with photoionization detector, integrator, and column (page 2534-1).
4. Vials, 4-mL, glass, and PTFE-lined caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-µL, readable to 0.1 µL.
7. Pipets, 1- and 2-mL.

SPECIAL PRECAUTIONS: Tetramethyl lead is extremely poisonous with delayed symptoms [1]. Acute or chronic poisoning may occur if inhaled or absorbed through skin.

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 of 15 to 100 L.
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 2.0 mL pentane to each vial containing 400 mg sorbent, and 1.0 mL pentane to each vial containing 200 mg sorbent. Cap each vial.
   NOTE: A suitable internal standard (e.g., 0.1% v/v nonane) may be added to samples and blanks at this step [2].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to pentane in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain tetramethyl lead concentrations in the range 0.2 to 5 µg/mL (as Pb).
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph [peak area or peak height vs. µg tetramethyl lead (as Pb)].
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of 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 with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. µg tetramethyl lead (as Pb) recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2534-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE 1: Under these conditions, t_r = 6 min for tetramethyl lead.
NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with pentane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area or peak height.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of tetramethyl lead (as Pb) 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 tetramethyl lead (as Pb) in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Method S384 was issued on April 15, 1977 [3], and validated with generated atmospheres [2,4]. Average recovery was 97.4% ± 6.5% (18 samples) in the range 0.04 to 0.18 mg/m³ for 24-L samples. No breakthrough occurred after sampling for 240 min at 0.2 L/min from an atmosphere containing 0.312 mg/m³ tetramethyl lead (as Pb) at 82% RH. Desorption efficiency for eighteen spiked samples in the range 0.89 to 3.6 µg per sample averaged 0.84 with s_r = 0.091. Sample migration between front and back sorbent sections was found to be negligible after storage for 10 days at room temperature.

REFERENCES:

[1] 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.
[2] A. D. Little, Inc. Backup Data Report S384 prepared under NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB-275-834 from NTIS, Springfield, VA 22161.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S384, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY: G. David Foley, NIOSH/DPSE.

FORMULA:  ; C_7H_8

M.W.: 92.14

TOLUENE

METHOD: 4000
ISSUED: 8/15/87

OSHA: 200 ppm; C 300 ppm; P 500 ppm
NIOSH: 100 ppm; 200 ppm/10 min [1,2]
ACGIH: 100 ppm; 150 ppm (STEL)
(1 ppm = 3.77 mg/m³ @ NTP)

PROPERTIES: liquid; d 0.866 g/mL @ 20 °C;
BP 110.6 °C; MP -95 °C;
VP 3.8 kPa (28 mm Hg; 3.7% v/v) @ 25 °C;
explosive range 1.3 to 7.1% v/v in air

SYNONYMS: methylbenzene, CAS #108-88-3.

SAMPLING

SAMPLER: PASSIVE
(activated carbon)

SAMPLE TIME-MIN: 15 min @ 200 ppm
-MAX: 8 hr @ 20 to 200 ppm

SHIPMENT: see step 2 - if necessary, transfer sorbent pad to septum-capped vial; otherwise, routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C if stored in septum-capped vial

FIELD BLANKS: 10% of samples
BULK SAMPLE: desirable

ACCURACY

RANGE STUDIED: 75 to 2250 mg/m³ [3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): 0.038 [3]

MEASUREMENT

!
!TECHNIQUE: GAS CHROMATOGRAPHY, FID
!
!ANALYTE: toluene
!
!DESORPTION: 1.5 mL carbon disulfide; stand
! 30 min
!
!INJECTION VOLUME: 5 µL
!
!TEMPERATURE-INJECTION: 175 °C
! -DETECTOR: 200 °C
! -COLUMN: 100 °C
!
!CARRIER GAS: He or N_2, 30 mL/min
!
!COLUMN: 3.6 m x 3 mm OD SP-1000 on 80/100 mesh
! Chromosorb WHP
!
!CALIBRATION: analyte solutions in CS_2
!
!RANGE: 0.05 to 15 mg per sample
!
!ESTIMATED LOD: 0.01 mg per sample
!
!PRECISION (s_r): 0.022 [3]
!

APPLICABILITY: The working range is 13 to 660 ppm (50 to 2500 mg/m³) for a 4-hour sample. The method is applicable to ceiling determinations. The method determines toluene vapor only (not aerosol). Competitive adsorption by water vapor and other volatile organic solvents affects sampler capacity.

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

OTHER METHODS: NIOSH Methods 1500 and 1501 employ active sampling on charcoal tubes with overall sensitivity about the same as this method.

REAGENTS:

1. Eluent: carbon disulfide (CS_2), chromatographic quality.*
2. Toluene, reagent grade.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: passive monitor with activated charcoal collection element. Monitors must be of known sampling rate for toluene.
2. Gas chromatograph, FID, integrator and column (page 4000-1).
3. Vials, glass, 2-mL, with PTFE-lined septum caps.
4. Pipet, TD, 1.5-mL, and pipet bulb.
5. Syringes, 5-, 10-, 25- and 100-µL.
6. Volumetric flasks, 10-mL.
7. Tweezers.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Remove sampler from package and remove caps if applicable. Attach sampler in worker's breathing zone. Make sure sampler inlets are unobstructed. Record start of sampling time. Follow manufacturer's recommendations to estimate appropriate sampling time based on relative humidity and suspected concentration of toluene.
   NOTE: The uptake constant is only valid for samplers in air with ambient velocity higher than ca. 10 cm/sec. For area samples, ensure adequate air movement.
2. Terminate sampling by sealing the sampler as recommended by the manufacturer or by transferring, in a toluene-free environment, the activated charcoal collection element to a vial and sealing the vial with a septum cap. Use tweezers for handling the collection element, taking care not to touch any activated charcoal.
   NOTE: Some sampler designs (e.g., 3M 3500 [4]) do not require transfer of the collection element; others (e.g., DuPont G-AA and G-BB) require transfer of sorbent pad to a sealed vial. Some sampler designs (e.g., Draeger ORSA-5) use granular sorbent.

SAMPLE PREPARATION:

3. Add 1.5 mL CS_2 to each collection element.
4. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least five working standards.
   a. Add known amounts of toluene to CS_2 in 10-mL volumetric flasks and dilute to the mark to produce toluene concentrations in the range 0.01 to 10 mg/mL.
   b. Analyze with samples and blanks (steps 8 through 10).
   c. Prepare calibration graph (peak area vs. mg toluene).
6. Determine desorption efficiency (DE) in the calibration range at least once for each lot of samplers used. Prepare three samplers at each of five concentrations plus three media blanks.
   a. Place the collection element of a media blank sampler into a vial and cap.
   b. Inject a known amount of toluene directly onto the collection element with a microliter syringe.
   c. Allow to stand overnight.
   d. Desorb (steps 3 and 4) and analyze with working standards.
   e. Prepare a graph of DE vs. mg toluene recovered.

7. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

8. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 4000-1.
9. Inject sample aliquot manually using solvent flush technique or with an autosampler.
   NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with CS_2, reanalyze, and apply the appropriate dilution factor in calculations.
10. Measure peak area.

CALCULATIONS:

11. Determine the mass, mg (corrected for DE), of toluene found on the sample collection element (W) and on the average media blank (B).
    NOTE: If W > sampler capacity x 0.33, the sampler may be saturated [6]. Evaluate each result on the basis of other organics present in the sampled atmosphere, the concentrations of all the adsorbable organics present, the ambient relative humidity, the sampling rate for the organics present and the sampling time.
12. Calculate concentration, C (mg/m^3), of toluene in the air sampled:

$$C = \frac{(W - B) \cdot 10^6}{t \cdot K} .$$

where: t = length of sampling period (min)
K = uptake constant (cm^3 toluene/min).

NOTE: The uptake constant must be known accurately (either be supplied by the sampler manufacturer or determined by the user by calibration with standard toluene-in-air mixtures [5]). K can be estimated from the diffusion coefficient, D (cm^2/min), the cross-sectional area, A (cm^2), and the diffusion pathlength, L (cm), of the sampler:

$$K = \frac{D \cdot A}{L} .$$

EVALUATION OF METHOD:

Precisions and biases listed in the method were determined by analyzing generated atmospheres containing various concentrations of toluene at a range of humidities and in the presence of other volatile organics [3]. Generated concentrations were independently verified.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Toluene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 73-11023 (1973).

[2] 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.

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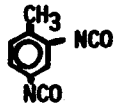
METHOD WRITTEN BY: Mary Lynn Woebkenberg, NIOSH/DPSE.

FORMULA:  ; $C_9H_6N_2O_2$

M.W.: 174.16

TOLUENE-2,4-DIISOCYANATE

NIOSH METHOD: 2535

ISSUED: 8/15/87

OSHA: 0.02 ppm (ceiling)
NIOSH: 35 µg/m³/10 hrs; 140 µg/m³/10 min
ACGIH: TWA 0.005 ppm; STEL 0.02 ppm
(1 ppm = 7.12 mg/m³ @ NTP)

PROPERTIES: liquid; MP 19.5-21.5 °C; BP 251 °C; density 1.2244 g/mL @ 20 °C; VP ca. 1.3 Pa (0.01 mm Hg ; 0.96 mg/m³) @ 20 °C

SYNONYMS: 2,4-TDI; 2,4-bis(carbonylamino)toluene; CAS #584-84-9.

SAMPLING

SAMPLER: TUBE WITH REAGENT-COATED GLASS WOOL (N-[(4-nitrophenyl)methyl]-propylamine on glass wool)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 2 L @ 0.14 mg/m³
-MAX: 170 L

SHIPMENT: protect from light

SAMPLE STABILITY: at least 14 days @ 25 °C [1]

STABILITY OF REAGENT ON GLASS WOOL:
≤ 7 days @ 25 °C; ≥ 4 weeks @ -21 °C

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 0.039 to 0.53 mg/m³[1] (67-L samples)

BIAS: none found [1]

OVERALL PRECISION (s_r): 0.033 [1]

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 3,3'-bis[(4-nitrophenyl)methyl]-3,3'-dipropyl-1,1'-(4-methyl-1,3-phenylene) diurea (2,4-TDIU)

RECOVERY: 2 mL CH_3OH; ultrasonic bath, 3 min

INJECTION VOLUME: 50 µL

MOBILE PHASE: 55:45 (v/v) CH_3CN:H_2O with 0.08% Et_3N and 0.16% H_3PO_4; 1.0 mL/min

DETECTOR: UV @ 254 nm

COLUMN: 25 cm x 4.6 mm; octadecylsilylated silica, 5-µm particle size

CALIBRATION: standard solutions of 2,4-TDIU in CH_3OH

RANGE: 0.3 to 25 µg 2,4-TDI per sample

ESTIMATED LOD: 0.1 µg 2,4-TDI per sample

PRECISION (s_r): 0.067 [1]

APPLICABILITY: The working range is 0.004 to 0.35 ppm (0.03 to 2.5 mg/m³) for a 10-L air sample. This method is applicable to isocyanate vapors (2,4-TDI vapor, 2,6-TDI vapor, and hexamethylene diisocyanate (HDI) vapor) [2,3], but not aerosols because of inefficient collection of aerosols and incomplete reaction of aerosol isocyanates with reagent.

INTERFERENCES: The reagent is slightly unstable in the dark at 25 °C. Tailing during HPLC, a result of reagent deterioration, may raise detection limits .

OTHER METHODS: This revises P&CAM 326 [4]. Sangö used similar HPLC conditions [5]. Melcher reviewed methods for isocyanates [6].

REAGENTS:

1. 2,4-TDI* (see APPENDIX A).
2. N-[(4-nitrophenyl)methyl]-propylamine hydrochloride.
3. 2,4-TDIU (see APPENDIX B).
4. Methanol, chromatographic quality.
5. Calibration stock solution, 10 mg/mL. Dissolve 50 mg 2,4-TDIU in methanol to make 5 mL solution.
6. Water, distilled.
7. NaOH, 1 M.
8. Toluene, reagent grade.
9. Dichloromethane, reagent grade.
10. Hexane, reagent grade.*
11. Nitrogen, purified, compressed.
12. Mobile phase. Mix 0.8 mL triethylamine and 1.6 mL H_3PO_4 with 1 L 55:45 CH_3CN:H_2O (v/v).*
13. Dibutylamine, 99% pure.
14. Tetrahydrofuran, reagent grade.*
15. Bromocresol purple indicator solution.
16. HCl, 0.05 M, standardized.
17. 2,4-TDI stock solution, 100 mg/mL. Dissolve 500 mg 2,4-TDI in dichloromethane to make 5 mL solution.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 4 cm x 6 mm ID, containing two sections of reagent-coated glass wool (see APPENDIX C); front section, 7 mm long; back section, 5 mm long. Reagent-coated glass wool is compressed tightly. Seal ends of sampler with plastic caps. Wrap midsection of sampler with black tape. Protect sampler from light. Sampler may be stored at -21 °C in the dark for at least four weeks. Limit period of storage of sampler at 25 °C in the dark to seven days.
2. Separatory funnels, 125-mL.
3. Beakers, 50- and 125-mL.
4. Aluminum foil.
5. Glass wool, silanized.
6. Glass rod, 15 cm x 4 mm.
7. Tweezers.
8. Glass tube with right-angle bend, 4.5 cm x 6 mm ID, wrapped with black tape.
9. Rubber tubing, opaque 1.5 cm x ca. 8 mm ID.
10. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
11. High pressure liquid chromatograph, 254-nm UV detector, integrator, and column (page 2535-1).
12. Vials, glass, 2-mL, caps lined with PTFE.
13. Pipets, 2-, 15-, and 25-mL.
14. Ultrasonic bath.
15. Syringes, 100-µL, readable to 1 µL.
16. Syringes, 10-µL, readable to 0.1 µL.
17. Volumetric flasks, 5-mL.
18. Buret, 50-mL.
19. U-tube, glass, 25 cm x 15 mm ID, glass stopcocks.
20. Sorbent tube, glass, 7 cm x 6 mm, coconut shell charcoal, ca. 150 mg.

SPECIAL PRECAUTIONS: 2,4-TDI can irritate the eyes and skin, and can cause bronchial asthma and allergic eczema. Flash points of hexane, tetrahydrofuran and triethylamine are -26 °C, -17 °C, and -6 °C, respectively.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove plastic caps from sampler. Attach one end of glass tube with right-angle bend directly to inlet of sampler with short piece of opaque rubber tubing.
3. Sample 2 to 170 L of air at 0.2 to 1 L/min. Seal ends of sampler with plastic caps.

SAMPLE PREPARATION:

4. Transfer front and back sections of reagent-coated glass wool to separate vials. Add 2 mL methanol. Seal vials.
5. Place vials into ultrasonic bath for 3 min.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least five working standards over the range 0.3 to 80 µg 2,4-TDIU per sample (equivalent to 0.1 to 25 µg 2,4-TDI per sample).
   a. Prepare a series of standard solutions of 2,4-TDIU in methanol over the range of 0.15 to 40 µg/mL.
   b. Analyze together with samples and blanks (steps 8 and 9).
   c. Prepare calibration graph (peak area vs. µg 2,4-TDIU).
7. Determine recoveries from samplers in the range 0.3 to 25 µg 2,4-TDI per sample. Prepare three samples at each of three levels plus three media blanks.
   NOTE: Recoveries should be quantitative. If recoveries are not quantitative, attempt to determine the reason for error.
   a. Prepare a series of standard solutions of 2,4-TDI in dichloromethane in the range 0.06 to 5 mg/mL.
   b. Connect a U-tube to the inlet of a sampler with a short piece of tubing.
   NOTE: The length of tubing should be minimal to prevent losses of TDI by adsorption or reaction on the inside wall of the tubing.
   c. Connect charcoal sorbent tube to inlet of U-tube (charcoal can adsorb contaminants of air which would react with 2,4-TDI).
   d. Draw ambient air through the charcoal tube, U-tube, and sampler with a sampling pump at 1 L/min.
   e. Place 5 µL of a standard solution of 2,4-TDI into the U-tube.
   f. Allow operation of the pump to continue for 20 min.
   g. Analyze the sampler for 2,4-TDIU (steps 6 and 7 and 10 through 12).

MEASUREMENT:

8. Establish chromatographic conditions indicated on page 2535-1.
9. Inject sample aliquot manually or with autosampler. Measure peak area.

CALCULATIONS:

10. Determine the mass (µg) of 2,4-TDIU found on the sample front (W_f) and back (W_b) sections and in the average media blank front (B_f) and back (B_b) sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
11. Calculate concentration, C, of 2,4-TDI in the air volume sampled, V (L):

$$C = \frac{0.310\ (W_f + W_b - B_f - B_b)}{V}\ mg/m^3,$$

where 0.310 = M.W. of 2,4-TDI/M.W. of 2,4-TDIU.

EVALUATION OF METHOD:

A variation of this method which involved normal-phase HPLC (Method P&CAM 326) was tested with fortified samplers and atmospheres generated with a diffusion cell [1,4]. Average recoveries of 2,4-TDIU from front sections of reagent-coated glass wool were 0.97 to 0.99 after applications of 1.0-, 2.1-, 9.9-, and 20.0-µg quantities of 2,4-TDI from a U-tube; s_r was 0.067 (21 samples, pooled). s_r was 0.033 (29 samples, pooled) for 67-L samples at 0.039 to 0.53 mg/m³. The independent method used for evaluation was that of Meddle and Wood [7]. Average concentrations ranged from 0.054 to 0.46 mg/m³ by the independent method [1]. Conclusive evidence for bias in the reagent-coated glass wool method was not found. Breakthrough volume was 71 L (0.53 mg/m³, 1 L/min); breakthrough volume was 279 L (0.14 mg/m³, 1 L/min). 2,4-TDIU was stable on coated glass wool at room temperature in the dark for 14 days. The reagent, N-[(4-nitrophenyl)methyl]propylamine, is unstable [1].

Evaluation of samplers with 2,4-TDI aerosols was not performed. However, samplers were inefficient collectors when aerosol particles were present in an atmosphere of 4,4'-methylenediphenylisocyanate (MDI). The collection efficiency of each sampler for MDI was about 90% (flow rate, 1 L/min; total concentration of MDI in vapor and aerosol forms, about 0.52 mg/m^3; mass median diameter of MDI particles, about 0.6 µm; geometric standard deviation, about 2.2) [1].

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METHOD REVISED BY: Samuel P. Tucker, Ph.D., NIOSH/DPSE.

APPENDIX A: Determination of Purity of 2,4-TDI

Dissolve 480 µL (365 mg, 0.00282 mole) dibutylamine in 10 mL tetrahydrofuran. Add 100 µL (122 mg, 0.000701 mole) 2,4-TDI. Stir the mixture and allow to stand 6 min. Add a few drops of bromocresol purple indicator solution. Prepare two additional samples in this manner. Titrate excess dibutylamine with 0.05 M HCl. Calculate percent purity, P, of 2,4-TDI for each sample:

$$P = \frac{(B - V \cdot M)}{2W} \cdot 100.$$

where: B = Molar quantity of dibutylamine before reaction (0.00282)
V = Volume of 0.05 M HCl (L)
M = Concentration of HCl (0.05M)
2 = Number of moles of dibutylamine required to react with 1 mole of 2,4-TDI
W = Molar quantity of 2,4-TDI added to tetrahydrofuran solution (0.000701)

APPENDIX B: Preparation of 2,4-TDIU [8]

Dissolve 1.03 g (0.00446 mole) N-[(4-nitrophenyl)methyl]-propylamine hydrochloride in 25 mL water in a 125-mL separatory funnel. Add 15 mL 1 M NaOH and shake the mixture. Extract the N-[(4-nitrophenyl)methyl]propylamine with 50 mL toluene, and separate the phases. Add a solution of 262 µL (321 mg, 0.00184 mole) 2,4-TDI in 30 mL toluene to the solution of N-[(4-nitrophenyl)methyl]propylamine. Collect the precipitate by filtration. Purify the product by dissolving it in a small volume of dichloromethane and precipitating it with hexane. Dry the product in vacuo (MP = 136 to 139 °C).

APPENDIX C: Preparation of Reagent-Coated Glass Wool

Dissolve 300 mg (0.00130 mole) N-[(4-nitrophenyl)methyl]propylamine hydrochloride in 25 mL water in a 125-mL separatory funnel. Add 15 mL 1 M NaOH and shake the mixture. Extract the N-[(4-nitrophenyl)methyl]propylamine with 50 mL hexane. Transfer 40 mL of the hexane solution to a 50-mL beaker which is wrapped with aluminum foil and contains 1.82 g silanized glass wool. Under dim light, evaporate hexane from the beaker with the aid of a stream of nitrogen. Knead the glass wool with a glass rod to produce a uniform coating. Continue to evaporate hexane until the glass wool appears dry. Protect the coated glass wool from bright light. The quantity of coated glass wool is sufficient for the preparation of the front and back sections for twenty samplers.

FORMULA: Cl_2=CHCl; C_2HCl_3

M.W.: 131.39

TRICHLOROETHYLENE

METHOD: 1022
ISSUED: 8/15/87

OSHA: 100 ppm; C 200 ppm; P 300 ppm
NIOSH: 100 ppm; C 150 ppm/10 min; suspect carcinogen [1,2,3]
ACGIH: 50 ppm; STEL 200 ppm
(1 ppm = 5.37 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.46 g/mL @ 20 °C; [3,4] BP 87 °C; MP -86 °C; VP 9.9 kPa (74 mm Hg; 9.8% v/v) @ 25 °C;

SYNONYMS: trichloroethene; CAS #79-01-6.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 477 to 2025 mg/m³ (3.4-L samples) [5]

BIAS: not significant [5]

OVERALL PRECISION (s_r): 0.082 [5]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: trichloroethylene

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 70 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: 3 m x 3 mm OD stainless steel, packed with 10% OV-101 on 100/120 mesh Chromosorb WHP

CALIBRATION: standard solutions of trichloroethylene in CS_2

RANGE: 0.5 to 10 mg per sample

ESTIMATED LOD: 0.01 mg per sample [6]

PRECISION (s_r): 0.038 @ 1.6 to 6.4 mg per sample [5]

APPLICABILITY: The working range is 27 to 875 ppm (150 to 4700 mg/m³) for a 3.4-L air sample. The method is applicable to 10-min ceiling determinations. The method was used for samples containing 0.5 to 5 mg trichloroethylene from a tool-degreasing operation [6].

INTERFERENCES: None studied. Alternate columns which have been used are: stainless steel, 6 m x 3 mm OD, packed with 10% SP-1000 on 80/100 mesh Supelcoport [6] and fused silica capillary, 60 m x 0.32 mm, coated with 0.25 µm OV-351 [7].

OTHER METHODS: This combines and revises methods S336 [8] and P&CAM 127 [9]. The criteria document method is similar [3]. Method 3701 uses a portable gas chromatograph for field readout.

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. Trichloroethylene (TCE), reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*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.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (see page 1022-1).
4. Vials, 2-mL, PTFE-lined septum caps.
5. Syringes, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Trichloroethylene is a suspect carcinogen and a narcotic [1,2,3]. Work with these substances only in a 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 of 1 to 30 L.
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 ethylbenzene [5], undecane [6], or octane [7] at 0.1% (v/v) may be added at this step.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of TCE to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain TCE concentrations in the range 0.01 to 10 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg TCE).

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of TCE, or a standard solution thereof in CS_2, 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 with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg TCE recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1022-1. 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 an aliquot of the desorbed liquid 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 TCE 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 TCE 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:

Method S336 was issued on June 6, 1975 [8], and validated with generated atmospheres using a calibrated syringe drive [5]. Average recoveries were 92 to 94% (16 samples) in the range 477 to 2025 mg/m³ for 3.4-L samples. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 99 min at 0.187 L/min from an atmosphere containing 2266 mg/m³ trichloroethylene in dry air. Desorption efficiency for SKC Lot 105 activated coconut charcoal in the range 1.6 to 6.4 mg per sample averaged 96.4% with s_r = 0.7% (18 samples). n-Octane was used as an internal standard in the chromatographic measurements. The semi-quartile ranges of desorption efficiencies in two rounds of the Proficiency Analytical Testing (PAT) program were 0.97 to 1.0 for charcoal tubes spiked with 0.6 to 1.1 mg trichloroethylene [10].

REFERENCES:

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METHOD WRITTEN BY: G. David Foley, NIOSH/DPSE.

FORMULA: $Cl_2C=CHCl$; C_2HCl_3

M.W.: 131.39

TRICHLOROETHYLENE by portable GC

METHOD: 3701

ISSUED: 8/15/87

OSHA: 100 ppm; C 200 ppm; P 300 ppm
NIOSH: 100 ppm; 150 ppm/10 min; suspect carcinogen [1,2,3]
ACGIH: 50 ppm; 200 ppm STEL
(1 ppm = 5.37 mg/m³ @ NTP)

PROPERTIES [3,4]: liquid; d 1.46 g/mL @ 20 °C; BP 87 °C; MP -86 °C; VP 7.7 kPa (58 mm Hg; 7.6% v/v) @ 20 °C; explosive range 11 to 41% v/v in air

SYNONYMS: trichloroethene; CAS #79-01-6.

SAMPLING

SAMPLER: AIR BAG (Tedlar)

FLOW RATE: 0.02 to 0.05 L/min or higher; fill bag to ≤80% of capacity; spot samples possible (step 2.a.)

SAMPLE STABILITY: bags should be analyzed as soon after collection as possible (≤4 hrs)

FIELD BLANKS: clean air, either in bag or from a non-work area

ACCURACY

RANGE STUDIED: 25 to 100 ppm

BIAS: not determined

OVERALL PRECISION (s_r): 0.078

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: trichloroethylene (TCE)

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 10 to 1000 ppm

ESTIMATED LOD: 0.25 ng per injection (0.1 ppm for a 1-mL injection)

PRECISION (s_r): 0.078

APPLICABILITY: The working range is 10 to 1000 ppm (54 to 5400 mg/m³) in relatively non-complex atmospheres where trichloroethylene is known to be present (see EVALUATION OF METHOD).

INTERFERENCES: None found.

OTHER METHODS: Method 1022 uses activated charcoal sampler tubes.

REAGENTS:

1. Trichloroethylene (TCE)* in air, working standards prepared in the field by filling Tedlar bags with commercially prepared and certified standards (preferred) or prepared in the field by injecting known amounts of pure trichloroethylene into Tedlar bags containing a metered volume of pure air or nitrogen.
2. Cylinder of air, nitrogen or helium for use as carrier gas and field blanks.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with photoionization detector, preferably with gas sampling loop and (if appropriate) strip chart recorder.
2. Personal sampling pump, 0.02 to 0.05 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
3. Bags, Tedlar, 2- to 20-L or other appropriate sizes.
4. Syringes, gas-tight, of various sizes appropriate to the GC, and for preparation of bag standards.
   NOTE: To reduce the possibility of contamination, use separate, previously unused syringes for working standards and samples. Test syringes for contamination occasionally by filling them with clean air and analyzing the contents.
5. Label tape and marking pen for labelling bags.

SPECIAL PRECAUTIONS: TCE is a suspect carcinogen [1]. Shipment of compressed gases must comply with 49 CFR 171-177 regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC instrument and recorder and allow to warm up according to manufacturer's instructions.
   NOTE: A straight line baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
   a. Spot sample. Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
      NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
      (1) use a gas sampling loop for injections, if available;
      (2) make at least three replicate determinations per sample;
      (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration; and
      (4) set conditions such that peaks are at least 50% of full scale.
   b. Integrated air sample for TWA determination.
      (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
      NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
      (2) Attach the sample bag to a personal sampling pump suitable for bag filling with a minimum length of flexible tubing.
      (3) Pump the air to be sampled into the sample bag at a rate calculated to fill $\leq$80% of the sample bag capacity over the sampling period.
      NOTE: The flow rate must remain within $\pm$5% of the initial setting throughout the sampling period.

(4) Within 4 hrs after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2.a).

3. Obtain the TCE peak height of the injected sample.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory before field work begins:
   a. Establish a laboratory calibration graph by at least three replicate determinations of at least five working standards. Plot peak height vs. mass of TCE.
   b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
   c. Determine the ability of the GC column to separate the TCE peak from other substances known or predicted to be present in the field samples.
5. Establish a daily calibration graph (peak height vs. mass of TCE) by triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate mass, W (ng), of TCE in sample by comparison of peak height with daily calibration graph (step 5). Determine concentration, C, of TCE in the injected sample, V (mL):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

NOTE: Some GCs perform this calculation electronically.

EVALUATION OF METHOD:

This method was evaluated using an AID Model 590 portable GC. Gas bags containing known amounts of TCE in air were used to establish the calibration graph. The response of the portable GC was then compared to the concentration obtained from analysis of replicate charcoal tube samples taken from the same bag. A six-inch strip chart recorder was used to obtain peak height data from the portable GC.

A limitation in the use of this type of portable GC (e.g., packed column, room temperature isothermal) is the limited ability to separate the analyte from any interferences present. In the evaluation of this method, a six-foot DC 200 column was used. Its ability to separate the TCE peak from other contaminants was not evaluated. However, the use of this or any other packed column operated at room temperature to separate complex mixtures is severely limited. Therefore, the application of this method should be confined to relatively uncomplicated atmospheres.

REFERENCES:

[1] NIOSH Current Intelligence Bulletin 2, Trichloroethylene, NIOSH (June 6, 1975), U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-127 (1979).
[2] Special Occupational Hazard Review with Control Recommendations — Trichloroethylene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-130 (1978).
[3] Criteria for a Recommended Standard...Occupational Exposure to Trichloroethylene, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 73-11025 (1973).
[4] NIOSH/OSHA Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 78-210 (1978).

METHOD WRITTEN BY: J. C. Posner, Ph.D., NIOSH/DPSE

FORMULA: CCl_3F

M.W.: 137.37

TRICHLOROFLUOROMETHANE

METHOD: 1006
ISSUED: 8/15/87

OSHA: 1000 ppm
NIOSH: no recommended standard [1]
ACGIH: C 1000 ppm
(1 ppm = 5.62 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.53 g/mL @ 0 °C;
BP 23.8 °C; MP -111 °C;
VP 92 kPa (690 mm Hg; 91% v/v) @ 20 °C;
not combustible

SYNONYMS: Freon 11; fluorotrichloromethane; CAS #75-69-4.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal,
400 mg/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.3 L
-MAX: 7 L

SHIPMENT: refrigerate

SAMPLE STABILITY: quantitative recovery
after 7 days @ 25 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 2390 to 10500 mg/m³ [2]
(4-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.072 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: trichlorofluoromethane

DESORPTION: 5 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 220 °C
-COLUMN: 65 °C

CARRIER GAS: nitrogen, 30 mL/min

COLUMN: 6 m x 3 mm OD stainless steel packed
with 10% FFAP on 100/120 Chromosorb WHP

CALIBRATION: standard solutions of analyte in
CS_2

RANGE: 2 to 40 mg per sample

ESTIMATED LOD: not determined

PRECISION (s_r): 0.063 @ 11 to 32 mg per
sample [2]

APPLICABILITY: The working range is 500 to 10000 mg/m³ (90 to 1800 ppm) for a 4-L air sample.

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

OTHER METHODS: This revises Method S102 [3].

REAGENTS:

1. Eluent: carbon disulfide,* chromatographic quality, containing 0.1% (v/v) nonane as internal standard.
2. Trichlorofluoromethane, 99%.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 8 mm OD, 6 mm ID, flame-sealed ends with plastic caps, containing two sections of 20/40 mesh activated (600 °C) coconut shell charcoal (front = 400 mg; back = 200 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 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1006-1).
5. Vials, glass, 10-mL, PTFE-lined septum crimp caps.
6. Syringes, 10-µL, readable to 0.1 µL.
7. Syringes, gas-tight, 10-µL to 10-mL.
8. Syringe needle, 22-gauge.
9. Volumetric flasks, 10-mL.
10. Pipet, TD, 5-mL.
11. Balance, 0.1-mg sensitivity.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). Work with it only in a hood and away from spark sources.

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 0.05 L/min for a total sample size of 0.3 to 7 L.
4. Cap the sampler. Pack securely for shipment in an insulated container with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler in separate vials. Discard the glass wool plugs. Seal each vial with a septum and crimp seal.
6. Insert a syringe needle through the septum to serve as a vent.
7. Add 5.0 mL eluent to each vial with a syringe. Remove the vent from the septum.
8. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least five working standards over the range 0.01 to 40 mg trichlorofluoromethane per sample. Use serial dilutions for the smallest concentrations.
   a. Add 5.0 mL eluent to each of a series of vials. Attach septum with crimp seal to each vial.

b. Weigh each vial.
c. Inject amounts (2 to 30 µL) of neat liquid trichlorofluoroethylene (or of a standard solution in CS_2) into the vials.
d. Reweigh the vials. Calculate the mass of trichlorofluoromethane added.
e. Analyze with samples and blanks (steps 12 and 13).
f. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg trichlorofluoromethane).

10. 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 levels plus three media blanks.
a. Add 400 mg charcoal (e.g., an unused front section) to each of a series of vials.
b. Seal each vial with a septum and crimp seal.
c. Weigh each vial.
d. Inject amounts (2 to 30 µL) of neat trichlorofluoromethane (or of a standard solution in CS_2) into the vials.
e. Reweigh each vial. Calculate the mass of trichlorofluoromethane added. Allow to stand overnight.
f. Desorb (steps 6 through 8) and analyze with freshly prepared working standards (steps 12 and 13).
g. Prepare a graph of DE vs. mg trichlorofluoromethane recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1006-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
NOTE 1: t_r = 3 min for trichlorofluoromethane and 4.5 min for nonane under these conditions.
NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
13. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of trichlorofluoromethane found in the sample front (W_f) and back (W_b) sorbent tubes, and in the average media blank front (B_f) and back (B_b) sorbent tubes.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of trichlorofluoromethane 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:

Method S102 was issued on October 29, 1976 [3], and validated with atmospheres generated by a cooled, calibrated syringe drive [2]. Average recovery was 0.98 with s_r = 0.046 (17 samples) in the range 2388 to 10520 mg/m³ for 4-L samples. No significant difference in recovery

was seen between samples (with or without backup sections) stored one or seven days at room temperature. In a separate experiment to check for migration, no significant difference in recovery was seen in samples stored for seven days, with and without backup sections, and no analyte was detectable in any of the backup sections.

Results of breakthrough (effluent concentration = 5% of test concentration) experiments were:

Charcoal, mg	Breakthrough Volume, L	Breakthrough Capacity, mg	Test Concentration, mg/m³	Rate L/min	Humidity, % RH	Ref.
100	2	25	12502	0.05	0	[4]
400	10.5	112	10660	0.187	0	[2]
400	6.2	63	10170	0.187	90	[2]

Desorption efficiency for seventeen 400-mg samples of SKC Lot 105 charcoal spiked with 10.5 to 32 mg trichlorofluoromethane averaged 1.04 with s_r = 0.063.

REFERENCES:

[1] 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.

[2] Backup Data Report for Fluorotrichloromethane, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB-271-712 from NTIS, Springfield, VA 22161.

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S102, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] Failure Report S102, prepared under Contract No. CDC (NIOSH) 99-74-45 (NIOSH, unpublished, 1977).

METHOD REVISED BY: G. David Foley, NIOSH/DPSE.

FORMULA: $CCl_2F-CClF_2$

M.W.: 187.38

1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE

METHOD: 1020
ISSUED: 8/15/87

OSHA: 1000 ppm
NIOSH: no recommended standard [1]
ACGIH: 1000 ppm; STEL 1250 ppm
(1 ppm = 7.66 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.55 g/mL @ 20 °C;
BP 47.6 °C; MP -35 °C;
VP 38 kPa (384 mm Hg; 51% v/v) @ 20 °C;
not combustible

SYNONYMS: Refrigerant 113; TTE; CAS #76-13-1.

SAMPLING

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

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 0.1 L @ 1000 ppm
-MAX: 2.5 L

SHIPMENT: refrigerated

SAMPLE STABILITY: not determined

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 3300 to 14200 mg/m³ [2]
(1.5-L samples)

BIAS: not significant [2]

OVERALL PRECISION (s_r): 0.07 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: 1,1,2-trichloro-1,2,2-trifluoroethane

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 200 °C
-DETECTOR: 200 °C
-COLUMN: 150 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 1.9 m x 6 mm OD, packed with 50/80 mesh Porapak Q

CALIBRATION: standard solutions of analyte in CS_2

RANGE: 1 to 20 mg per sample

ESTIMATED LOD: not determined

PRECISION (s_r): 0.02 @ 5.6 to 23 mg per sample [2]

APPLICABILITY: The working range is 670 to 13300 mg/m³ (86 to 1740 ppm) for a 1.5-L air sample.

INTERFERENCES: None studied.

OTHER METHODS: This revises Method S129 [3].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. 1,1,2-Trichloro-1,2,2-trifluoroethane (TTE), reagent grade.*
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, filtered, compressed.

*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.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Refrigerant, bagged, and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see page 1020-1).
5. Vials, 2-mL, PTFE-lined caps.
6. Syringes, 10- to 100-µL, readable to 0.5%.
7. Volumetric flasks, 10-mL.
8. Pipet, TD 1-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C). 1,1,2-Trichloro-1,2,2-trifluoroethane is a narcotic [1]. Work with these compounds only in a 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 0.05 L/min for a total sample size of 0.1 to 2.5 L.
4. Cap the samplers. Pack securely for shipment in a refrigerated container.

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.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of TTE to CS_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain TTE concentrations in the range 0.1 to 20 mg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg TTE).
9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. 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 (2 to 20 µL) of TTE or a standard solution of TTE in CS_2 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 with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg TTE recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1020-1. 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 an aliquot of the desorbed liquid 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 TTE 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 TTE 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:

Method S129 was issued on May 9, 1975 [3], and validated with generated atmospheres using calibrated syringe drive and independent verification by gas chromatography [2]. Average recovery was 100.3% (18 samples) in the range 3300 to 14,200 mg/m³ for 1.5-L samples. Breakthrough (effluent = 5% of test concentration) occurred after sampling for 60 min at 0.046 L/min from an atmosphere containing 14,500 mg/m³ 1,1,2-trichloro-1,2,2-trifluoroethane in dry air. Desorption efficiency for 18 samples of SKC Lot 105 activated coconut charcoal spiked with 5.6 to 23 mg 1,1,2-trichloro-1,2,2-trifluoroethane averaged 1.01 with $s_r = 0.02$.

REFERENCES:

[1] 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.
[2] Documentation of the NIOSH Validation Tests, S129, 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.
[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2, S129, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

METHOD REVISED BY: G. David Foley, NIOSH/DPSE; S129 originally validated under NIOSH Contract CDC-99-74-45.

FORMULA: (1): V_2O_5; (2): V_2O_3

M.W.: (1): 181.88; (2): 149.88

VANADIUM OXIDES

METHOD: 7504

ISSUED: 8/15/87

OSHA: C 0.5 mg/m³ (as V) (V_2O_5 dust);
C 0.1 mg/m³ (as V) (V_2O_5 fume); 1 mg/m³ (FeV)

NIOSH: 0.05 mg/m³/15 min (as V) (compounds);
1.0 mg/m³ (as V) (V, VC) [1,2]

ACGIH: 0.05 mg/m³ (respirable, as V_2O_5); 1.0 mg/m³ (FeV)

PROPERTIES: solids; MP 658 °C (1);
MP 1967 °C (2)

SYNONYMS: (1): vanadic anhydride; vanadium pentoxide; CAS #1314-62-1.
(2): vanadic oxide; vanadium sesquioxide; vanadium trioxide; CAS #1314-34-7.

SAMPLING

SAMPLER: CYCLONE + FILTER
(10-mm nylon cyclone + 5-µm PVC membrane)

FLOW RATE: 1.7 L/min

VOL-MIN: 200 L @ 0.5 mg/m³
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 10% of samples

BULK SAMPLE: high-volume respirable (preferred) or settled dust to identify interferences

ACCURACY

RANGE STUDIED: (1): 0.8-2.6 mg/m³;
(2): 0.2-2.6 mg/m³ [3]

BIAS: Table 1

OVERALL PRECISION (s_r): Table 1

ANALYSIS

!
!METHOD: X-RAY POWDER DIFFRACTION
!
!ANALYTE: vanadium pentoxide, vanadium trioxide,
! or ammonium metavanadate
!
!SAMPLE PREPARATION: dissolve filter in
! tetrahydrofuran; redeposit
! on Ag filter
!
!XRD: Cu target X-ray tube
! optimize for intensity; 1°2θ slit
! graphite monochromator
! scintillation detector
! integrated intensity with background
! subtraction
! slow step scan (10 seconds/0.02° 2θ)
!
!CALIBRATION: standard suspensions of analytes
! deposited on Ag filters
!
!RANGE: 0.1 to 2 mg V per sample
!
!ESTIMATED LOD: Table 1
!
!PRECISION (s_r): Table 1
!
!
!

APPLICABILITY: The working range is 0.2 to 4 mg/m³ (as V) for a 500-L air sample. The method will determine V_2O_5, V_2O_3, and NH_4VO_3 on the same sample.

INTERFERENCES: Silica (likely to be found in mineral samples) interferes (Table 1) but alternative diffraction lines are available. Most other compounds likely to be in the sample do not interfere [3].

OTHER METHODS: This replaces P&CAM 364 [4]. Methods 7101 [Vanadium (soluble and insoluble) by graphite atomizer AAS] and 7300 (Elements by ICP-AES) determine total V.

REAGENTS:

1. V_2O_5, V_2O_3 or NH_4VO_3 (≥99%). Grind in freezer mill. Sieve through 10-µm sieve in isopropanol (for V_2O_3 or NH_4VO_3) or acetonitrile (for V_2O_5). Dry at 110 °C for one hour. Store in desiccator.
2. Tetrahydrofuran (THF), reagent grade.*
3. Isopropanol, reagent grade.
4. Acetonitrile, reagent grade.
5. Glue or tape for securing silver filters to XRD holders.
6. Desiccant.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Personal sampler: 10-mm nylon cyclone; two-piece filter cassette containing membrane filters, polyvinyl chloride, 37-mm diameter, 5-µm pore size (e.g., FWS-B, MSA, Pittsburgh, PA 15208).
2. Personal sampling pump calibrated to ±5% at 1.7 L/min, with flexible connecting tubing.
3. Area Sampler: 0.5-inch HASL cyclone; polyvinyl chloride membrane filters, 37-mm diameter, 5-µm pore size; 3 piece filter cassette, with high-volume pump (9 L/min).
4. Filters, silver membrane, 25-mm diameter, 0.45-µm pore size (Osmonics, Inc., Minnetonka, MN 55343).
5. X-ray powder diffractometer with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard. Source: Gem Dugout, State College, PA, 16801) for data normalization.
7. Filtration apparatus and side arm vacuum flask, with 25-mm filter holders (Millipore XX10 025 30).
8. Sieve, 10-µm, for wet-sieving (Buckbee-Mears, Box 43210, St. Paul, MN 55164).
9. Centrifuge tubes, wide-mouth, 40-mL.
10. Ultrasonic bath or probe.
11. Analytical balance (0.01 mg).
12. Magnetic stirrer with thermally-insulated top.
13. Bottles, reagent, 1-L, with ground glass stoppers.
14. Drying oven.
15. Polyethylene wash bottle.
16. Desiccator.
17. Pipets, TD, 2- to 25-mL.

SPECIAL PRECAUTIONS: THF is extremely flammable and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump to 1.7 L/min with a representative sampler in line.
2. Sample at 1.7 L/min for a total sample size of 200 to 1000 L. Do not exceed 2 mg dust loading on the filter.
   NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to more than 90 °C from vertical may deposit over-sized material from the cyclone body onto the filter.
3. Obtain an area high-volume respirable sample in the vicinity of the personal sampling area.

SAMPLE PREPARATION:

4. Place sample filter in a centrifuge tube. Add 10 mL THF. Place centrifuge tube in ultrasonic bath for 10 min.
   NOTE: The filter should dissolve almost instantaneously.

5. Mount a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL THF onto the filter. Pour the sample suspension from the beaker into the funnel. Rinse centrifuge tube twice with 5-mL portions of THF, adding rinses to the funnel, and apply vacuum.
6. Control filtration rate to keep liquid level near top of funnel during filtering. Do not wash the walls or add THF to the funnel when the liquid level is lower than 4 cm above the filter. Leave vacuum on after filtration for sufficient time to dry the filter. Transfer filter with forceps to sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL:

7. Select six silver membrane filters as media blanks, randomly from the same box of filters to be used for depositing the samples. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL THF through the filter. Remove, let dry and mount on XRD holders.
   NOTE: These will be used to test for sample self-absorption.
8. Prepare standard suspensions.
   a. Weigh 10- and 50-mg portions of the dry analytes to the nearest 0.01 mg. Quantitatively transfer to 1-L glass-stoppered bottles. Add 1.00 L acetonitrile (for V_2O_5) or isopropanol (for V_2O_3 or NH_4VO_3).
   b. Disperse the powder in the liquid using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer and add a stirring bar to the suspension. Allow the solution to return to room temperature before withdrawing aliquots.
9. Prepare a series of standard filters over the range 0.05 to 2 mg V per sample.
   a. Mount a filter on the filtration apparatus. Wet the filter with ca. 3 mL of acetonitrile (for V_2O_5) or isopropanol (for V_2O_3 or NH_4VO_3).
   b. Turn off the stirrer and shake the bottle vigorously by hand. Immediately remove the lid and withdraw an aliquot (2 to 25 mL) from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot.
   c. Transfer the aliquot from the pipet to the funnel. Keep the tip of the pipet near the surface but not submerged in the suspension. Rinse the pipet with ca. 5 mL of acetonitrile (for V_2O_5) or isopropanol (for V_2O_3 or NH_4VO_3), draining the rinse into the funnel. Repeat the rinse three more times.
   d. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down sides of funnel after deposit is in place (to avoid rearranging the material on the filter).
   e. Transfer the filter to the XRD sample holder.
10. Perform step scans on the standards and reference specimen using the same conditions as for samples. Use steps 12 and 13 to determine normalized intensity, $\hat{I}_X^\circ$, for each peak measured. Use exactly the same normalization factor, N, as for samples (step 13).
11. Prepare calibration graph ($\hat{I}_X^\circ$ vs. mg of each standard). Determine slope, m (counts/µg).
    NOTE 1: The intercept with the $\hat{I}_X^\circ$ axis should be ca. zero. A large negative intercept indicates an error in determining background (e.g., incorrectly measuring the baseline, or interference by another phase at the angle of background measurement). A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.
    NOTE 2: Poor repeatability at a given level indicates problems in the sample preparation technique and new standards should be made. Eliminate curvature with absorption corrections based on the mass absorption coefficient of the analyte (step 15, or from Tables 2 through 4).

MEASUREMENT:

12. Obtain a qualitative X-ray diffraction scan (broad 2θ range) of high-volume sample to determine the presence of interferences.
    NOTE: If quantitative analysis is to be done on the bulk sample, wet-sieve it first through a 10-μm sieve.
13. Mount the filter (sample, standard, or blank) in the XRD instrument and perform the following:
    a. Determine net intensity, I_r^o, of the reference specimen before filter is scanned. Select a convenient scale factor, N, which is approximately equivalent to the net count for the reference specimen peak; use this for all analyses.
    b. Step-scan the most intense, interference-free diffraction peak of each compound to be determined, integrating the counts.
       NOTE: Useful analytical lines for the analytes are given in Table 1. Use strongest line of the analyte which does not have a matrix interference. Avoid lines in the proximity of Ag (JCPDS #4-0783 [5]) and AgCl (JCPDS #31-1238 [6]) (the latter often exists on the surface of silver filters).
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain total (average) background.
    d. Calculate net intensity, I_x, (different between peak integrated count and total background count).
    e. Calculate and record the normalized intensity for the analyte peak on each sample and standard:

$$\hat{I}_x = \left(\frac{I_x}{I_r^o}\right) \times N.$$

       For each media blank, determine the net count for the analyte diffraction peak. Calculate the average normalized intensity, I_b, for the 6 media blanks.
    f. Determine net count, I_{Ag}, of an interference-free silver peak on the filter following the same procedure. Scan times should be shorter for the silver peak (e.g., about 5% of scan times for analyte peaks) and should be consistent throughout the method. For each media blank, determine the net count for the silver peak. Calculate the average value, $\hat{I}_{Ag}^o$, for the 6 media blanks.
       NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently. In this case, the net intensities of the analyte, blank, and silver peaks (I_x, I_b, and I_{Ag}) should be normalized to the most recently measured reference intensity.
14. Scan each field blank over the same 2θ range used for the analyte and silver peaks. The analyte peak should be absent. The normalized intensity of the silver peak of the field blanks should match that of the media blanks.
    NOTE: These analyses serve only to verify that contamination of the filters has not occurred.

CALCULATIONS:

15. Calculate absorption correction factors (Tables 2, 3, and 4) [7]:

$$f(T) = \frac{-R \ln T}{1 - T^R}$$

where: $R = (\sin \theta_{Ag})/(\sin\theta_x)$ and

$T = \hat{I}_{Ag} / \hat{I}_{Ag}^o$ = transmittance of sample.

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

$$C = \frac{([\hat{I}_x \cdot f(T)] - \hat{I}_b)}{m \cdot V}$$

EVALUATION OF METHOD:

VANADIUM PENTOXIDE: The V_2O_5 method was evaluated [3] using both spiked and generated samples of V_2O_5. With the spiked samples, using the 31.05° line and loadings of 433 to 699 µg/filter, the overall s_r was 8.3% with an average bias of -7.3%. Five sets of generated samples, ranging from 184 to 2400 µg V_2O_5 per filter, gave an average bias of 10.12% with a pooled s_r of 6.9%. The samples were generated using an aerosol which had been sized using a cyclone with characteristics similar to the 10-mm nylon cylone; however, individual 10-mm nylon cyclones on the cassettes were not used. The 10-mm nylon cyclones must be tightly sealed and used carefully; otherwise, serious imprecision may be introduced.

VANADIUM TRIOXIDE: The method was evaluated [3] using both spiked and generated samples of V_2O_3. With the spiked samples, using the 24.39° line and loadings of 107 to 321 µg per filter, the overall s_r was 8.2% with an average bias of 12.2%. Five sets of generated samples, from atmospheres of 0.24 to 2.57 mg V_2O_3/m^3, gave an average bias of -10.1% with a pooled s_r of 13.4% (24.39° line). As above, the samples were generated using an aerosol which had been sized using a cyclone with characteristics similar to the 10-mm nylon cylone; however, individual 10-mm nylon cyclones on the cassettes were not used.

AMMONIUM METAVANADATE: The method was evaluated [3] with spiked NH_4VO_3 samples over the range of 109 to 277 µg NH_4VO_3 per filter, and with generated samples generated as described above, with atmospheres of 0.037 to 0.435 mg m^3 of NH_4VO_3. The 18.10 °2θ line provided an overall s_r of 26.3%, with a bias of -10.2% over the generation range. The stability of the compound is critical and analysis should occur within two weeks of sampling, unless refrigeration storage is employed. Sampling is quantitative using the two-filter technique described.

For the analytes, biases of spiked samples were determined assuming the volume of suspension as "true." Biases of generated samples were determined assuming the 'true' concentration from the analysis of monitor AAWP filters by ICP-AES.

Instrumental imprecision increases with smaller depositions. For low loading levels, higher counting times will increase precision, as should sample spinning. The stated lower limit of quantitation of ca. 100 µg per analyte using the recommended analytical lines is an estimate was based on numerous spiked and generated sample experiments.

REFERENCES:

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

[2] Criteria for a Recommended Standard...Occupational Exposure to Vanadium, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-222 (1977).

[3] T. Carsey, "Quantitation of Vanadium Oxides in Airborne Dusts by X-Ray Diffraction," Anal. Chem., 57: 2125-2130 (1985).

[4] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 8 (unpublished, 1982).

[5] Powder Diffraction File Search Manual, International Centre for Diffraction Data (JCPDS), Swarthmore, PA, 19081, p. 809 (1981).
[6] Ibid., p. 810.
[7] M. Abell, D. Dollberg, J. Crable, "Quantitative Analysis of Dust Samples from Occupational Environments Using Computer-Automated X-ray Diffraction," in Advances in X-Ray Analysis, Vol. 24, Plenum, p. 37 (1981).
[8] E. Bertin: Principles and Practice of X-ray Spectrometric Analysis, 2nd Ed., Plenum, New York, p. 471 (1975).

METHOD WRITTEN BY: Thomas P. Carsey, Ph.D., NIOSH/DPSE.

Table 1. Characteristics of analytical lines.

d-space (A)	Relative Intensity[1]	Peak 2θ[1]	Scan Min 2θ	Scan Max 2θ	Detection Limit[2] (µg)	Calibration Slope (ct/µg)	Precision[3] (% s_r)	Bias[4] (%)	Comments
					Vanadium Pentoxide (PDF # 9-0387)				
4.38	100	20.27	19.4	20.9	4	205.0	11.5	-28.9	Silica interf. 20.85 °2θ
4.09	35	21.73	20.9	22.4	13	57.1	-	-	silica interf. 20.85 °2θ
3.40	90	26.21	25.5	26.6	10	54.2	11.3	-22.3	silica interf. 26.69 °2θ
2.88	65	31.05	30.3	31.4	9	73.0	8.3	10.1	good
2.185	17	41.32	40.5	41.6	28	24.9	-	-	weak; V2O3 interf. 41.42 °2θ
					Vanadium Trioxide (PDF # 26-278)				
3.65	60	24.39	24.75	23.5	6	75.1	14.7	-10.1	good
2.70	80	33.18	33.5	32.5	5	78.3	16.0	0.0	AgCl interf. 32.32 °2θ
2.47	60	36.37	36.8	35.7	9	70.6	15.6	14.2	Silica interf. 36.53 °2θ
2.18	20	41.42	41.7	40.6	62	11.7	-	-	weak; V2O5 interf. 41.32 °2θ
1.83	25	49.83	50.4	49.3	21	30.2	-	-	weak
1.69	100	54.28	54.5	53.3	5	91.2	20.7	-10.1	good
1.43	30	65.25[5]							
					Ammonium Metavanadate (PDF # 9-411)				
5.88	50	15.07	14.3	15.4	7	133.8	24.0	11.4	good
4.90	75	18.10	17.7	18.2	7	101.4	26.3	-10.2	good
4.14	95	21.46	21.0	21.8	10	49.8	-	13.2	weak; V2O5 interf. 21.73 °2θ
3.77	40	23.60	23.1	23.9	18	38.5	-	-	weak; V2O5 interf. 41.32 °2θ
3.164	100	28.21[6]			50.3	-	-		AgCl interf. at 27.88 °2θ
2.912	60	30.74	30.1	30.9	21	33.9	-	-	weak
2.628	45	34.12	33.5	34.4	20	36.0	-	-	weak

[1] From Reference 2, p. 979 (λ = 1.5418Å).

[2] Reference 8.

[3] $s_r = \sqrt{(GRSD^2 + 0.1667 \cdot SRSD^2 + .05^2)}$, where GRSD is the generated-sample pooled relative standard deviation, and SRSD is the spiked-sample pooled relative standard deviation. This is the estimated relative standard deviation for the total (sampling plus measurement) air-monitoring method.

[4] From generated samples.

[5] Not evaluated because of an Ag interference at 64.48 °2θ.

[6] Not evaluated because of an AgCl interference at 27.88 °2θ.

Table 2. Matrix absorption correction factors for vanadium pentoxide/silver peaks by degrees two-theta.

V_2O_5	20.27°	26.13°	31.00°		20.27°	26.13°	31.00°
Silver	38.12°	38.12°	38.12°		38.12°	38.12°	38.12°
T	(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)
1.00	1.0000	1.0000	1.0000	0.74	1.3053	1.2332	1.1952
0.99	1.0094	1.0073	1.0062	0.73	1.3203	1.2445	1.2046
0.98	1.0189	1.0147	1.0124	0.72	1.3356	1.2560	1.2141
0.97	1.0285	1.0222	1.0187	0.71	1.3512	1.2677	1.2238
0.96	1.0384	1.0298	1.0251	0.70	1.3672	1.2796	1.2337
0.95	1.0483	1.0375	1.0317	0.69	1.3835	1.2918	1.2438
0.94	1.0585	1.0454	1.0383	0.68	1.4002	1.3043	1.2541
0.93	1.0688	1.0533	1.0450	0.67	1.4172	1.3170	1.2646
0.92	1.0794	1.0614	1.0518	0.66	1.4346	1.3300	1.2753
0.91	1.0901	1.0697	1.0587	0.65	1.4524	1.3432	1.2862
0.90	1.1009	1.0780	1.0658	0.64	1.4706	1.3567	1.2973
0.89	1.1120	1.0865	1.0729	0.63	1.4892	1.3706	1.3087
0.88	1.1233	1.0952	1.0801	0.62	1.5083	1.3847	1.3203
0.87	1.1348	1.1040	1.0875	0.61	1.5278	1.3992	1.3322
0.86	1.1465	1.1129	1.0950	0.60	1.5478	1.4139	1.3444
0.85	1.1584	1.1220	1.1026	0.59	1.5682	1.4291	1.3568
0.84	1.1705	1.1312	1.1103	0.58	1.5892	1.4445	1.3695
0.83	1.1828	1.1406	1.1182	0.57	1.6107	1.4604	1.3825
0.82	1.1954	1.1502	1.1261	0.56	1.6327	1.4766	1.3957
0.81	1.2082	1.1599	1.1343	0.55	1.6553	1.4932	1.4094
0.80	1.2213	1.1698	1.1425	0.54	1.6784	1.5102	1.4233
0.79	1.2346	1.1799	1.1509	0.53	1.7022	1.5277	1.4376
0.78	1.2482	1.1902	1.1595	0.52	1.7266	1.5456	1.4522
0.77	1.2620	1.2006	1.1682	0.51	1.7516	1.5640	1.4672
0.76	1.2762	1.2113	1.1770	0.50	1.7774	1.5828	1.4826
0.75	1.2906	1.2221	1.1860	0.49	1.8039	1.6022	1.4984

T = Sample transmittance (see step 15)
f(T) = Sample correction factor (see step 15)

Table 3. Matrix absorption correction factors for vanadium trioxide/silver peaks by degrees two-theta.

V_2O_3	24.39°	33.18°	36.37°	54.28		24.39°	33.18°	36.37°	54.28°
Silver	38.15°	38.15°	38.15°	38.15°		38.15°	38.15°	38.15°	38.15°
T	f(T)	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)	f(T)
1.00	1.00000	1.00000	1.00000	1.00000	0.74	1.25097	1.18219	1.16591	1.11173
0.99	1.00779	1.00576	1.00527	1.00360	0.73	1.26315	1.19089	1.17379	1.11696
0.98	1.01571	1.01161	1.01061	1.00725	0.72	1.27558	1.19975	1.18182	1.12228
0.97	1.02375	1.01753	1.01603	1.01095	0.73	1.28825	1.20877	1.19000	1.12769
0.96	1.03191	1.02354	1.02152	1.01469	0.70	1.30119	1.21797	1.19832	1.13320
0.95	1.04021	1.02964	1.02709	1.01849	0.69	1.31439	1.22734	1.20681	1.13880
0.94	1.04863	1.03583	1.03274	1.02233	0.68	1.32786	1.23689	1.21546	1.14450
0.93	1.05719	1.04211	1.03847	1.02622	0.67	1.34162	1.24663	1.22427	1.15030
0.92	1.06589	1.04848	1.04429	1.03016	0.66	1.35567	1.25657	1.23326	1 15621
0.91	1.07474	1.05494	1.05019	1.03416	0.65	1.37002	1.26670	1.24242	1.16223
0.90	1.08372	1.06151	1.05617	1.03822	0.64	1.38469	1.27705	1.25177	1.16837
0.89	1.09286	1.06817	1.06225	1.04232	0.63	1.39968	1.28761	1.26131	1.17462
0.88	1.10215	1.07494	1.06842	1.04649	0.62	1.41500	1.29839	1.27105	1.18099
0.87	1.11160	1.08181	1.07468	1.05071	0.61	1.43068	1.30941	1.28100	1.18749
0.86	1.12122	1.08879	1.08104	1.05500	0.60	1.44672	1.32066	1.29116	1.19411
0.85	1.13099	1.09589	1.08749	1.05934	0.59	1.46313	1.33216	1.30153	1.20088
0.84	1.14094	1.10309	1.09405	1.06375	0.58	1.47993	1.34392	1.31214	1.20778
0.83	1.15107	1.11042	1.10072	1.06823	0.57	1.49713	1.35595	1.32298	1.21483
0.82	1.16137	1.11786	1.10749	1.07277	0.56	1.51475	1.36825	1.33408	1.22203
0.81	1.17186	1.12543	1.11437	1.07738	0.55	1.53281	1.38084	1.34542	1.22939
0.80	1.18255	1.13313	1.12137	1.08206	0.54	1.55133	1.39374	1.35704	1.23691
0.79	1.19342	1.14096	1.12848	1.08681	0.53	1.57031	1.40695	1.36893	1.24460
0.78	1.20450	1.14892	1.13571	1.09164	0.52	1.58979	1.42048	1.38111	1.25246
0.77	1.21579	1.15702	1.14306	1.09654	0.51	1.60978	1.43435	1.39359	1.26051
0.76	1.22729	1.16526	1.15055	1.10152	0.50	1.63030	1.44858	1.40639	1.26875
0.75	1.23902	1.17365	1.15816	1.10659	0.49	1.65139	1.46318	1.41952	1.27719

T = Sample transmittance (see step 15)
f(T) = Sample correction factor (see step 15)

Table 4. Matrix absorption correction factors for ammonium metavanadate/silver peaks by degrees two-theta.

NH_4VO_3	15.07°	18.10°	21.46°	23.60		15.07°	18.10°	21.46°	23.60°
Silver	38.15°	38.15°	38.15°	38.15°		38.15°	38.15°	38.15°	38.15°
T	f(T)	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)	f(T)
1.00	1.0000	1.0000	1.0000	1.0000	0.74	1.0000	1.0000	1.0000	1.0000
0.99	1.0126	1.0105	1.0088	1.0081	0.73	1.0126	1.0105	1.0088	1.0081
0.98	1.0254	1.0211	1.0178	1.0162	0.72	1.0254	1.0211	1.0178	1.0162
0.97	1.0384	1.032	1.0270	1.0245	0.71	1.0384	1.0320	1.0270	1.0245
0.96	1.0517	1.043	1.0362	1.0330	0.70	1.0517	1.0430	1.0362	1.0330
0.95	1.0653	1.0542	1.0457	1.0415	0.69	1.0653	1.0542	1.0457	1.0415
0.94	1.0791	1.0656	1.0553	1.0503	0.68	1.0791	1.0656	1.0553	1.0503
0.93	1.0932	1.0773	1.0650	1.0591	0.67	1.0932	1.0773	1.0650	1.0591
0.92	1.1075	1.0891	1.0749	1.0681	0.66	1.1075	1.0891	1.0749	1.0681
0.91	1.1221	1.1011	1.0850	1.0773	0.65	1.1221	1.1011	1.0850	1.0773
0.90	1.1371	1.1134	1.0953	1.0866	0.64	1.1371	1.1134	1.0953	1.0866
0.89	1.1523	1.1259	1.1057	1.0960	0.63	1.1523	1.1259	1.1057	1.0960
0.88	1.1678	1.1386	1.1164	1.1056	0.62	1.1678	1.1386	1.1164	1.1056
0.87	1.1836	1.1516	1.1272	1.1154	0.61	1.1836	1.1516	1.1272	1.1154
0.86	1.1997	1.1648	1.1382	1.1254	0.60	1.1997	1.1648	1.1382	1.1254
0.85	1.2162	1.1783	1.1494	1.1355	0.59	1.2162	1.1783	1.1494	1.1355
0.84	1.2330	1.1920	1.1608	1.1458	0.58	1.2330	1.1920	1.1608	1.1458
0.83	1.2501	1.2060	1.1724	1.1563	0.57	1.2501	1.2060	1.1724	1.1563
0.82	1.2676	1.2202	1.1842	1.1669	0.56	1.2676	1.2202	1.1842	1.1669
0.81	1.2855	1.2348	1.1963	1.1778	0.55	1.2855	1.2348	1.1963	1.1778
0.80	1.3038	1.2496	1.2086	1.1889	0.54	1.3038	1.2496	1.2086	1.1889
0.79	1.3224	1.2647	1.2211	1.2002	0.53	1.3224	1.2647	1.2211	1.2002
0.78	1.3414	1.2801	1.2338	1.2116	0.52	1.3414	1.2801	1.2338	1.2116
0.77	1.3609	1.2959	1.2468	1.2233	0.51	1.3609	1.2959	1.2468	1.2233
0.76	1.3807	1.3120	1.2601	1.2353	0.50	1.3807	1.3120	1.2601	1.2353
0.75	1.4474	1.3284	1.2736	1.2474	0.49	1.4010	1.3284	1.2736	1.2474

T = Sample transmittance (see step 15)
f(T) = Sample correction factor (see step 15)

FORMULA: $CH_2=CCl_2$; $C_2H_2Cl_2$

M.W.: 96.94

VINYLIDENE CHLORIDE

METHOD: 1015
ISSUED: 8/15/87

OSHA: no standard
NIOSH: lowest possible (carcinogen) [1]
ACGIH: 5 ppm; STEL 20 ppm
(1 ppm = 3.96 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.213 g/mL @ 20 °C;
BP 31.7 °C; MP -122.5 °C ; flammable

SYNONYMS: 1,1-dichloroethene; 1,1-dichloroethylene; CAS #75-35-4.

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 2.5 L @ 1 ppm
-MAX: 7 L

SHIPMENT: routine

SAMPLE STABILITY: 7 days @ 25 °C;
21 days @ 5 °C [2]

FIELD BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: 7.6 to 10 mg/m³ [3]

BIAS: not significant [3]

OVERALL PRECISION (s_r): not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinylidene chloride

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 150 °C
-DETECTOR: 200 °C
-COLUMN: 65 °C

CARRIER GAS: He or N_2, 30 mL/min

COLUMN: silanized glass, 3 m x 6 mm OD packed with Durapak OPN 100/120 mesh or equivalent

CALIBRATION: standard solutions of vinylidene chloride in CS_2

RANGE: 0.01 to 0.1 mg per sample

ESTIMATED LOD: 0.007 mg per sample [3]

PRECISION (s_r): 0.048 @ 0.012 to 0.085 mg per sample [3]

APPLICABILITY: The working range is 0.5 to 5 ppm (2 to 20 mg/m³) for a 5-L air sample. The capacity of charcoal for vinylidene chloride decreased rapidly with increasing relative humidity and was also found to be a function of concentration.

INTERFERENCES: The GC column will not separate vinyl chloride and carbon disulfide. Other GC packings that separate vinyl chloride and CS_2 may not separate vinylidene chloride and CS_2. If determination of both of these monomers is to be performed, use two different GC columns.

OTHER METHODS: This revises P&CAM 266 [2].

REAGENTS:

1. Carbon disulfide (CS_2), chromatographic quality.*
2. Vinylidene chloride, 99%.
3. Cyclohexane.
4. Calibration stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in CS_2 to make 10 mL solution. Prepare in duplicate.
5. DE stock solution, 10 mg/mL. Dissolve 0.1 g vinylidene chloride in cyclohexane to make 10 mL solution. Prepare in duplicate.
6. Nitrogen or helium, purified.
7. Hydrogen, prepurified.
8. 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 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 1015-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipets, volumetric, 10- to 100-µL, and 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Vinylidene chloride is a suspect carcinogen [1]. Carbon disulfide and vinylidene chloride are toxic and severe fire and explosion hazards (flash point = -30 °C for CS_2 and -10 °C for vinylidene chloride); work with both compounds only in a hood. Vinylidene chloride polymerizes above 0 °C, especially in the presence of oxygen or catalysts; explosive reaction products may result [4].

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 of 2.5 to 7 L.
4. Cap the samplers. Pack securely for shipment.
   NOTE: Refrigerated shipment will decrease migration of vinylidene chloride to back sorbent section.

SAMPLE PREPARATION:

5. Allow samples to equilibrate to room temperature before uncapping. Place the front and back sorbent sections of the sampler tube in separate vials.
6. Add 1.0 mL CS_2 to each vial. Cap vial immediately.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards.
   a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the mark. Prepare working standards in the range 0.01 to 0.1 mg vinylidene chloride/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or peak height vs. mg vinylidene chloride).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the range of interest. 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 (2 to 10 µL) of DE 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 with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg vinylidene chloride recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 1015-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If response 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 or peak height.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of vinylidene chloride 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 vinylidene chloride 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:

Method P&CAM 266 was issued on November 21, 1977 [2]. The method was tested with sample loadings between 13 and 85 µg vinylidene chloride per charcoal tube [3]. The samples were collected from atmospheres containing vinylidene chloride in the range 7.6 to 10.0 mg/m³ and having relative humidity in the range 10 to 95%. The pooled relative standard deviation of the measurement was 4.8% for the analysis of 36 samples over the range 12 to 85 µg vinylidene chloride per sample. Desorption efficiency was determined to be 80% for a loading of 7 µg vinylidene chloride at a vinylidene chloride concentration of 10 mg/m³ and high relative humidity; the breakthrough volume was 7.3 L when sampling at 0.2 L/min from this atmosphere. At 87% relative humidity, the breakthrough volume was 10% of the breakthrough volume at 10% relative humidity.

REFERENCES:

[1] NIOSH/OSHA Current Intelligence Bulletin 28, Vinyl Halides Carcinogenicity, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-102 (1978).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, P&CAM 266, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Foerst, D. "A Sampling and Analytical Method for Vinylidene Chloride in Air," Am. Ind. Hyg. Assoc. J., 40: 888-893 (1979).
[4] Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).

METHOD REVISED BY: Ardith A. Grote, NIOSH/DPSE.

V. A. INDEX OF THIRD EDITION METHOD NUMBERS

3rd ed. Method Number	Substance
0500	NUISANCE DUST, TOTAL
0600	NUISANCE DUST, RESPIRABLE
1000	ALLYL CHLORIDE
1001	METHYL CHLORIDE Chloromethane
1002	CHLOROPRENE
1003	HYDROCARBONS, HALOGENATED: Benzyl chloride Bromoform Carbon tetrachloride Chlorobenzene Chlorobromomethane Chloroform o-Dichlorobenzene p-Dichlorobenzene 1,1-Dichloroethane 1,2-Dichloroethylene Ethylene dichloride Hexachloroethane Methylchloroform Tetrachloroethylene 1,1,2-Trichloroethane 1,2,3-Trichloropropane
1004	sym-DICHLOROETHYL ETHER
1005	METHYLENE CHLORIDE
1006	TRICHLOROFLUOROMETHANE Fluorotrichloromethane Freon 11
1007	VINYL CHLORIDE
1008	ETHYLENE DIBROMIDE
1009	VINYL BROMIDE
1010	EPICHLOROHYDRIN
1011	ETHYL BROMIDE
1012	DIBROMODIFLUOROMETHANE
1013	1,2-DICHLOROPROPANE
1014	METHYL IODIDE
1015	VINYLIDENE CHLORIDE 1,1-Dichloroethene 1,1-Dichloroethylene
1016	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE Refrigerant 112 Refrigerant 112a
1017	BROMOTRIFLUOROMETHANE Refrigerant 13B1 Trifluorobromomethane
1018	DICHLORODIFLUOROMETHANE and 1,2-DICHLOROTETRAFLUOROETHANE Cyrofluorane Difluorodichloromethane Refrigerant 12 Refrigerant 114
1019	1,1,2,2-TETRACHLOROETHANE Acetylene tetrachloride
1020	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE Refrigerant 113 TTE
1022	TRICHLOROETHYLENE TCE Trichloroethane
1024	1,3-BUTADIENE
1300	KETONES I: Acetone Diisobutyl ketone 2-Hexanone Hexone 2-Pentanone
1301	KETONES II: Camphor Ethyl butyl ketone Mesityl oxide Methyl (n-amyl) ketone 5-Methyl-3-heptanone
1400	ALCOHOLS I: tert-Butyl alcohol Ethanol Isopropyl alcohol
1401	ALCOHOLS II: n-Butyl alcohol sec-Butyl alcohol Isobutyl alcohol n-Propyl alcohol
1402	ALCOHOLS III: Allyl alcohol Cyclohexanol Diacetone alcohol Isoamyl alcohol Methyl isobutyl carbinol

3rd Ed. Method Number	Substance
1403	ALCOHOLS IV:
	2-Butoxyethanol
	2-Ethoxyethanol
	Methyl cellosolve
1450	ESTERS I:
	n-Amyl acetate
	sec-Amyl acetate
	n-Butyl acetate
	sec-Butyl acetate
	tert-Butyl acetate
	2-Ethoxyethyl acetate
	Ethyl acrylate
	Isoamyl acetate
	Isobutyl acetate
	Methyl isoamyl acetate
	n-Propyl acetate
1500	HYDROCARBONS, BP 36 - 126 °C:
	Benzene
	Cyclohexane
	Cyclohexene
	n-Heptane
	n-Hexane
	Methylcyclohexane
	n-Octane
	n-Pentane
	Toluene
1501	HYDROCARBONS, AROMATIC:
	Benzene
	p-tert-Butyl toluene
	Cumene
	Ethylbenzene
	α-Methylstyrene
	Naphthalene
	Styrene
	Toluene
	Vinyl toluene
	Xylene
1550	NAPHTHAS:
	Coal tar naphthas
	Kerosene
	Mineral spirits
	Petroleum ether
	Petroleum naphtha
	Rubber solvent
	Stoddard solvent
1551	TURPENTINE
1600	CARBON DISULFIDE (rev. 5/15/85)
1601	1,1-DICHLORO-1-NITROETHANE
1602	DIOXANE
1603	ACETIC ACID
1604	ACRYLONITRILE
1606	ACETONITRILE
1607	ETHYLENE OXIDE
1608	GLYCIDOL
1609	TETRAHYDROFURAN
1610	ETHYL ETHER
1611	METHYLAL
1612	PROPYLENE OXIDE
1613	PYRIDINE
1614	ETHYLENE OXIDE
	1,2-Epoxyethane
	EtO
	Oxirane
2000	METHANOL
2001	CRESOLS
2002	AMINES, AROMATIC:
	Aniline
	N,N-Dimethyl aniline
	N,N-Dimethyl-p-toluidine
	o-Toluidine
	2,4-Xylidine
2003	1,1,2,2-TETRABROMOETHANE
2004	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE
2005	NITROBENZENES:
	4-Chloronitrobenzene
	Nitrobenzene
	Nitrotoluene
2007	AMINOETHANOL COMPOUNDS:
	2-Aminoethanol
	2-Dibutylaminoethanol
	2-Diethylaminoethanol
2008	CHLOROACETIC ACID
	Chloroethanoic acid
	Monochloroacetic acid
2500	2-BUTANONE
2501	ACROLEIN
2502	FORMALDEHYDE (oxazolidine)
2503	MEVINPHOS (Phosdrin)
2504	TETRAETHYL PYROPHOSPHATE (TEPP)
2506	ACETONE CYANOHYDRIN
2507	NITROGLYCERIN/EGDN
2508	ISOPHORONE
2510	1-OCTANETHIOL
2513	ETHYLENE CHLOROHYDRIN
2514	ANISIDINE
2515	DIAZOMETHANE

3rd Ed. Method Number	Substance
2516	DICHLOROFLUOROMETHANE
2517	PENTACHLOROETHANE
2518	HEXACHLORO-1,3-CYCLOPENTADIENE
2519	ETHYL CHLORIDE
2520	METHYL BROMIDE
2521	METHYL CYCLOHEXANONE
2523	1,3-CYCLOPENTADIENE
2524	DIMETHYL SULFATE
2526	NITROETHANE
2527	NITROMETHANE Nitrocarbol
2528	2-NITROPROPANE Dimethylnitromethane
2529	FURFURAL 2-Furaldehyde 2-Furancarboxaldehyde
2530	BIPHENYL Diphenyl
2533	TETRAETHYL LEAD (as Pb) Lead tetraethyl TEL
2534	TETRAMETHYL LEAD (as Pb) Lead tetramethyl
2535	TOLUENE-2,4-DIISOCYANATE
3500	FORMALDEHYDE (chromotropic acid)
3501	FORMALDEHYDE (Girard T)
3502	PHENOL
3503	HYDRAZINE
3505	TETRAMETHYL THIOUREA
3506	ACETIC ANHYDRIDE
3507	ACETALDEHYDE Ethanal
3508	METHYL ETHYL KETONE PEROXIDE 2-Butanone peroxide
3700	BENZENE by portable GC
3701	TRICHLOROETHYLENE by portable GC Trichloroethene
3702	ETHYLENE OXIDE 1,2-Epoxyethane Oxirane
4000	TOLUENE Methylbenzene
5000	CARBON BLACK
5001	2,4-D and 2,4,5-T
5002	WARFARIN
5003	PARAQUAT (rev. 5/15/85)
5004	HYDROQUINONE
5005	THIRAM

3rd Ed. Method Number	Substance
5006	CARBARYL (Sevin) (rev. 5/15/85)
5007	ROTENONE
5008	PYRETHRUM
5009	BENZOYL PEROXIDE
5010	BROMOXYNIL and BROMOXYNIL OCTANOATE
5011	ETHYLENE THIOUREA
5012	EPN, MALATHION, and PARATHION
5013	DYES, BENZIDINE, o-ANISIDINE, and o-TOLIDINE (rev. 5/15/85)
5014	CHLORINATED TERPHENYL
5016	STRYCHNINE
5017	DIBUTYL PHOSPHATE
5018	2,4,7-TRINITROFLUOREN-9-ONE
5019	AZELAIC ACID
5020	DIBUTYL PHTHALATE and DI(2-ETHYLHEXYL) PHTHALATE
5021	o-TERPHENYL
5022	ARSENIC, ORGANO-: p-Aminophenylarsonic acid Dimethylarsenic acid Methylarsonic acid
5023	COAL TAR PITCH VOLATILES
5025	CHLORINATED DIPHENYL ETHER Chlorinated diphenyl oxide
5026	MINERAL OIL MIST Airborne mist of white mineral oil Cable oil Cutting oil Drawing oil Engine oil Heat-treating oils Hydraulic oils Machine oil Transformer oil
5500	ETHYLENE GLYCOL
5502	ALDRIN and LINDANE
5503	POLYCHLOROBIPHENYLS
5504	ORGANOTIN COMPOUNDS (as Sn) Bibutyltin bix(isooctyl mercaptoacetate) Tetrabutyltin Tributyltin chloride Tricyclohexyltin hydroxide
5505	ISOCYANATE GROUP (rev. 5/15/85)
5506	POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC)
5508	KEPONE
5509	BENZIDINE and 3,3'-DICHLOROBENZIDINE

3rd Ed. Method Number	Substance
5514	DEMETON
5515	POLYNUCLEAR AROMATIC HYDROCARBONS (GC)
5517	POLYCHLOROBENZENES
	Pentachlorobenzene
	1,2,4,5-Tetrachlorobenzene
	1,2,4-Trichlorobenzene
5518	NAPHTHYLAMINES
	α-Naphthylamine
	β-Naphthylamine
	1-Naphthylamine
	2-Naphthylamine
6000	MERCURY
6001	ARSINE
6004	SULFUR DIOXIDE
6005	IODINE
6006	DIBORANE
	Boroethane
6007	NICKEL CARBONYL
6008	STIBINE
	Antimony trihydride
6402	PHOSPHORUS TRICHLORIDE
6600	NITROUS OXIDE
6601	OXYGEN
6700	NITROGEN DIOXIDE
6701	AMMONIA
7013	ALUMINUM
7020	CALCIUM
7024	CHROMIUM
7027	COBALT
7029	COPPER (fume and dust)
7030	ZINC
7048	CADMIUM
7056	BARIUM, soluble compounds
7074	TUNGSTEN (soluble and insoluble) (rev. 5/15/85)
7082	LEAD
7102	BERYLLIUM
7200	WELDING AND BRAZING FUME:
	Cadmium
	Chromium
	Copper
	Iron
	Manganese
	Nickel
	Silver
	Zinc

3rd Ed. Method Number	Substance
7300	ELEMENTS (ICP):
	Aluminum
	Arsenic
	Beryllium
	Cadmium
	Calcium
	Chromium
	Cobalt
	Copper
	Iron
	Lead
	Lithium
	Magnesium
	Manganese
	Molybdenum
	Nickel
	Phosphorus
	Platinum
	Selenium
	Silver
	Sodium
	Tellurium
	Thallium
	Tin
	Titanium
	Tungsten
	Vanadium
	Yttrium
	Zinc
	Zirconium
7400	FIBERS
	Actinolite asbestos
	Anthophyllite asbestos
	Chrysotile asbestos
	Crocidolite asbestos
	Fibrous glass
	Grunerite asbestos
	Tremolite asbestos
7401	ALKALINE DUSTS
7402	ASBESTOS FIBERS
	Actinolite asbestos
	Anthophyllite asbestos
	Chrysotile asbestos
	Crocidolite asbestos
	Grunerite asbestos
	Tremolite asbestos

3rd Ed. Method Number	Substance
7500	SILICA, CRYSTALLINE (XRD)
7501	SILICA, AMORPHOUS
7502	ZINC OXIDE
7504	VANADIUM OXIDES
	Vanadic anhydride
	Vanadic Oxide
	Vanadium pentoxide
	Vanadium sesquioxide
	Vanadium trioxide
7505	LEAD SULFIDE
7506	BORON CARBIDE
7600	CHROMIUM, HEXAVALENT
7601	SILICA, CRYSTALLINE (color)
7602	SILICA, CRYSTALLINE (IR)
7900	ARSENIC (hydride AAS)
7901	ARSENIC TRIOXIDE (graphite AAS)
7902	FLUORIDES (aerosol and gas)
7903	ACIDS, INORGANIC (IC):
	Hydrogen bromide
	Hydrogen chloride
	Hydrogen fluoride
	Nitric acid
	Phosphoric acid
	Sulfuric acid
7904	CYANIDES (aerosol and gas)
7905	PHOSPHORUS
	White phosphorus
	Yellow phosphorus
8000	ALAD in blood
8001	PENTACHLOROPHENOL in blood
8002	2-BUTANONE, ETHANOL, and TOLUENE in blood
8003	LEAD in blood and urine
8004	POLYCHLORINATED BIPHENYLS in serum
8005	ELEMENTS in blood or tissue
	Antimony
	Cadmium
	Chromium
	Copper
	Iron
	Lanthanum
	Lead
	Lithium
	Magnesium
	Manganese
	Molybdenum
	Nickel
	Platinum
	Silver
	Strontium
	Thallium
	Vanadium
	Zinc
	Zirconium
8300	HIPPURIC ACID in urine (color)
8301	HIPPURIC and METHYL HIPPURIC ACIDS in urine (HPLC)
8302	MBOCA in urine (rev. 5/15/85)
8303	PENTACHLOROPHENOL in urine
8304	BENZIDINE in urine (TLC)
8305	PHENOL and p-CRESOL in urine
8306	BENZIDINE in urine (GC)
8308	FLUORIDE in urine
8310	METALS in urine:
	Aluminum
	Barium
	Cadmium
	Chromium
	Copper
	Iron
	Lead
	Manganese
	Molybdenum
	Nickel
	Platinum
	Silver
	Strontium
	Tin
	Titanium
	Zinc
9000	CHRYSOTILE ASBESTOS (bulk)

V. B. INDEX OF SECOND EDITION METHOD NUMBERS

[The Second Edition Method Number is the method number as it appeared in the indicated volume of the NIOSH Manual of Analytical Methods, 2nd Edition, Vols 1 through 7].

CRDT = Criteria Document
SDS = Sampling Data Sheet from NIOSH Publication 77-159
NR = Not revised
TBR = To be revised in future supplements

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method [Number]
P&CAM	102	1	Lead in blood (Dithizone)	LEAD [7082]; LEAD IN BLOOD OR URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	106	1	Silica (colorimetric)	SILICA, CRYSTALLINE [7601]
	107	1	Antimony in urine	NR
	108	1	Nitrogen oxides	NITROGEN DIOXIDE [6700]
	109	1	Silica (XRD)	SILICA, CRYSTALLINE [7500]
	110	1	Silica (Infrared)	SILICA, CRYSTALLINE [7602]
	112	1	Carbon monoxide	TBR
	113	1	Carbon monoxide in blood	NR
	114	1	Fluoride in urine	FLUORIDE IN URINE [8308]
	115	1	Hydrogen chloride	ACIDS, INORGANIC [7903]
	116	1	Cyanide	CYANIDES [7904]
	117	1	Hydrogen fluoride	FLUORIDES [7902]; ACIDS, INORGANIC [7903]
	118	1	Acrolein	ACROLEIN [2501]
	121	1	Beryllium	BERYLLIUM [7102]; ELEMENTS-ICP [7300]
	124	1	Selenium in urine	NR
	125	1	Formaldehyde	FORMALDEHYDE [3500, 2502, 3501]
	126	1	Hydrogen sulfide	TBR
	127	1	Acetone	KETONES I [1300]
	127	1	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; BENZENE [3700]; HYDROCARBONS, AROMATIC [1501]
	127	1	2-Butanone	2-BUTANONE [2500]
	127	1	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	p-Dioxane	DIOXANE [1602]
	127	1	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
	127	1	Methylene chloride	METHYLENE CHLORIDE [1005]
	127	1	Styrene	HYDROCARBONS, AROMATIC [1501]
	127	1	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1003]
	127	1	Toluene	HYDROCARBONS, BP 35-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]
	127	1	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1003]
	127	1	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
	127	1	Xylene	HYDROCARBONS, AROMATIC [1501]
	139	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	139	1	Arsenic in urine	NR
	140	1	Arsenic in urine	NR

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method [Number]
P&CAM	141	1	TDI	TOLUENE-2,4-DIISOCYANATE [2535]
	142	1	MDI	NR
	145	1	Mercury in urine	MERCURY IN URINE [8309]
	146	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	152	1	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]
	153	1	Ozone	NR
	154	1	Ozone	NR
	158	1	Parathion	EPN, MALATHION and PARATHION [5012]
	159	1	Oil mist	MINERAL OIL MIST [5026]
	160	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	163	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	165	1	Mercury in urine	NR
	167	1	Mercury in blood	NR
	168	1	Aniline	AMINES, AROMATIC [2002]
	168	1	o-Toluidine	AMINES, AROMATIC [2002]
	168	1	2,4-Xylidine	AMINES, AROMATIC [2002]
	168	1	Dimethylaniline	AMINES, AROMATIC [2002]
	169	1	Chromic acid	CHROMIUM, HEXAVALENT [7600]
	173	1,5	Aluminum	ALUMINUM [7013]; ELEMENTS-ICP [7300]
	173	1	Antimony	NR
	173	1,5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	173	1,5	Barium	TBR
	173	1,5	Beryllium	BERYLLIUM [7102]; ELEMENTS-ICP [7300]
	173	1,5	Bismuth	TBR
	173	1,5	Cadmium	CADMIUM [7048]; ELEMENTS-ICP [7300]
	173	1,5	Calcium	CALCIUM [7020]; ELEMENTS-ICP [7300]
	173	1,5	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]
	173	1,5	Cobalt	COBALT [7027]; ELEMENTS-ICP [7300]
	173	1,5	Copper	COPPER [7029]; ELEMENTS-ICP [7300]
	173	1,5	Indium	NR
	173	1,5	Iron	ELEMENTS-ICP [7300]
	173	1,5	Lead	LEAD [7082]; ELEMENTS-ICP [7300]
	173	1,5	Lithium	ELEMENTS-ICP [7300]
	173	1,5	Magnesium	ELEMENTS-ICP [7300]
	173	1,5	Manganese	ELEMENTS-ICP [7300]
	173	1,5	Molybdenum	ELEMENTS-ICP [7300]
	173	1,5	Nickel	ELEMENTS-ICP [7300]
	173	1,5	Palladium	NR
	173	1,5	Potassium	NR
	173	1,5	Rubidium	NR
	173	1,5	Silicon	NR
	173	1,5	Silver	ELEMENTS-ICP [7300]
	173	1,5	Sodium	ELEMENTS-ICP [7300]
	173	1,5	Strontium	ELEMENTS-ICP [7300]
	173	1,5	Tellurium	ELEMENTS-ICP [7300]
	173	1,5	Thallium	ELEMENTS-ICP [7300]
	173	1,5	Vanadium	ELEMENTS-ICP [7300]
	173	1,5	Zinc	ZINC [7030]; ELEMENTS-ICP [7300]

	2nd Ed. Method Number	2nd Ed. Vol. Number	Substance	3rd Ed. Method [Number]
P&CAM	175	5	Mercury	MERCURY [6000]
	176	1	Tin	ELEMENTS-ICP [7300]
	177	1	Gallium	NR
	178	1	Vinyl chloride	VINYL CHLORIDE [1007]
	179	1	Carbon disulfide	CARBON DISULFIDE [1600]
	180	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	181	1	Selenium	ELEMENTS-ICP [7300]
	182	1	Chromium	CHROMIUM [7024]; CHROMIUM HEXAVALENT [7600]; ELEMENTS-ICP [7300]
	183	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	184	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	186	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	187	1	Sulfuric acid	ACIDS, INORGANIC [7903]
	188	1	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	189	1	Antimony	NR
	190	1	Indium	NR
	191	1	Cadmium	CADMIUM [7048]; ELEMENTS-ICP [7300]
	191	1	Lead	LEAD [7082]; ELEMENTS-ICP [7300]
	192	1	Arsenic in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	193	1	Antimony in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	194	1	Indium in blood	NR
	195	1	Lead in blood	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	196	1	Arsenic in urine	NR
	197	1	Antimony in urine	NR
	198	1	Gallium in urine	NR
	199	1	Indium in urine	NR
	200	1	Lead in urine	LEAD IN BLOOD AND URINE [8003]; METALS IN URINE [8310]
	201	1	Methyl chloride	METHYL CHLORIDE [1001]
	202	1	Acrylonitrile	ACRYLONITRILE [1604]
	203	1	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
	204	1	Sulfur dioxide	SULFUR DIOXIDE [6004]
	205	1	Ammonia	AMMONIA [6701]
	206	1	Polynuclear aromatic hydrocarbons	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	208	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]; METALS IN URINE [8310]
	209	1	Chlorine	NR
	211	1	Acrolein	ACROLEIN [2501]
	212	1	Fluorides	FLUORIDES [7902]; ACIDS, INORGANIC [7903]
	213	1	bis-(Chloromethyl)ether	NR

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P&CAM	214	1	Lead in air or blood	LEAD [7082]; ELEMENTS-ICP [7300]; LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]
	215	1	Phosphate in urine	NR
	216	1	Phosphoric acid	ACIDS, INORGANIC [7903]
	217	1	Benzene solubles	COAL TAR PITCH VOLATILES [5023]
	219	1	Phosgene	NR
	220	1	Chloromethyl methyl ether	NR
	221	1	Aliphatic amines	TBR
	222	1	Zinc oxide	ZINC OXIDE [7502]
	223	1	Cadmium in blood	ELEMENTS IN BLOOD OR TISSUE [8005]
	224	1	Cadmium in urine	METALS IN URINE [8310]
	225	1	Kepone	KEPONE [5508]
	226	1	2,6-Di-t-butyl-p-cresol	TBR
	227	1	Polymethylsiloxane	TBR
	228	1	Thiram	THIRAM [5005]
	230	1	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	231	1	Nitrogen oxides	NITROGEN DIOXIDE [6700]
	232	1	Formic acid	NR
	234	1	Dyes, benzidine, o-tolidine	DYES [5013]
	235	1	Formaldehyde	FORMALDEHYDE [2502, 3500, 3501]
	236	1	MOCA	TBR
	237	1	Tissue preparation	ELEMENTS IN BLOOD OR TISSUE [8005]
	239	1	Asbestos	FIBERS [7400]; ASBESTOS FIBERS [7402]
	241	1	Sodium hydroxide	ALKALINE DUSTS [7401]
	242	1	Phosphorus	PHOSPHORUS [7905]
	243	1	Benzidine	BENZIDINE and 3,3'-DICHLOROBENZIDINE [5509]
	244	1	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
	245	1	Asbestos (chrysotile, bulk)	CHRYSOTILE ASBESTOS [9000]
	246	1	3,3'-Dichlorobenzidine	BENZIDINE and 3,3'-DICHLOROBENZIDINE [5509]
	247	1	Methanol	METHANOL [2000]
	248	1	1,1-Dimethyl hydrazine	TBR
	248	1	Hydrazine	HYDRAZINE [3503]
	248	1	Methyl hydrazine	TBR
	248	1	Phenyl hydrazine	TBR
	250	4	Zirconium oxide	TBR
	251	1	Benzo(a)pyrene	POLYNUCLEAR AROMATIC HYDROCARBONS [5506, 5515]
	252	1	Dimethylnitrosamine	TBR
	253	1	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
	255	1	Thiophene	TBR
	256	1	Azelaic acid	AZELAIC ACID [5019]
	257	1	Phosphorus	PHOSPHORUS [7905]
	259	1,5	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
	260	4	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
	261	4	Antimony	TBR

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P&CAM	262	1	Lead in blood and urine	LEAD IN BLOOD AND URINE [8003]; ELEMENTS IN BLOOD OR TISSUE [8005]; METALS IN URINE [8310]
	263	4	Hexamethylenetetramine	TBR
	264	4	Naphthylamines	NAPHTHYLAMINES [5518]
	265	4	Arsine	ARSINE [6001]
	266	4	Vinylidene chloride	VINYLIDENE CHLORIDE [1015]
	267	5	Sulfuric acid	ACIDS, INORGANIC [7903]
	268	5	Sulfur dioxide, sulfates, sulfites	SULFUR DIOXIDE [6004]
	269	4	4-Aminobiphenyl	TBR
	270	4	Aminoethanol compounds	AMINOETHANOL COMPOUNDS [2007]
	271	4	Tungsten	TUNGSTEN [7074], ELEMENTS-ICP [7300]
	272	4	2-Nitropropane	2-NITROPROPANE [2528]
	273	4	4-Nitrobiphenyl	TBR
	276	4	Ethylenediamine	TBR
	277	4	Methylamine	TBR
	278	4	Vinyl acetate	TBR
	279	4	Beryllium in tissue	ELEMENTS IN BLOOD OR TISSUE [8005]
	280	4	N,N-Dimethyl-p-toluidine	AMINES, AROMATIC [2002]
	281	4	Ethylene thiourea	ETHYLENE THIOUREA [5011]
	282	4	Tetramethyl thiourea	TETRAMETHYL THIOUREA [3505]
	283	4	Oil mist	MINERAL OIL MIST [5026]
	284	4	4-Dimethylaminoazobenzene	TBR
	285	5	Crotonaldehyde	TBR
	286	5	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	288	5	Beryllium	BERYLLIUM [7102]; ELEMENTS-ICP [7300]
	290	5	Vanadium	ELEMENTS-ICP [7300]
	291	5	α-Chloroacetophenone	NR
	294	5	Cyclopentadiene	1,3-CYCLOPENTADIENE [2523]
	295	5	Dichlorovos	TBR
	296	6	Hydrogen sulfide	TBR
	297	5	Dibutyl phosphate	DIBUTYL PHOSPHATE [5017]
	298	5,7	Nickel	ELEMENTS-ICP [7300]
	299	5	Dimethylnitrosamine	TBR
	300	5	Ethylenimine (aziridine)	TBR
	301	5	Dimethyl sulfate	TBR
	302	5	Maleic anhydride	TBR
	303	5	Styrene oxide	TBR
	304	5	OCBM	TBR
	305	5	Phosphorus trichloride	PHOSPHORUS TRICHLORIDE [6402]
	307	5	Hexachlorobutadiene	TBR
	308	5	Hexachlorocyclopentadiene	HEXACHLORO-1,3-CYCLOPENTADIENE
	309	5	Chrysotile asbestos (bulk)	CHRYSOTILE ASBESTOS [9000]
	310	5	Hydrogen chloride	ACIDS, INORGANIC [7903]
	313	6	Warfarin	WARFARIN [5002]
	314	5	Trichloroisocyanuric acid	TBR
	315	5	Benzidine in urine	BENZIDINE IN URINE [8304, 8306]

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P&CAM	316	6	Silica, amorphous	SILICA, AMORPHOUS [7501]
	317	6	Diethylcarbmoyl chloride	TBR
	318	6	Formaldehyde	FORMALDEHYDE [2502, 3500, 3501]
	319	6	Chromium (VI)	CHROMIUM, HEXAVALENT [7600]
	320	6	Arsenic, organo-	ARSENIC, ORGANO- [5022]
	321	6	1,2-Dichloropropane	1,2-DICHLOROPROPANE [1013]
	322	6	Trimellitic anhydride	TBR
	323	6	Titanium diboride	TBR
	324	6	Boron carbide	BORON CARBIDE [7506]
	325	6	Benzidine, o-anisidine and o-tolidine dyes	DYES [5013]
	326	6	TDI	TOLUENE-2,4-DIISOCYANATE [2535]
	327	6	Hippuric acid in urine	HIPPURIC ACID IN URINE [8300]
	328	6	ALAD in blood	ALAD IN BLOOD [8000]
	329	6	PCB in blood	POLYCHLORINATED BIPHENYLS IN SERUM [8004]
	330	6	Phenol and Cresol in urine	PHENOL and p-CRESOL IN URINE [8305]
	331	6	Methyl ethyl ketone peroxide	METHYL ETHYL KETONE PEROXIDE [3508]
	332	6	Chloroacetic acid	CHLOROACETIC ACID [2008]
	333	6	Bisphenol A	TBR
	335	6	Pentachloroethane	PENTACHLOROETHANE [2517]
	336	6	Tetraethyl pyrophosphate	TETRAETHYL PYROPHOSPHATE-TEPP [2504]
	337	7	p-Chlorophenol	TBR
	338	7	Ethylene glycol	ETHYLENE GLYCOL [5500]
	339	7	Inorganic acids	ACIDS, INORGANIC [7903]
	340	7	Acetone cyanohydrin	ACETONE CYANOHYDRIN [2506]
	341	7	Diborane	DIBORANE [6006]
	342	7	MOCA in urine	MBOCA IN URINE [8302]
	343	7	Polychlorobenzenes	POLYCHLOROBENZENES [5517]
	344	7	Nickel carbonyl	NICKEL CARBONYL [6007]
	345	7	Welding and brazing fume	WELDING AND BRAZING FUME [7200]
	346	7	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
	347	7	MDI	ISOCYANATE GROUP [5505]
	348	7	2,4,7-Trinitro-9-fluorenone	2,4,7-TRINITROFLUOREN-9-ONE [5018]
	349	7	Vinyl bromide	VINYL BROMIDE [1009]
	350	7	Lead sulfide	LEAD SULFIDE [7505]
	351	7	Elements by ICP	ELEMENTS-ICP [7300]
	354	7	Formaldehyde	FORMALDEHYDE [2502, 3500, 3501]
	355	-	Talc, respirable	TBR
	357	-	n-Octanethiol	1-OCTANETHIOL [2510]
	358	-	Pentachlorophenol in urine	PENTACHLOROPHENOL IN URINE [8303]
	359	-	Benzidine in urine	BENZIDINE IN URINE [8304, 8306]
	360	-	Hippuric Acid in urine	HIPPURIC ACID IN URINE [8300]; HIPPURIC and METHYL HIPPURIC ACIDS IN URINE [8301]
	361	-	2-Butanone, ethanol, and toluene in blood	2-BUTANONE, ETHANOL, AND TOLUENE IN BLOOD [8002]
	362	-	Pentachlorophenol in blood	PENTACHLOROPHENOL IN BLOOD [8001]
	363	-	Polychlorinated terphenyls	CHLORINATED TERPHENYL [5014]
	364	-	Vanadium oxides	VANADIUM OXIDES [7504]

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P&CAM	365	-	2-Butanone	2-BUTANONE [2500]
	368	-	Tin, organo-	ORGANOTIN COMPOUNDS [5504]
	374	-	Acrolein	ACROLEIN [2501]
	S1	2	Acetone	KETONES I [1300]
	S2	2	Antimony	NR
	S3	2	2-Butanone	2-BUTANONE [2500]
	S4	2	Hydrogen sulfide	TBR
	S5	2	Manganese	ELEMENTS-ICP [7300]
	S7	5	p-Nitroaniline	TBR
	S8	2	Ozone	NR
	S10	2	Camphor	KETONES II [1301]
	S11	5	Chloroacetaldehyde	TBR
	S12	2	Mesityl oxide	KETONES II [1301]
	S13	2	5-Methyl-3-heptanone	KETONES II [1301]
	S15	2	Methyl (n-amyl) ketone	KETONES II [1301]
	S16	2	Ethyl butyl ketone	KETONES II [1301]
	S17	5	Furfural	FURFURAL [2529]
	S18	2	Hexone (MIBK)	KETONES I [1300]
	S19	2	Cyclohexanone	KETONES I [1300]
	S20	2	2-Pentanone	KETONES I [1300]
	S22	2	p-tert-Butyltoluene	HYDROCARBONS, AROMATIC [1501]
	S23	2	Cumene	HYDROCARBONS, AROMATIC [1501]
	S24	4	Diphenyl	BIPHENYL [2530]
	S25	2	Vinyl toluene	HYDROCARBONS, AROMATIC [1501]
	S26	2	α-Methyl styrene	HYDROCARBONS, AROMATIC [1501]
	S27	2	Terphenyl	o-TERPHENYL [5021]
	S28	2	Cyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
	S29	2	Ethylbenzene	HYDROCARBONS, AROMATIC [1501]
	S30	2	Styrene	HYDROCARBONS, AROMATIC [1501]
	S31	2	sec-Amyl acetate	ESTERS I [1450]
	S32	2	tert-Butyl acetate	ESTERS I [1450]
	S33	2	Dibutyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
	S35	2	Ethyl acrylate	ESTERS I [1450]
	S36	2	Ethyl formate	TBR
	S37	2	Methyl isoamyl acetate	ESTERS I [1450]
	S38	2	Methyl acrylate	TBR
	S39	2	Methyl cellosolve acetate	TBR
	S40	2	Di-2-ethylhexyl phthalate	DIBUTYL PHTHALATE and DI[2-ETHYLHEXYL] PHTHALATE [5020]
	S41	2	2-Ethyoxyethyl acetate	ESTERS I [1450]
	S42	2	Methyl acetate	TBR
	S43	6	Methyl methacrylate	TBR
	S44	2	Isobutyl acetate	ESTERS I [1450]
	S45	2	Isoamyl acetate	ESTERS I [1450]
	S46	2	sec-Butyl acetate	ESTERS I [1450]
	S47	2	n-Butyl acetate	ESTERS I [1450]
	S48	2	n-Propyl acetate	ESTERS I [1450]
	S49	2	Ethyl acetate	TBR

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S50	2	Isopropyl acetate	TBR
S51	2	n-Amyl acetate	ESTERS I [1450]
S52	2	Allyl alcohol	ALCOHOLS III [1402]
S53	2	sec-Butyl alcohol	ALCOHOLS II [1401]
S54	2	Cyclohexanol	ALCOHOLS III [1402]
S55	2	Diacetone alcohol	ALCOHOLS III [1402]
S56	2	Ethanol	ALCOHOLS I [1400]
S57	2	Hydroquinone	HYDROQUINONE [5004]
S58	2	Isoamyl alcohol	ALCOHOLS III [1402]
S59	2	Methanol	METHANOL [2000]
S60	2	Methyl isobutyl carbinol	ALCOHOLS III [1402]
S62	2	n-Propyl alcohol	ALCOHOLS II [1401]
S63	2	tert-Butyl alcohol	ALCOHOLS I [1400]
S64	2	Isobutyl alcohol	ALCOHOLS II [1401]
S65	2	Isopropyl alcohol	ALCOHOLS I [1400]
S66	2	n-Butyl alcohol	ALCOHOLS II [1401]
S67	2	Chlorinated camphene	TBR
S69	2	Dipropylene glycol methyl ether	TBR
S70	2	Glycidol	GLYCIDOL [1608]
S71	2	Methylal	METHYLAL [1611]
S72	2	Phenyl ether	TBR
S73	2	Phenyl ether-biphenyl mixture	TBR
S74	2	Phenyl glycidyl ether	TBR
S75	2	Propylene oxide	PROPYLENE OXIDE [1612]
S76	2	2-Butoxyethanol	ALCOHOLS IV [1403]
S77	2	Isopropyl glycidyl ether	TBR
S78	2	Tetrahydrofuran	TETRAHYDROFURAN [1609]
S79	2	2-Methoxyethanol	ALCOHOLS IV [1403]
S80	2	Ethyl ether	ETHYL ETHER [1610]
S81	2	n-Butyl glycidyl ether	TBR
S82	2	Cyclohexene	HYDROCARBONS, BP 36-126 °C [1500]
S84	5	Methyl acetylene (propyne)	TBR
S85	6	Methyl acetylene/propadiene	TBR
S86	2	Naphtha, coal tar	NAPHTHAS [1550]
S87	2	Propane	TBR
S88	2	Turpentine	TURPENTINE [1551]
S89	2	Heptane	HYDROCARBONS, BP 36-126 °C [1500]
S90	2	Hexane	HYDROCARBONS, BP 36-126 °C [1500]
S91	2	Butadiene	1,3-BUTADIENE [1024]
S92	2	Ketene	TBR
S93	2	LPG	TBR
S94	2	Methylcyclohexane	HYDROCARBONS, BP 36-126 °C [1500]
S95	2	Propylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S96	2	Pentachloronaphthalene	NR
S97	2	Octachloronaphthalene	TBR
S98	2	Methyl iodide	METHYL IODIDE [1014]
S99	4	Methyl chloride	METHYL CHLORIDE [1001]

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S100	2	Hexachloronaphthalene	TBR
S101	2	Hexachloroethane	HYDROCARBONS, HALOGENATED [1003]
S102	2	Fluorotrichloromethane	TRICHLOROFLUOROMETHANE [1006]
S103	2	Ethylene chlorohydrin	ETHYLENE CHLOROHYDRIN [2513]
S104	2	Ethylene dibromide	ETHYLENE DIBROMIDE [1008]
S105	4	Ethyl chloride	ETHYL CHLORIDE [2519]
S106	2	Ethyl bromide	ETHYL BROMIDE [1011]
S107	2	Dibromodifluoromethane	DIBROMODIFLUOROMETHANE [1012]
S108	2	Dichlorotetrafluoroethane	DICHLORODIFLUOROMETHANE and 1,2-DICHLORO-TETRAFLUOROETHANE [1018]
S109	2	Dichlorofluoromethane	DICHLOROFLUOROMETHANE [2516]
S110	2	1,2-Dichloroethylene	HALOGENATED HYDROCARBONS [1003]
S111	2	Dichlorodifluoromethane	DICHLORODIFLUOROMETHANE and 1,2-DICHLORO-TETRAFLUOROETHANE [1018]
S112	2	Chloroprene	CHLOROPRENE [1002]
S113	2	Chlorobromomethane	HYDROCARBONS, HALOGENATED [1003]
S114	2	Bromoform	HYDROCARBONS, HALOGENATED [1003]
S115	2	Benzyl chloride	HYDROCARBONS, HALOGENATED [1003]
S116	2	Allyl chloride	ALLYL CHLORIDE [1000]
S117	2	Acetylene tetrabromide	1,1,2,2-TETRABROMOETHANE [2003]
S118	2	Epichlorohydrin	EPICHLOROHYDRIN [1010]
S119	2	Chlorinated diphenyl oxide	CHLORINATED DIPHENYL ETHER [5025]
S120	4	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S121	2	Polychlorinated biphenyls	POLYCHLOROBIPHENYLS [5503]
S122	2	Ethylene dichloride	HYDROCARBONS, HALOGENATED [1003]
S123	2	1,1-Dichloroethane	HYDROCARBONS, HALOGENATED [1003]
S124	2	1,1,2,2-Tetrachloroethane	1,1,2,2-TETRACHLOROETHANE [1019]
S125	2	Trifluorobromomethane	BROMOTRIFLUOROMETHANE [1017]
S126	2	1,2,3-Trichloropropane	HYDROCARBONS, HALOGENATED [1003]
S128	2	Trichloronaphthalene	NR
S129	2	1,1,2-Trichloro-1,2,2-trifluoroethane	1,1,2-TRICHLORO-1,2,2-TRIFLUOROETHANE [1020]
S130	2	Tetrachloronaphthalene	NR
S131	2	1,1,1,2-Tetrachloro-difluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUORO-ETHANE [1016]
S132	2	1,1,2,2-Tetrachloro-difluoroethane	1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE and 1,1,2,2-TETRACHLORO-1,2-DIFLUORO-ETHANE [1016]
S133	2	Chlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S134	2	1,1,2-Trichloroethane	HYDROCARBONS, HALOGENATED [1003]
S135	3	o-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S137	3	Diazomethane	DIAZOMETHANE [2515]
S138	4	n-Butylamine	TBR
S139	3	Diethylamine	TBR
S140	5	Diethylaminoethanol	AMINOETHANOL COMPOUNDS [2007]
S141	4	Diisopropylamine	TBR
S142	3	Dimethylamine	TBR
S143	3	1,1-Dimethyl hydrazine	TBR

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S144	3	Ethylamine	TBR
S146	3	N-Ethyl morpholine	TBR
S147	3	Isopropylamine	TBR
S148	6	Methylamine	TBR
S149	3	Methyl hydrazine	TBR
S150	3	Morpholine	TBR
S152	3	Triethylamine	TBR
S153	3	Monomethylaniline	TBR
S155	3	Tetramethylsuccinonitrile	TBR
S156	3	Acrylonitrile	ACRYLONITRILE [1604]
S158	4	2-Aminopyridine	TBR
S160	3	Phenyl hydrazine	TBR
S161	3	Pyridine	PYRIDINE [1613]
S162	3	2,4-Xylidine	AMINES, AROMATIC [2002]
S163	5	Anisidine (o and p-)	ANISIDINE [2514]
S164	3	Dimethylaniline	AMINES, AROMATIC [2002]
S165	3	Acetonitrile	ACETONITRILE [1606]
S166	5	Dinitro-o-cresol	TBR
S167	3	Cresol	CRESOLS [2001]
S168	3	o-Toluidine	AMINES, AROMATIC [2002]
S169	4	Acetic acid	ACETIC ACID [1603]
S170	3	Acetic anhydride	ACETIC ANHYDRIDE [3506]
S173	5	Formic acid	TBR
S174	3	Sulfuric acid	ACIDS, INORGANIC [7903]
S175	3	Hydrogen bromide	ACIDS, INORGANIC [7903]
S176	3	Hydrogen fluoride	FLUORIDES [7902]; ACIDS, INORGANIC [7903]
S178	3	2-Hexanone	KETONES I [1300]
S179	3	Phthalic anhydride	NR
S181	4	Quinone	TBR
S182	5	Silver	ELEMENTS-ICP [7300]
S183	3	Tin	ELEMENTS-ICP [7300]
S185	3	Zirconium	ELEMENTS-ICP [7300]
S186	3	Copper	COPPER [7029]; ELEMENTS-ICP [7300]
S187	3	Tellurium hexafluoride	TBR
S188	3	Rhodium, fume and dust	TBR
S189	3	Rhodium, soluble	TBR
S190	3,7	Selenium	ELEMENTS-ICP [7300]
S191	3,7	Platinum	ELEMENTS-ICP [7300]
S193	3	Molybdenum	ELEMENTS-ICP [7300]
S194	5	Hafnium	TBR
S198	3	Barium	BARIUM [7056]
S199	4	Mercury	MERCURY [6000]
S200	3	Yttrium	ELEMENTS-ICP [7300]
S201	5	Tantalum	ELEMENTS-ICP [7300]
S203	4	Cobalt	COBALT [7027]; ELEMENTS-ICP [7300]
S204	3,7	Tellurium	ELEMENTS-ICP [7300]
S205	3	Calcium	CALCIUM [7020]; ELEMENTS-ICP [7300]
S206	3	Nickel	ELEMENTS-ICP [7300]
S208	3	Tributyl phosphate	TBR

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S209	3	Triorthocresyl phosphate	TBR
S210	3	Triphenyl phosphate	TBR
S211	5	1-Chloro-1-nitropropane	TBR
S213	3	1,1-Dichloro-1-nitroethane	1,1-DICHLORO-1-NITROETHANE [1601]
S214	4	Dinitrobenzene	TBR
S215	4	Dinitrotoluene	TBR
S216	3	Nitroglycerin/EGDN	NITROGLYCERIN/EGDN [2507]
S217	3	Nitrobenzene	NITROBENZENES [2005]
S218	3	p-Nitrochlorobenzene	NITROBENZENES [2005]
S219	4,6	Nitroethane	NITROETHANE [2526]
S220	6	Nitromethane	NITROMETHANE [2527]
S223	3	Nitrotoluene	NITROBENZENES [2005]
S224	3	Tetranitromethane	NR
S225	3	Tetryl	TBR
S227	3	n-Propyl nitrate	TBR
S228	4	Picric acid	TBR
S229	3	Arsine	ARSINE [6001]
S237	3	Hydrazine	HYDRAZINE [3503]
S243	4	Stibine	STIBINE [6008]
S244	5	Sulfur hexafluoride	TBR
S245	6	Sulfuryl fluoride	TBR
S246	3	Hydrogen chloride	ACIDS, INORGANIC [7903]
S248	3	Carbon disulfide	CARBON DISULFIDE [1600]
S249	3	Carbon dioxide	TBR
S250	3	Cyanide	CYANIDES [7904]
S253	4	Benzoyl peroxide	BENZOYL PEROXIDE [5009]
S254	3	Dimethylacetamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S255	3	Dimethylformamide	DIMETHYLACETAMIDE and DIMETHYLFORMAMIDE [2004]
S256	5	Thiram	THIRAM [5005]
S257	5	Phosphorus pentachloride	TBR
S262	3	Carbon black	CARBON BLACK [5000]
S264	3	Ethyl silicate	TBR
S272	3	Oil mist	MINERAL OIL MIST [5026]
S273	3	Carbaryl (Sevin)	CARBARYL [5006]
S274	3	DDT	TBR
S275	3	Aldrin	ALDRIN and LINDANE [5502]
S276	5	ANTU	TBR
S278	6	Chlordane	TBR
S279	5	2,4-D	2,4-D and 2,4,5-T [5001]
S280	6	Demeton	DEMETON [5514]
S281	3	p-Dichlorobenzene	HYDROCARBONS, HALOGENATED [1003]
S283	3	Dieldrin	TBR
S284	6	Endrin	TBR
S285	3	EPN	EPN, MALATION, and PARATHION [5012]
S286	3	Ethylene oxide	ETHYLENE OXIDE [1614, 3702]
S287	5	Heptachlor	TBR
S288	4	Hydrogen cyanide	CYANIDES [7904]

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S290	3	Lindane	ALDRIN and LINDANE [5502]
S291	5	Methyl formate	NR
S292	3	Naphthalene	HYDROCARBONS, AROMATIC [1501]
S293	3	Nicotine	TBR
S294	5	Paraquat	PARAQUAT [5003]
S295	3	Parathion	EPN, MALATHION, and PARATHION [5012]
S296	6	Mevinphos (Phosdrin)	MEVINPHOS [2503]
S297	4	Pentachlorophenol	TBR
S298	6	Pyrethrum	PYRETHRUM [5008]
S299	6	Ronnel	TBR
S300	5	Rotenone	ROTENONE [5007]
S301	5	Sodium fluoroacetate	TBR
S302	5	Strychnine	STRYCHNINE [5016]
S303	5	2,4,5-T	2,4-D and 2,4,5-T [5001]
S306	3	Thallium	ELEMENTS-ICP [7300]
S308	4	Sulfur dioxide	SULFUR DIOXIDE [6004]
S309	3	Arsenic	ARSENIC [7900]; ARSENIC TRIOXIDE [7901]; ELEMENTS-ICP [7300]
S310	3	Aniline	AMINES, AROMATIC [2002]
S311	3	Benzene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; BENZENE [3700]
S312	3	Cadmium	CADMIUM [7048]; ELEMENTS-ICP [7300]
S313	3	Cadmium fume	CADMIUM [7048]; ELEMENTS-ICP [7300]
S314	3	Carbon tetrachloride	HYDROCARBONS, HALOGENATED [1003]
S315	3	Silica, crystalline	SILICA, CRYSTALLINE [7500, 7601, 7602]
S316	4	Zinc oxide	ZINC OXIDE [7502]
S317	3	Chromium, hexavalent	CHROMIUM, HEXAVALENT [7600]
S318	3	Xylene	HYDROCARBONS, AROMATIC [1501]
S319	4	Nitric acid	ACIDS, INORGANIC [7903]
S320	4	Nitrogen dioxide	NITROGEN DIOXIDE [6700]
S321	4	Nitric oxide	TBR
S323	3	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]
S327	4	Formaldehyde (Girard T)	FORMALDEHYDE [3501, 2502, 3500]
S328	3	Methyl chloroform	HYDROCARBONS, HALOGENATED [1003]
S329	3	Methylene chloride	METHYLENE CHLORIDE [1005]
S330	3	Phenol	PHENOL [3502]
S332	5	Phosphine	TBR
S333	3	Phosphoric acid	ACIDS, INORGANIC [7903]
S334	4	Phosphorus	PHOSPHORUS [7905]
S335	3	Tetrachloroethylene	HYDROCARBONS, HALOGENATED [1003]
S336	3	Trichloroethylene	TRICHLOROETHYLENE [1022, 3701]
S339	3	Beryllium	BERYLLIUM [7102]; ELEMENTS-ICP [7300]
S340	4	Carbon monoxide	TBR
S341	3,7	Lead	LEAD [7082]; ELEMENTS-ICP [7300]
S342	6	Mercury, organo	TBR
S343	3	Toluene	HYDROCARBONS, BP 36-126 °C [1500]; HYDROCARBONS, AROMATIC [1501]; TOLUENE [4000]

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S345	5	Acetaldehyde	ACETALDEHYDE [3507]
S346	4	Allyl glycidyl ether	TBR
S347	5	Ammonia	AMMONIA [6701]
S348	5	Ammonium sulfamate	TBR
S349	3	Boron oxide	NUISANCE DUST TOTAL [0500]
S350	4	n-Butyl mercaptan	TBR
S351	3	Chloroform	HYDROCARBONS, HALOGENATED [1003]
S352	3	Chromium	CHROMIUM [7024]; ELEMENTS-ICP [7300]
S354	4	Copper fume	COPPER [7029]; ELEMENTS-ICP [7300]
S356	5	Crag herbicide I	NR
S357	3	sym-Dichloroethyl ether	sym-DICHLOROETHYL ETHER [1004]
S358	3	Diisobutyl ketone	KETONES I [1300]
S360	3	Dioxane	DIOXANE [1602]
S361	5	2-Ethoxyethanol	ALCOHOLS IV [1403]
S365	4	Furfuryl alcohol	TBR
S366	4	Iron oxide fume	ELEMENTS-ICP [7300]
S367	3	Isophorone	ISOPHORONE [2508]
S368	3	Isopropyl ether	TBR
S369	3	Magnesium oxide fume	ELEMENTS-ICP [7300]
S370	3	Malathion	EPN, MALATHION, and PARATHION [5012]
S371	4	Methoxychlor	TBR
S372	3	Methyl bromide	METHYL BROMIDE [2520]
S374	4	Methylcyclohexanol	TBR
S375	4	Methylcyclohexanone	METHYL CYCLOHEXANONE [2521]
S376	3	Molybdenum	ELEMENTS-ICP [7300]
S378	3	Octane	HYDROCARBONS, BP 36-126 °C [1500]
S379	3	Pentane	HYDROCARBONS, BP 36-126 °C [1500]
S380	3	Naphtha, petroleum	NAPHTHAS [1550]
S381	4	Sodium hydroxide	ALKALINE DUSTS [7401]
S382	3	Stoddard solvent	NAPHTHAS [1550]
S383	4	Tetraethyl lead	TETRAETHYL LEAD [2533]
S384	4	Tetramethyl lead	TETRAMETHYL LEAD [2534]
S385	3	Titanium dioxide	TBR
S388	4	Vanadium	ELEMENTS-ICP [7300]
S391	3	Vanadium	ELEMENTS-ICP [7300]
CRDT	-	Fibrous glass	CARBON BLACK [5000]; FIBERS [7400]
CRDT	-	Nitrous oxide	NITROUS OXIDE [6600]
CRDT	-	Organotins	ORGANOTIN COMPOUNDS [5504]
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