NIOSH Manual of Analytical Methods

Volume 6

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

NIOSH MANUAL OF ANALYTICAL METHODS

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VOLUME 6

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Public Health Service
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National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
Cincinnati, Ohio

August 1980

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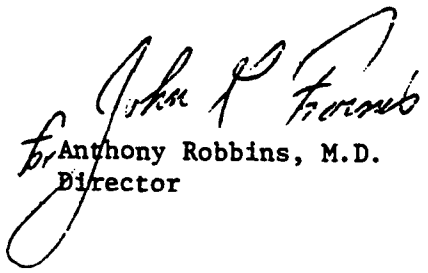
DHHS (NIOSH) Publication No. 80-125

FOREWORD

Environmental monitoring methods have played an important role in the evaluation and control of occupational diseases. They provide the information needed to modify and improve our control systems and to protect the worker from occupational health hazards.

These methods are also a necessary part of all standards which set environmental limits for toxic exposures. Many of the methods in this book have been recommended to the Occupational Safety and Health Administration for use in their compliance monitoring program. It is a pleasure to present this volume for your use.



for Anthony Robbins, M.D.
Director

PREFACE

This volume of the NIOSH Manual of Analytical Methods presents 35 new methods for monitoring exposure to toxic substances in the workplace. The second edition of the Manual (Volumes 1-3) was published in 1977 and presents 337 methods. Volumes 4 and 5, published in 1978 and 1979, supplement those methods with 117 new methods.

As a companion to the earlier books, Volume 6 presents methods that expand the scope of the Manual and together provide the largest set of sampling and analytical techniques available for industrial hygiene monitoring. Like Volume 5, errata pages for earlier methods have been included in this book. The method numbering system is the same and methods can be located by P&CAM- or S-numbers in the Contents. Also, a Cumulative Index in alphabetical order covering all the chemical substances in the six volumes can be found at the end of this book.

For your convenience, three franked postcards are attached to the back cover. You may want to offer suggestions for changes or corrections in the Manual. We welcome your comments.

Copies of the previous volumes may be obtained by sending a self-addressed label with your order to: Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Stock Numbers: 017-033-00267-3 (Volume 1), 017-033-00260-6 (Volume 2), 017-033-00261-4 (Volume 3), 017-033-00317-3 (Volume 4), and 017-033-00349-1 (Volume 5).

ABSTRACT

This sixth volume of the Manual provides an additional 35 methods for monitoring toxic substances. The procedures give step-by-step instructions on how to sample as well as how to analyze for these compounds in the workplace.

Many of the methods have been validated using an improvement of the protocol developed in 1974 for the joint NIOSH/OSHA Standards Completion Program. Other methods have been only partly evaluated and are presented for information and trial use.

CONTENTS OF VOLUME 6

CUMULATIVE INDEX (VOLUMES 1-6)

ACKNOWLEDGMENTS

All of the P&CAM-numbered methods have an author line following the references of each individual method. The S-numbered methods were developed and validated under Contract 210-76-0123 by either SRI International or Arthur D. Little, Inc. Their contributions to this volume are gratefully acknowledged.

The aid of Drs. Laurence J. Doemeny, Janet C. Haartz, Larry K. Lowry, and Alexander W. Teass and Messers Barry R. Belinky, Robert A. Glaser, and John L. Holtz for monitoring contracts or supervising sections producing methods is acknowledged. Thanks are due to Karen A. Eaton, Grace A. Fannin, Helen Fley, Patricia L. Munch, Eleanor P. Robers, Anna B. Silvers, and Frankie J. Smith for preparing the manuscript. Special thanks go to Teri A. McKee for her extra help in completing the manuscript.

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ERRATA TO VOLUMES 1-5

The following additions, changes or corrections to the methods appearing in Volumes 1-5 of the NIOSH Manual of Analytical Methods are given below. Other changes were presented in Volumes 4 and 5.

Page Number; Section	Change
	Volume 1
179-3; 7.3	"0.1 M" to "0.01 M"
	Add "Dilute 1.0 mL of the resulting solution to 100 mL with water."
209-3; 10.	"24.450" to "24,450"
235-4; 7.3	"4.190 g" to "4.4703 g"
	Volume 2
S8-3; 7.3	"phospheric" to "phosphoric"
S29-1; Box	Precision "0.041" to "0.08"
S29-2; 4.1	"17 mg/cu m" to "35 mg/cu m"
	Volume 4
S384-1; Box	OSHA Standard "0.07" to "0.075"
	Volume 5
x	Page No. "165" to "163-5"
	Page No. "178-1" to "178-10"
	179-5; 8.3.2 - Delete change
	179-5; 7.3 - Delete change
xiii	Page No. "xiii" to "S114-4"
xiv	Page No. "xiv" to "S114-5"

268-7; 10.2	In SO_2 formula: "0.08002" <u>to</u> "0.8002"
305-7;10.3.1	In formula: " $\sqrt{P_1P_2/T_1T_2} \times \frac{298}{760}$" <u>to</u> " $\sqrt{\frac{P_1T_2}{P_2T_1}}$
S332-5; 7.16	"$Fe(NH_4)_2(SO_4)_2$" <u>to</u> "$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$"
S332-5; 7.17	"$SnCl_2$" <u>to</u> "$SnCl_2 \cdot 2H_2O$"
Cumulative Index	Beryllium "S399" <u>to</u> "S339"
	DDVP "S295" to "295"

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HYDROGEN SULFIDE

Measurements Research Branch

Analytical Method

Analyte:	Sulfide	Method No:	P&CAM 296
Matrix:	Air	Range:	15-60 mg/m^3
Procedure:	Adsorption on molecular sieve, thermal desorption GC-FPD	Precision:	0.066
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 A known volume of air is drawn through a desiccant tube containing sodium sulfate to remove water vapor, followed by a tube containing molecular sieve to trap hydrogen sulfide.

1.2 Hydrogen sulfide is desorbed from the molecular sieve using thermal desorption, and the sample is analyzed by gas chromatography.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was evaluated over the range of 15-60 mg/m^3 at an atmospheric temperature of 25°C and an atmospheric pressure of 745 mm Hg, using a 5-L sample. This sample size is based on both the capacity of molecular sieve to trap hydrogen sulfide and the sensitivity of the flame photometric detector. The method is capable of measuring smaller amounts, with satisfactory desorption efficiency. (Ref. 11.1) Desorption efficiency must be determined over the range used.

2.2 The upper limit of the method depends on the adsorption capacity of the molecular sieve. This capacity may vary with the concentrations of hydrogen sulfide and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 400 mg of molecular sieve) reaches 5% of the concentration in the test gas

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mixture. A breakthrough test was conducted at a concentration of 17.1 mg/m^3 and 85% relative humidity. Breakthrough occurred in 173 minutes at an average sampling rate of 0.137 L/min. This corresponds to a breakthrough capacity of 0.359 mg and volume of 23.7 L.

3. Interferences

3.1 Humidity is the single largest interference in this method. It is advantageous to record the relative humidity of a sampling site if possible. Use of the recommended desiccant tube eliminates the effects of humidity when sampling for hydrogen sulfide.

3.2 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 Any sulfur containing compound that has the same retention time as hydrogen sulfide at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The relative standard deviation for the total analytical and sampling method in the range of 7.5-30 mg/m^3 was 0.066. This value corresponds to a 1.9 mg/m^3 standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2.

4.2 The relative standard deviation is a good measure of accuracy of the method. Experiments performed in development studies are described in Reference 11.3. In these experiments the desorption efficiency was greater than 0.988 for a loading of 0.1-0.4 mg on the sorbent. On the average, the concentrations obtained at 0.5X, 1X, and 2X the OSHA standard level were 0.07% lower than the "true" concentration for 18 samples collected from dynamically generated test atmospheres. This difference could represent the random variation from the experimentally determined "true" concentration. Storage stability studies indicated that the mean concentration of samples analyzed after seven days was 20% lower than the mean concentration of samples analyzed immediately after collection. Thus, storage represents a source of bias that would need to be corrected in the method.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be

eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 Thermal desorption eliminates the use of desorbing liquids and hence the background disturbance they cause. In doing so, thermal desorption improves sensitivity. In addition, thermal desorption eliminates any lengthy desorption time period.

5.3 One disadvantage of the method is the fact that hydrogen sulfide is not stable on molecular sieve. In addition, the capacity of molecular sieve is dramatically reduced in the presence of water vapor (humidity). Use of the recommended desiccant tube eliminates the humidity problem.

5.4 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for using one tube only.

6. Apparatus

6.1 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within 5% at the desired flow rate. Each personal sampling pump must be calibrated with a representative molecular sieve and desiccant tube in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Molecular sieve tubes. Glass tube with both ends flame sealed, 7 cm long with a 8-mm O.D. and 6-mm I.D., containing two sections of molecular sieve, 5-angstrom, separated by a 2-mm portion of urethane foam. The adsorbing section contains 400 mg of molecular sieve, the backup section contains 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 2.5 inch of mercury at a flow of 0.2 L/min.

6.3 Desiccant tubes. The desiccant tube was a 7-cm long Teflon tube with 13-mm I.D. containing 9.0 g of anhydrous sodium sulfate.

6.4 Gas chromatograph equipped with a flame photometric detector in the sulfur mode.

6.5 Column (36' x 1/8" FEP Teflon) packed with 40/60 mesh Chromosorb T coated with 12% polyphenyl ether and 0.5% H_3PO_4.

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6.6 Glass lined thermal desorption unit with a sample splitter or a glass lined thermal desorption unit and a 500-mL evacuated glass vessel with a septum port.

6.7 An electronic integrator or some other suitable method of determining peak areas.

6.8 Milliliter syringes, 5-mL and other convenient sizes for preparing standards.

6.9 Mercury Manometer (if evacuated vessel from 6.6 is used).

6.10 Tedlar bags of varying size for H_2S standard preparation.

7. Reagents

7.1 Nitrogen, or equivalent, pre-purified with 99.995% minimum purity.

7.2 Air, or equivalent, dry.

7.3 Hydrogen, or equivalent, pre-purified with 99.995% minimum purity.

7.4 H_2S, or equivalent, 95.5% minimum purity.

7.5 H_2S permeation tube, or equivalent, 230 cm, standard emission from Metronics, Inc.

8. Procedure

8.1 Collection and Shipping of Samples

8.1.1 Immediately before sampling, break the ends of the molecular sieve tube to provide an opening at least one-half the internal diameter of the tube. Uncap the ends of the desiccant tube. The molecular sieve tubes must be from the same manufacturer's lot.

8.1.2 The smaller section of molecular sieve is used as a backup and should be positioned nearer the sampling pump. The dessiccant tube should be connected to the molecular sieve tube (at the end of the tube with the larger amount of molecular sieve) with the shortest possible piece of tubing.

8.1.3 The desiccant and molecular sieve tubes should be placed in a vertical direction during sampling to minimize channeling through the molecular sieve.

8.1.4 Air being sampled should not be passed through any hose or tubing before entering the desiccant tube.

8.1.5 A sample size of 5 L is recommended. Sample at a known flow rate of 0.15-0.2 L/min. Record the sampling time, flow rate, and type of sampling pump used.

8.1.6 The temperature, pressure and relative humidity of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.1.7 The molecular sieve tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.1.8 With each batch or partial batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank.

8.1.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Hydrogen sulfide samples must be shipped immediately and in cold storage, if possible, because H_2S does not store well on molecular sieve.

8.2 Analysis of Samples

8.2.1 Preparation of Samples. In preparation for analysis, each molecular sieve tube is scored with a file in front of the first section of molecular sieve and broken open. The glass wool is removed and discarded. The molecular sieve in the first (larger) section is transferred to the appropriate housing in the thermal desorption unit. The separation section of foam is removed and discarded; the second section is transferred to a 2-mL stoppered sample vial. These two sections are analyzed separately.

8.2.2 Desorption of Samples. The samples are positioned in the thermal desorption unit. One of two steps is taken:

1. For small concentrations, the sample can desorb directly into the gas chromatograph for separation and analysis.

2. For samples of large concentration, the sample must go through a sample splitter or be desorbed into an evacuated vessel of known volume.

The temperature for thermal desorption of H_2S is 180°C.

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8.2.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

50 mL/min (50 psig) nitrogen carrier gas flow;
170 mL/min (30 psig) hydrogen gas flow to detector;
200 mL/min (60 psig) air flow to detector;
100°C injector temperature;
50°C column temperature.

A retention time of 2-3 minutes can be expected for H_2S under these conditions and using the column recommended in 6.5.

8.2.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. With thermally desorbed samples, the injection may be carried out in one of two manners:

1. directly from the thermal desorption unit via a heated 3-mL gas sampling loop; or

2. via 3 mL gas-lock syringe injection if the sample was thermally desorbed into the evacuated vessel mentioned in 6.6

Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.2.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.3 Determination of Desorption Efficiency

In practical application, thermal desorption is 100% efficient.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1-2 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/3.0 mL versus peak area. NOTE: Since no internal standard is used in this method, standard gases must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FPD response.

9.1 From a gas cylinder of pure hydrogen sulfide and clean, dry air or nitrogen, bag standards should be made up to cover the range of 3 mg/m^3 to 70 mg/m^3. At least five working standards should be prepared.

9.2 Analyze the standards as per Section 8.3.

9.3 Prepare a standard calibration curve by plotting concentration of hydrogen sulfide in mg/3.0 mL versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed if the standard curve is based upon mg/3.0 mL hydrogen sulfide and the volume of the sample injected is identical to the volume of the standards injected.

10.2 Corrections for blank must be made for each sample.

$$M = M_S - M_b$$

where: M = weight of H_2S in mg
M_S = mg found in front section of sample tube
M_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total mass of the sample, M_T.

10.4 The concentration hydrogen sulfide in the air sampled can be expressed in mg/m^3.

$$C_M = \frac{M_T}{V_C\ (L)}\ (\text{Section } 10.3) \times 1000\ (L/m^3)$$

where: C_M = concentration in mg/m^3
M_T = total mass of sample in mg
V = volume of air sampled

10.5 Another method of expressing concentration is ppm.

$$C_A = \frac{C_M \times 24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

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where: C_A = air concentration in ppm
P = pressure (mm Hg) of air sampled
T = temperature (^oC) of air sampled
24.45 = molar volume (L/mole) at 25^oC and 760 mm Hg
MW = molecular weight (g/mole) of hydrogen sulfide
760 = standard pressure (mm Hg)
298 = standard temperature (^oK)

11. References

11.1 Black, M.S., R.P. Herbst, and D.R. Hitchcock: Solid Adsorbant Preconcentration and Gas Chromatographic Analysis of Sulfur Gases. Anal. Chem. 50: 848-851 (1978).

11.2 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2

Mary Lynn Woebkenberg
Measurements Systems Section

WARFARIN

Measurements Research Branch

Analytical Method

Analyte:	Warfarin	Method No.:	P&CAM 313
Matrix:	Air	Range:	0.054 - 0.244 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.056
Procedure:	Filter collection, extraction with methanol, HPLC		
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known volume of air is drawn through a polytetrafluoroethylene filter to trap the warfarin present. The filter is transferred to a sample jar and extracted in 5 mL of methanol. An aliquot of the sample is injected into a high performance liquid chromatograph equipped with a UV detector set at 280 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was evaluated over the range of 0.0539-0.244 mg/cu m using a 408-liter sample. This method may be extended to higher values by further dilution of the sample solution.

2.2 The detection limit of the analytical method is estimated to be at least 0.5 µg per mL for a 20-µL injection at a range of 0.04 absorbance units with a recorder range of 10 mV full scale.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any other compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data based on a single set of conditions cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.054-0.244 mg/cu m was 0.0555.

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This value corresponds to a 5.55 µg/cu m standard deviation at the OSHA standard level. Statistical information may be found in Reference 11.1.

4.2 In evaluation experiments, a collection efficiency of at least 98% was determined for the collection medium, thus no bias was introduced in the sample collection test. The analytical method recovery was determined to be 102.1% for a collection loading of 19.63 µg. In storage stability studies the mean of samples analyzed after seven days was within 7% of the mean of samples analyzed immediately after collection. Experiments performed in this study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

5.2 The accuracy of the method has not been adequately assessed.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of organic dust has the following components:

6.1.1 Filter. The filter unit consists of a 37-mm diameter, 1.0 micrometer pore size, polytetrafluoroethylene membrane filter and a 37-mm diameter cellulose backup pad.

6.1.2 Filter Holder. The filter is placed in a two-piece filter holder held together by tape or a shrinkable band.

6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate is needed. The pump must be calibrated with a representative filter unit in the line.

6.1.4 Thermometer.

6.1.5 Barometer.

6.1.6 Stopwatch.

6.2 High pressure liquid chromatograph equipped with a detector capable of UV detection at 280 nm.

6.3 HPLC column (30-cm x 3.9-mm I.D. stainless steel) packed with µ-Bondapak C_{18} or equivalent.

6.4 A syringe or fixed volume sample loop for HPLC injection. A 20-µL sample volume was used for these studies.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes in convenient sizes for making standard solutions.

6.7 Volumetric flasks in convenient sizes for making standard solutions.

6.8 Squat form 2-oz ointment jars with Teflon film gaskets and screw caps.

6.9 A 5-mL pipette.

6.10 Tweezers.

7. Reagents

Whenever possible reagents used should be ACS reagent grade or better.

7.1 Warfarin, 99%.

7.2 Methanol, distilled in glass.

7.3 0.0025N phosphoric acid. Prepare by dissolving 60 µL of 85% H_3PO_4 per liter of water.

7.4 Warfarin stock solution, 2 mg/mL. Prepare by dissolving 0.02 g in 10 mL methanol.

7.5 HPLC mobile phase, 30% by volume 0.0025N phosphoric acid - 70% by volume methanol.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter unit in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter holder and close firmly to insure that the edge of the filter is

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sealed. The filter is held in place by a cellulose backup pad and the filter holder is held together by tape or a shrinkable cellulose band. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.3.2 Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.

8.3.4 A sample size of 400 liters is recommended. Sample at a flow rate of between 1.5 and 2.0 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and readjusted as necessary. If the rotameter cannot be readjusted, terminate sampling.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If the pressure reading is not available, record the elevation.

8.3.7 After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Obtain a blank sample by handling one filter in the same manner as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples or partial batch of ten samples.

8.3.10 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a Teflon-lined cap.

8.3.11 The filter holders should be shipped in a suitable container designed to prevent damage in transit.

Never transport the bulk sample in the same container as the sample or blank filters.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the filter from the holder with the aid of tweezers and transfer to the 2-oz. ointment jar.

2. Add 5 mL of methanol to the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

8.4.2 Analysis by High Pressure Liquid Chromatograph. The mobile phase is 30% by volume 0.0025N H_3PO_4: 70% by volume methanol. The typical operating conditions for the liquid chromatograph are:

1. 1.5 mL/min solvent flow rate

2. Ambient column temperature

3. 800 psi system pressure

4. 280 nm UV detection wavelength

8.4.3 Injection. A 20-µL sample aliquot is recommended for this analysis. The sample may be injected either by using an appropriate syringe or by filling a fixed volume sample loop, provided that reproducibility requirements are satisfied. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery determinations should cover the concentration range of interest.

8.5.2 Procedure for Determining Recovery. A known amount of warfarin, equivalent to that present in a 400-liter sample at a selected level, is added to a PTFE filter

and air dried. A stock solution containing 2.0 milligrams of warfarin per milliliter of methanol is prepared. Ten, 20 and 40-microliter aliquots of the solution are added to the filter and air-dried to produce samples equivalent to 400-liter collections at 0.5, 1 and 2 times the OSHA standard. Six filters at each of the three levels are prepared and allowed to stand overnight. A parallel blank filter is also prepared except no sample is added to it. All filters are then extracted and analyzed as described in Section 8.4.

The sample recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered - Filter Blank (µg)}}{\text{Weight (µg) Added}}$$

9. Calibration and Standardization

A series of standards, varying in the concentration range corresponding to approximately 0.1 to 3 times the OSHA standard for the samples under study, is prepared and analyzed under the same HPLC conditions and during the same time period as the unknown samples.

9.1 From the stock solution listed in Section 7.4, prepare at least six standards to cover the concentration range of 4-120 µg/5 mL. This is done by adding from 2 to 60-microliter aliquots of the stock solution to 5 mL methanol in ointment jars. Analysis is done as described in Section 8.4.

9.2 The series of standards is analyzed under the same HPLC conditions and during the same time period as the unknown samples It is convenient to express concentration of standards in µg/5 mL, because samples are extracted in this amount of methanol. Curves are established by plotting concentrations in µg/5 mL versus peak area.

10. Calculations

10.1 Read the concentration in µg/5 mL corresponding to the sample peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg/5 mL and the volume of the sample injected is identical to the volume of standards injected.

10.2 Corrections for the sample blank (Section 8.3.9) must be made for each sample.

$$\text{µg} = \text{µg sample} - \text{µg blank}$$

where:

µg sample = µg found in sample filter
µg blank = µg found in sample blank filter

10.3 Divide the weight of analyte found on each filter by the recovery (Section 8.5) to obtain the corrected µg/sample.

$$\text{Corrected µg/sample} = \frac{\text{Weight found}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min). If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/L, by

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.3)}}{\text{Air Volume Sampled (L)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.

31.

11.2 Backup Data Report for Warfarin, 313, prepared under NIOSH Contract No. 210-76-0123, 4/13/79.

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ARTHUR D. LITTLE, INC.
NIOSH Contract No. 210-76-0123

AMORPHOUS SILICA

Measurements Research Branch

Analytical Method

Analyte:	Cristobalite	Method No.:	P&CAM 316
Matrix:	Airborne dust	Range:	1 - 12.5mg/m^3
Procedure:	Filter collection, thermal conversion, X-ray diffraction	Precision:	0.10 (Analytical)
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

1. Synopsis

   1.1 A known volume of air is drawn through a PVC membrane filter to trap airborne dust.

   1.2 The filter samples are scanned by X-ray diffraction to determine other phases which may cause matrix interference.

   1.3 The filters are ashed, heat treated to quantatively convert the amorphous silica to cristobalite, and the residue redeposited on silver membrane filters.

   1.4 The mass of amorphous silica present is determined by measuring the diffraction peak intensity of the cristobalite and the silver filter. The mass is calculated from calibration data.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The range of the method is 1 to 12.5 mg/m^3 for a 400-L air sample of pure amorphous silica.

   2.2 The detection limit is 3 μg on a 25-mm silver filter but quantitative measurements cannot be made at this level.

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3. Interferences

3.1 Several compounds (e.g., albite, ammonium phosphate, tridymite) have diffraction peaks that interfere with the major peak for cristobalite. The presence of phase interference can be verified by X-ray diffraction analysis. If interferences are present, analytical measurements are made using a different cristobalite peak, with a commensurate decrease in sensitivity and precision. In addition, quartz and cristobalite present initially must be quantitated prior to heat treatment and subtracted from the final quantity of cristobalite (Section 8.4.1).

3.2 The presence of specific elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

3.3 The interfering effect of matrix absorption by the sample result in attenuation of the diffracted beam; thus corrections must be made (Sections 10.3 to 10.5).

3.4 Alkali and alkaline earth oxides prevent 100% conversion of amorphous silica to cristobalite. This can be circumvented by an acid wash prior to heat treatment (Section 8.4.2(1)).

4. Precision and Accuracy

4.1 The relative standard deviation for the analytical method was determined to be related to the type of amorphous silica (gelled, fumed or precipitated) and was 4.4%, 8.2% and 4.7% respectively over the range 0.5 - 5 mg pure amorphous silica.

4.2 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

5.1 The X-ray diffraction method is specific and can be used to determine if the polymorphs of crystalline free silica are also present.

5.2 The equipment is relatively expensive, but the diffraction measurements can be automated.

5.3 There are no other specific methods for amorphous silica.

6. Apparatus

6.1 Personal Sampling Equipment. The sampling unit for respirable dust collection has the following components:

6.1.1 Ten-mm nylon cyclone.

6.1.2 Filter unit consisting of the filter media (Section 6.1.4) and appropriate three-piece cassette filter holder.

6.1.3 Personal sampling pump calibrated to ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.4 Polyvinyl chloride membrane filters, 37-mm, 5 µm pore size. (Gelman VM-1 filters are unacceptable because of the high background produced by the ash; Millipore BS-filters are unacceptable because they contain high levels of amorphous silica.)

6.2 Area Sampling Equipment. The sampling unit for high volume respirable dust collection has the following components:

6.2.1 Calibrated Gast 1022 vacuum pump equipped with a needle valve flow controller or equivalent.

6.2.2 HASL cyclone, one inch (Bendix No. 240 cyclone), or equivalent.

6.2.3 Polyvinyl chloride membrane filter, 47-mm, 1 µm pore size.

6.2.4 Filter holder.

6.3 X-ray diffraction instrument with a copper target X-ray tube. The instrument should be optimized for intensity rather than resolution.

6.4 Silver membrane filters, 25-mm diameter and 0.45 µm pore size: Selas Flotronics, Spring House, Pennsylvania 19477, or equivalent.

6.5 Filtration apparatus (Gelman No. 1107 or equivalent) and side arm vacuum flask.

6.6 Canada balsam pitch-resin, or other glue.

6.7 Sieve, 10-µm.

6.8 Low temperature radiofrequency asher (LTA).

6.9 Agate mortar and pestle.

6.10 Pyrex beakers, 50-mL.

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6.11 Instrument calibration reference specimen, mica, Arkansas stone (alpha quartz) or other stable standard.

6.12 Desiccator.

6.13 Filter storage cassettes.

6.14 Forceps.

6.15 Polyethylene wash bottle.

6.16 Analytical balance.

6.17 Ultrasonic bath or probe.

6.18 Furnace capable of maintaining a temperature of 1100°C for six hours and of temperature programming to 500°C at 50°C/minute or less.

6.19 Platinum crucibles with covers for high temperature furnace.

7. Reagents

ACS Analytical Reagent Grade or equivalent.

7.1 Pure fumed amorphous silica, grade M-5 or MS-7 (Cabot Corporation, 125 High St., Boston MA.)

7.2 Glue, tape or other material necessary for attaching silver filters to filter holders.

7.3 Isopropanol.

7.4 Desiccant (Drierite).

7.5 NaCl, powder.

8. Procedure

8.1 Cleaning of Equipment. All glassware should be detergent washed, thoroughly rinsed with tap water followed by distilled water and dried.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. Cyclone assemblies should be cleaned before using and a visual check for scoring of the surfaces made. Replace the cyclone if it is scored.

8.3 Collection and Shipping of Samples

8.3.1 Attach the cassette and cyclone assembly to the worker.

8.3.2 Collect the sample at a flow rate of 1.7 liters per minute. A 400-L air sample is recommended as it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and the sampling should be terminated at any evidence of a problem.

8.3.3 Terminate sampling after the predetermined time and note sample flow rate, collection time, date, ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.4 After sample collection, the filter cassette should be firmly sealed with plugs in both the inlet and outlet ends.

8.3.5 Carefully record sample and identify all relevant sample data.

8.3.6 With each batch of ten samples, submit one filter from the same lot of filters that was used for sample collection and which is handled in the same way as the samples except that no air is drawn through it. Label this as a blank.

8.3.7 The filter cassettes should be shipped in a suitable container designed to prevent damage in transit.

8.3.8 When possible, collect a bulk (settled dust) sample of the suspected parent material of the airborne dust in a suitable container and ship with the filter samples.

8.3.9 Collect a high volume respirable dust sample using the equipment listed under 6.2. A sample of 27,000 liters should be collected at 75 liters per minute.

8.4 Analysis of Samples

8.4.1 Obtain a qualitative X-ray diffraction scan (broad 2θ range) of the bulk and/or high volume respirable sample to determine the presence of free silica polymorphs and any matrix interference. The expected diffraction peaks are as follows:

Mineral	2 Theta, Primary	2 Theta, Secondary
Quartz	26.66	20.85
Cristobalite	21.93	36.11
Tridymite	21.62	20.50
Silver	38.12	44.28

8.4.2 Ash and heat the samples to convert the amorphous silica to cristobalite as follows:

1. If chemical interferences (CaO, Al_2O_3, MgO, SrO, BaO, Fe_2O_3, Cr_2O_3) were observed in the analysis of the bulk and/or high volume respirable samples, the samples must undergo a pretreatment step to eliminate non-stoichiometric conversion of the amorphous silica to cristobalite. If other free silica polymorphs are present, quantitative analysis for these analytes must be performed prior to heat treatment (see Reference 11.3). If interferences are not present, proceed to step 2. Using forceps, place the filter samples in 50 mL beakers and situate within the sample compartment of the low temperature asher so that the sample exposure to the plasma is optimized. The samples are ashed for two hours at 100 watts RF power at the oxygen flow rate recommended by the manufacturer using the techniques recommended in the instrument manual. After ashing, add 50 mL of 2% HCl to each beaker, agitate for several minutes and filter using PVC filters.

2. Fold the PVC filters, taking care that no sample is displaced, place in platinum crucibles, cover, and place the crucibles in the furnace. Raise the temperature slowly ($\leq$ 50°C/min) to 500°C to ash the filters. When ashing is complete (approximately 0.5 hours), raise temperature to 1100°C and maintain at 1100°C for six hours. Cool and remove from furnace.

8.4.3 Transfer residue to agate mortar and grind with approximately 10 mg of NaCl. Transfer to a 50-mL beaker and dissolve NaCl with 10 mL distilled water. Ultrasonically agitate the beaker contents for three minutes.

8.4.4 Place a silver filter in the filtration apparatus and attach the chimney. Pour several mL of water on the filter. With no suction, very little water will penetrate the filter. Pour the suspension from the beaker into the chimney, washing the beaker several times

with water from a wash bottle. Apply a vacuum to the filter flask so the suspension is filtered rapidly. Do not wash the chimney walls. Leave the vacuum on for sufficient time to produce a dry filter. Disassemble the filter funnel, release the vacuum and remove the filter with forceps.

8.4.5 Transfer the silver filter to a sample holder, attach using Canada balsam and insert in the diffractometer.

8.4.6 Analyze the most intense diffraction peak of cristobalite that is free from matrix interference by step scanning the peak and integrating the counts. Measure the background on each side of the peak for one half the time used for peak scanning and add the counts from each side for a total (average) background. The position of the background must be determined for each set of samples. The net count or intensity, I_c, is the difference between the peak integrated count and the total background count.

8.4.7 Determine the net count, I_{Ag}, of the appropriate silver peak following the procedure of 8.4.6. Scan times should be shorter for silver filters but should be consistent throughout the method.

8.4.8 After each unknown is scanned, determine the net count, I_r^o, of the reference specimen. Determine normalized intensities, $\hat{I}$, for each peak by dividing the peak intensity by that of the reference specimen. Examples for the cristobalite and silver peaks are:

$$\hat{I}_c = \frac{I_c}{I_r^o}$$

$$\hat{I}_{Ag} = \frac{I_{Ag}}{I_r^o}$$

Record the normalized intensities.

8.4.9 Remove the silver filter from the holder by dissolving the canada balsam with isopropyl alcohol. Turn the filter over so that the clean side is up and remount it in the sample holder. Determine the net count for the silver peak I_{Ag}^o (Section 8.4.8). Normalize the measured intensity.

$$\hat{I}^{o}_{Ag} = \frac{I^{o}_{Ag}}{I^{o}_{r}}$$

and record $\hat{I}^{o}_{Ag}$.

9. Calibration and Standardization

9.1 Preparation of Cristobalite Standards

9.1.1 Prepare suspensions of fumed amorphous silica in isopropanol by accurately weighing approximately 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg of the standard into 50-mL beakers, adding 10 mL of isopropanol and then ultrasonically agitating. Filter through PVC filters.

9.1.2 Use the heat treatment and filtering procedures (Section 8.4) to convert the amorphous silica standards to cristobalite standards on silver filters.

9.2 Perform step scans on the standards and reference specimen using the same conditions as those used for the samples. Determine and record the normalized intensity, $\hat{I}^{o}_{c}$, for each peak measured.

10. Calculations

10.1 Prepare a calibration curve by plotting $\hat{I}^{o}_{c}$ as a function of the weight (w) of cristobalite deposited on each standard filter. Poor reproducibility (> 10% RSD) at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line for low weights and curvature at high weights should be ignored when determining the line of best fit.

10.2 Determine the initial slope, m, of the calibration curve in counts/μg. The intercept, b, of the line with the $\hat{I}^{o}_{c}$ axis should be approximately zero. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from 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.

10.3 Using the normalized intensities, $\hat{I}_{Ag}$, for the silver peaks of each sample (Section 8.4.8) and the average $\hat{I}^{o}_{Ag}$ calculated for the clean silver filters, calculate the transmittance, T, of each sample as follows:

$$T = \frac{\hat{I}_{Ag}}{\text{ave } \hat{I}^{o}_{Ag}}$$

10.4 Determine the correction factor, f(T), for each sample according to the formula:

$$f(T) = \frac{-R \ln T}{1-T^R}$$

where: $R = \frac{\sin \theta_{Ag}}{\sin \theta_c}$

and θ_{Ag} and θ_c are the angles θ (not 2θ) of the silver and cristobalite peaks.

10.5 Calculate the weight (w) in milligrams of the cristobalite in each sample:

$$w(mg) = \left[\frac{\hat{I}_c - b}{m}\right] \times [f(T)]$$

Blank values should be zero within the precision of method. Nonzero blanks, if they are consistent, should be subtracted from the sample values.

10.6 For personal sampling pumps with rotameters only, the following correction should be made:

$$V_s = f \times t \left[\frac{P_1}{P_2} \times \frac{T_2}{T_1}\right]^{1/2}$$

where: V_s = corrected air volume (L)
f = sample flow rate (Lpm)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (^oK)
T_2 = temperature of air sampled (^oK)

10.7 Calculate the airborne concentration of amorphous silica dust (C) in mg per cubic meter:

$$C = \frac{W}{V_s}$$

11. References

11.1 Leroux, J. and C. Powers, "Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters," Occup. Health Rev. 21:26, 1970.

11.2 Lange, B. A. and J. C. Haartz, "Quantitative Determination of Synthetic Amorphous Silica Using X-Ray Diffraction," to be published.

11.3 NIOSH Method P&CAM 259 in "NIOSH Manual of Analytical Methods," Vol. 5, D. G. Taylor, Manual Coordinator, DHEW (NIOSH) Publication No. 79-141 (1979).

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DIETHYLCARBAMOYL CHLORIDE

Measurements Research Branch

Analytical Method

Analyte:	Diethylcarbamoyl chloride	Method No.:	P&CAM 317
		Range:	8-240 mg/m^3
Matrix:	Air		
Procedure:	Adsorption on Porapak P, desorption with ethyl acetate, GC analysis via FID	Precision:	0.077
Date Issued:	1/6/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known amount of air is drawn through a sorbent tube containing Porapak P to trap the analyte present. The Porapak P is transferred to a small stoppered sample container and the analyte is desorbed with ethyl acetate. An aliquot of the resulting solution is injected into a gas chromatograph equipped with a flame ionization detector. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

The method was evaluated over the range 8-240 mg/m^3 at a temperature and pressure of 20°C and 756 torr using 5-L samples. This corresponds to the collection of 40-1250 µg of analyte.

The upper limit of the method is dependent upon the capacity of the Porapak P to retain the analyte. No breakthrough was observed when 2.5 mg of the analyte in humid air was evaporated from a U-tube onto a 100 mg bed of the sorbent. In this experiment, 12 L of air were pulled through the sorbent bed at 0.2 L/min.

3. Interferences

3.1 Any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.2 The analyte reacts readily with amines and alcohols. In experiments in which the analyte was trapped with an amine co-contaminant, diethylamine and aniline proved to have no effect on sample stability, while benzylamine appeared to cause a decrease in the recovery which was significantly dependent on temperature and quantity of amine. In addition, the sampling medium has a negligible capacity for diethylamine, a potential co-contaminant. Since the reactive nature and concentration of co-contaminants may be unknown, it is advisable to refrigerate the samples immediately after collection. Analysis should be completed as soon as possible after collection.

4. Precision and Accuracy

4.1 The relative standard deviation for the total sampling and analytical method in the range 8-240 mg/m^3 was 7.7%. At the lower end of the analytical range, this corresponds to 0.62 mg/m^3.

4.2 Five-liter samples from bag standards containing 8 mg/m^3 diethylcarbamoyl chloride in dry air were collected on Porapak P and exposed to humid air (relative humidity > 70%) for one hour. The analyte was quantitatively recovered from these samples after storage for 28 days.

5. Advantages and Disadvantages

5.1 This method was developed for monitoring personal exposures. However, it has not been field tested.

5.2 Due to the hydrophobic nature of the Porapak P, water vapor is not efficiently trapped on the sorbent. Therefore, the capacity of the sampling tube should be unaffected by high relative humidity. The volume of air that can be sampled by the Porapak P is, therefore, high (at least 12 L). However, when the amount of DECC found on the backup section of the sampling tube exceeds 10% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the sampling train. This variation will affect the flow and cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of sampling at 0.2 L/min. The pump should be calibrated with a representative Porapak P tube in line.

6.2 Porapak P* tube. Glass tube, 7.0-cm long, 6-mm outside diameter, and 4-mm inside diameter containing 100-mg front and 50-mg backup sections of 50/80 mesh pre-extracted Porapak P. The sorbent beds are separated by a 2-mm portion of urethane foam and contained at the ends by silanized glass wool plugs. Prior to use, the sorbent is extracted with acetone in a Sohxlet apparatus for two hours, allowed to air-dry, and then placed in the drying tube of the apparatus shown in Figure 1. This apparatus is connected to the carrier gas inlet port of a GC oven and exhausted into the detector. Several grams of the sorbent are dried at 120 °C under helium flowing at 20 mL/min for several hours. The sorbent is allowed to cool in a clean dessiccator. Care should be taken to avoid excessive agitation of the Porapak P during handling. A static charge can be induced in the material and is not readily dissipated. This will cause the individual particles to agglomerate, making the material difficult to handle while packing the collection tubes. The tubes should be washed with acetone and thoroughly dried prior to packing with Porapak P. This prevents the sorbent from adhering to the tube walls. Cap the sorbent tubes with plastic caps prior to use.

6.3 Gas chromatograph equipped with a flame ionization detector. This must be an instrument with a 10-cm or shorter glass or glass-lined transfer line from the column to the detector. Silanize the transfer line prior to use.

6.4 GC column, 2-m long x 4-mm inside diameter silanized glass, packed with 3% Dexsil-300 on 80/100 Supelcoport.

6.5 Electronic integrator or some other suitable method of determining peak areas.

6.6 Vials, 2-mL, with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes, 10-µL and other convenient sizes, for preparing standards.

6.8 Pipets, delivery type, 10-mL and other convenient sizes.

*Porapak P is a styrene-divinylbenzene porous polymer manufactured by Waters Associates.

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6.9 Volumetric flasks, 10-mL and other convenient sizes, for preparing standard solutions.

6.10 Stopwatch.

6.11 Manometer.

6.12 Sohlet extractor.

6.13 Parafilm.

6.14 Glass tubes, 7-cm x 4-mm i.d., flame sealed at one end, used for desorption experiments.

6.15 Distillation apparatus.

7. Reagents

7.1 Acetone, chromatoquality.

7.2 Diethylcarbamoyl chloride. The technical grade material must be purified by distillation at 182 °C prior to use. It is stored over 10A molecular sieves and should be protected from light and heat.

7.3 Ethyl acetate, distilled in glass.

7.4 Helium, purified.

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the caps from the ends of the tube. All tubes must be packed with Porapak P from the same manufacturer's lot.

8.2.2 Connect the Porapak P tube to the sampling pump with a piece of flexible plastic tubing. The samller section of the Porapak P tube is used as a backup and should be positioned nearer the sampling pump.

8.2.3 The tube should be placed in a vertical position during sampling to minimize channeling through the Porapak P.

8.2.4 Air being sampled should not pass through any hose or tubing before entering the Porapak P tube.

8.2.5 The sampling volume will depend upon the concentration of the analyte in air. At least 12 L of air can be sampled. Record the collection time and the flow.

8.2.6 Record the temperature, pressure and relative humidity of the atmosphere being sampled. If the pressure reading is not available, record the elevation.

8.2.7 Seal the Porapak P tube with plastic caps immediately after sampling. Rubber caps should not be used.

8.2.8 With each batch of ten samples, submit at least one blank tube made from the same lot of Porapak P as used for sample collection. This tube should be subjected to exactly the same handling as the samples (break, seal, transport) except that no air is drawn through it.

8.2.9 Capped tubes must be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 Any samples of bulk material should be submitted to the laboratory in glass containers with a Teflon lined cap. These samples should not be transported in the same container as the Porapak P tubes.

8.2.11 Refrigerate the Porapak P tubes as soon after sampling as possible.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Porapak P tube. Remove the glass wool plug and transfer the first (longer) section of sorbent to a 2-mL stoppered vial. Remove the separating section of urethane foam and transfer the backup section of Porapak P to another stoppered vial. It may be necessary to tap the tube sharply to affect complete transfer of the Porapak P. Analyze the two sections separately.

8.3.2 Desorption of Samples. Pipette 1.0 mL of ethyl acetate into each sample container. Shake the sample a few times during the desorption period. Allow the samples to desorb for at least one hour. If preliminary analysis

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indicates that 10 μg or less of the analyte has been collected on the tube(s), the samples should be desorbed in a sonic bath for an additional hour. Analyses should be completed the same day that the samples are desorbed.

8.3.3 GC Conditions

	Flow Rates (mL/min)	Temperatures (°C)	
Helium	20	Injector	150
Hydrogen	40	Detector	150
Air	400	Column	60

The analyte has a retention time of approximately 9 minutes under these conditions using the column recommended in Section 6.4. The ethyl acetate will elute from the column before the analyte.

8.3.4 Injection. Inject a 5-μL aliquot into the gas chromatograph using the solvent-flush technique. It may not be advisable to use an automatic sample injector because of possible plugging of the syringe needle with Porapak P particles.

8.3.5 Measure the area of the sample peak by an electronic integrator or some other suitable form of area measurement.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of diethylcarbamoyl chloride may vary from one laboratory to another and, also, from one batch of Porapak P to another. Thus, it is necessary to determine the desorption efficiency for each batch of Porapak P used.

8.4.2 One hundred milligrams of Porapak P is measured into a 7-cm x 4-mm i.d. glass tube, flame sealed at one end. This Porapak P must be from the same batch as that used in obtaining the samples. The open end is capped with parafilm. A known amount of an ethyl acetate solution containing 1-10 μg/μL of DECC is injected directly into the Porapak P bed with a microliter syringe and the tube is capped with more parafilm. The amount injected is equivalent to that present in an air sample at a selected level.

Six tubes at each of three levels covering the range of interest are prepared in this manner and allowed to stand

overnight to assure complete adsorption of the DECC onto the Porapak P. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed as described in Section 8.4.

Standards are prepared by injecting the same volume of DECC solutions into a 1.0-mL of ethyl acetate with the same syringe as used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D) equals the average weight of DECC in µg recovered from the tube (Q_r) divided by the weight in µg added to the tube (Q_a).

$$D = \frac{Q_r}{Q_a}$$

If D varies significantly with sample weight, plot D vs. Q_r and use the curve to correct for adsorption losses in Section 10.4.

9. Calibration and Standardization

9.1 Prepare a stock standard solution containing 10 µg/µL of DECC in ethyl acetate.

9.2 From the stock solution, prepare at least five standards to cover the range 10-100 µg in 1.0-mL of ethyl acetate.

9.3 Analyze the standards with the samples.

9.4 Prepare a calibration curve by plotting concentration of DECC in µg/1.0 mL versus peak area.

10. Calculations

10.1 Read the weight in µg corresponding to each peak area from the standard curve.

10.2 No blank is expected. If the blank is significant, determine its source and eliminate or correct for it.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 If the desorption efficiency (D) is significantly different from 1.0 (Section 8.4.2), divide the total weight (W) by the desorption efficiency to obtain the corrected weight in µg (Wc).

$$W_c = \frac{W}{D}$$

10.5 The concentration (C) of DECC in the air sampled can be expressed in μg/L.

$$C = \frac{W_c}{V}$$

where V is the volume of air sampled in liters. This number is numerically equal to the concentration of DECC in mg/m^3.

10.6 C may be converted to the concentration in ppm (C') by use of the following formula:

$$C' = C \times \frac{24.45}{M} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:
- P = the pressure of air sampled in torr
- T = the temperature of air sampled in °C
- 24.45 = the molar volume of an ideal gas in liters
- M = molecular weight (g/mole) of diethylcarbamoyl chloride (135 g/mole)
- 760 = standard pressure in torr
- 298 = standard temperature in °K

11. References

11.1 R. A. Glaser. Unpublished report. Development of a Quantitative Sampling and Analytical Method for Diethylcarbamoyl Chloride. Report of Research performed during Fiscal Years 1978 and 1979.

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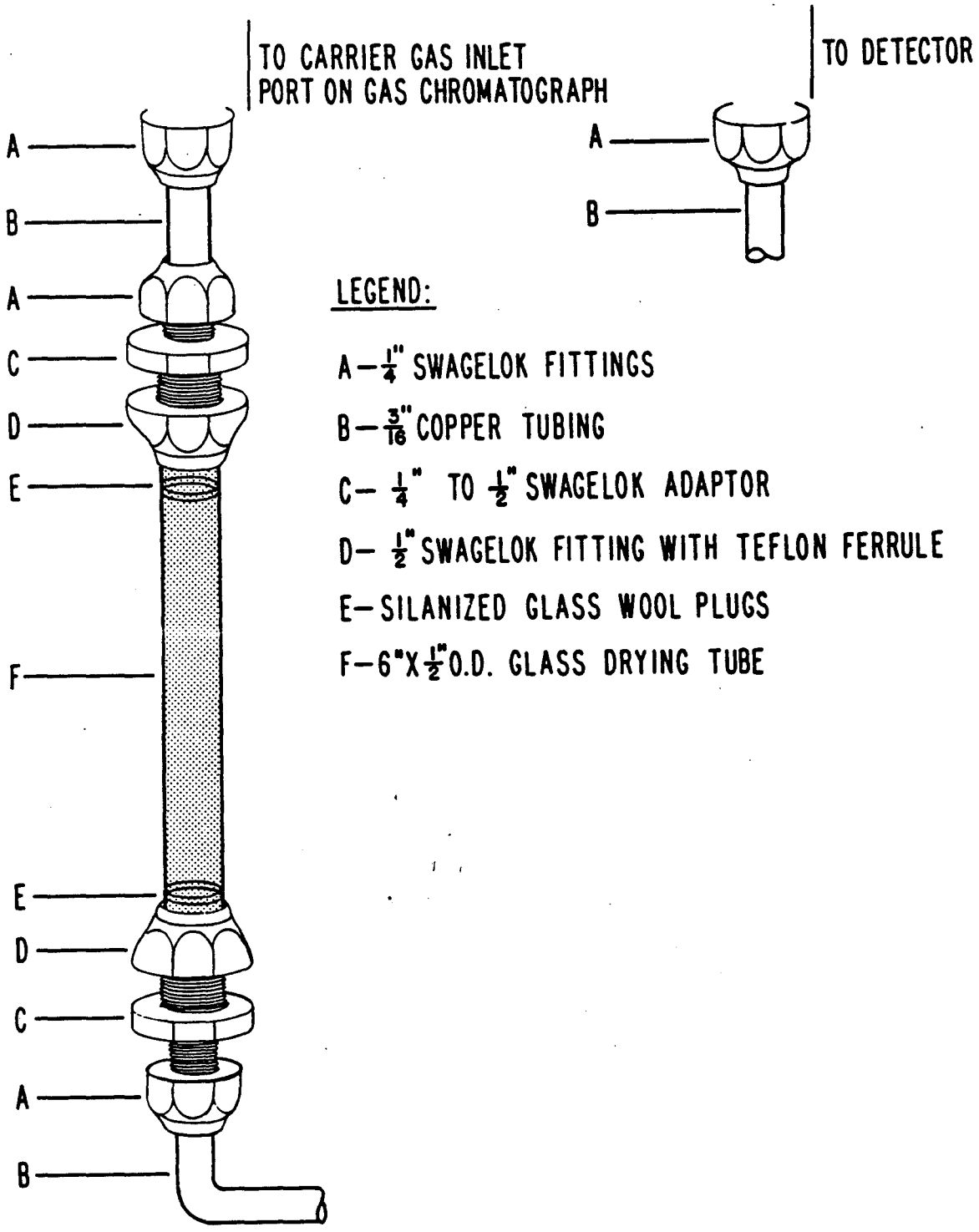
TO CARRIER GAS INLET
PORT ON GAS CHROMATOGRAPH
TO DETECTOR
A
B
A
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A
B
LEGEND:
A—1/4" SWAGELOK FITTINGS
B—3/16" COPPER TUBING
C— 1/4" TO 1/2" SWAGELOK ADAPTOR
D— 1/2" SWAGELOK FITTING WITH TEFLON FERRULE
E—SILANIZED GLASS WOOL PLUGS
F—6"X1/2"O.D. GLASS DRYING TUBE

Figure 1.

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FORMALDEHYDE

Measurement Support Branch

Analytical Method

Analyte:	Formate Ion	Method No.:	P&CAM 318
Matrix:	Air	Range:	0.03--2 mg/m^3
Procedure:	Adsorption on impregnated charcoal, desorption with hydrogen peroxide, ion exchange chromatography	Precision:	0.097
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 A known volume of air is drawn through an impregnated charcoal tube to trap the formaldehyde.

1.2 The charcoal in the tube is transferred to a centrifuge tube and formaldehyde is desorbed with hydrogen peroxide.

1.3 An aliquot of the desorbed sample is injected into an ion chromatograph.

1.4 The area or the height of the resulting formic acid peak is determined and compared with a calibration curve obtained from injections of standard solutions.

2. Working Range, Sensitivity and Detection Limit

2.1 The working range for a 96-liter air sample is 0.03-2 mg/cu m formaldehyde. This corresponds to about 3-200 µg formaldehyde per sample. This range can be extended by using a different sensitivity scale of the ion chromatograph or by diluting the samples.

2.2 The sensitivity of the analytical method is approximately 0.6 µg formaldehyde per sample per mm chart deflection. With a 0.1 mL volume actually being injected, this corresponds to an instrumental sensitivity of 6 ng/mm.

3. Interferences

3.1 Particulate formate and formic acid interfere with this method. The particulate formate can be removed by using a prefilter connected in front of the charcoal tube.

3.2 Maleic and phthalic acids do not interfere with the formaldehyde determination.

4. Precision and Accuracy

4.1 The precision of the overall method is 9.7% in the range 16-320 µg formaldehyde per sample.

4.2 The overall recovery in laboratory generated samples was 100%.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Transportation to the analytical laboratory is simplified with the solid sorbent tubes.

5.2 The sorbent tube has a high capacity even at high relative humidities. It can be used for eight hours to measure a workday concentration, or for short times to measure excursion concentrations.

5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.

5.4 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variation in pressure drop will affect the flow rate, and the sample volume will be imprecise since the pump is calibrated for one tube only.

5.5 Samples can be stored for at least one month without loss.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within 5% at the recommended flow rate.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6 mm o.d. and a 4 mm i.d., containing 2 sections of 20/40 mesh impregnated charcoal separated by a 2 mm portion of urethane foam. The impregnated charcoal tubes are commercially available from SKC, Inc., Eighty Four, Pennsylvania. (Catalog No. 226-45). The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3 mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across

the tube should be less than 2.5 inches of water at a flow rate of 0.2 liter per minute.

6.3 Ion chromatograph, equipped with electrical conductivity detector and recorder or integrator.

6.4 15 mL centrifuge tube.

6.5 10 mL pippette.

6.6 Ultrasonic bath.

6.7 10 mL plastic syringe with male Luer fittings.

6.8 In-line filter with Luer fitting, 25 mm.

6.9 Mixed cellulose ester membrane filter, 25 mm, 0.45 µm or less.

6.10 Volumetric flasks, assorted sizes.

6.11 Microburette.

7. Reagents

All reagents used should be ACS Reagent Grade or better.

7.1 Double deionized water. Conductivity--grade deionized water with a specific conductance of 10 µmho/cm or less is needed for preparation of eluents and other solutions used on the ion chromatograph.

7.2 Hydrogen peroxide (0.1%). Dilute 0.33 mL of 30% H_2O_2 to 100 mL with deionized water.

7.3 Borate eluent (0.005M). Dissolve 7.6284 g $Na_2B_4O_7 \cdot 10\ H_2O$ in deionized water and dilute to 4 liters.

7.4 Formaldehyde stock standard (1 mg/mL). Dilute 3 mL of 37% formaldehyde to 1 liter with deionized water. This solution is stable for at least 3 months. Standardize this solution as described in Section 9.1.

7.5 Iodine (0.1 N). Dissolve 25 g KI in about 25 mL of water, add 12.7 g of iodine, and dilute to 1 liter.

7.6 Iodine (0.01N). Dilute 100 mL of the 0.1N iodine solution to 1 liter. Standardize against sodium thiosulfate.

7.7 Starch solution (1%). Make a paste of 1 g of soluble starch and 2 mL of water and slowly add the paste to 100 mL boiling water. Cool, add several milliliters of chloroform as a

preservative, and store in a stoppered bottle. Discard when a mold growth is noticeable.

7.8 Buffer solution. Dissolve 80 g of anhydrous Na_2CO_3 in about 500 mL of water. Slowly add 20 mL of glacial acetic acid and dilute to 1 liter.

7.9 Sodium bisulfite (1%). Dissolve 1 g of $NaHSO_3$ in 100 mL of water. Prepare fresh weekly.

7.10 Sodium thiosulfate (0.05N). Dissolve 1.25 g of $Na_2S_2O_3 \cdot 5H_2O$ in 100 mL of freshly boiled water and age for about a week.

8. Procedure

8.1 Cleaning of Equipment

Glassware should be washed in detergent and rinsed in dilute (1-5%) nitric acid, followed by thorough rinsing with deionized water.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, the ends of the charcoal tubes are broken to provide an opening of at least one-half the internal diameter of the tube.

8.2.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.2.3 The charcoal tube is placed in a vertical position during sampling in order to minimize channeling through the charcoal.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.2.5 The sampling time, volume and flow rate are measured. The sample is taken at a flow rate of 200 mL per minute or less. The total volume sampled should be no more than 96 liters.

8.2.6 The temperature, pressure and relative humidity of the atmosphere being sampled are recorded.

8.2.7 To obtain a blank sample, a charcoal tube is handled in exactly the same manner as each sample except that no air is drawn through it. Submit at least one blank tube for each batch of 10 samples.

8.2.8 The charcoal tubes are capped with plastic caps immediately after sampling, and shipped to the laboratory for analysis.

8.3 Analysis of Samples

8.3.1 Preparation of Samples

Score each tube with a file in front of the glass wool plug that precedes the first sorbent section and break the tube. Transfer the plug and the initial section to a 15 cm centrifuge tube. Likewise, transfer the second plug and sorbent section to another centrifuge tube. Label each appropriately for separate analysis.

8.3.2 Desorption

Add 10 mL of 0.1% H_2O_2 solution. Seal the samples with parafilm. After one hour of occasional shaking, place the samples in an ultrasonic bath for 20 minutes.

8.3.3 Preparation

Pour the contents of the centrifuge tube into a syringe fitted with an in-line filter (0.45 µm) and collect the filtrate in a second syringe.

8.3.4 Inject the filtered sample into the chromatograph and record the sample identity and instrumental conditions. Typical operating conditions are:

Sensitivity:	30 µmho full scale
Eluent:	0.005 M, $Na_2B_4O_7$
Flow Rate:	138 mL/hr
Separator Column:	3 x 500 mm anion exchanger
Suppressor Column:	6 x 250 mm cation exchanger
Retention Time:	5 minutes

8.3.5 Measure and record the peak height or peak area and obtain the concentration from the standard curve.

9. Calibration and Standardization

9.1 Standardization of Formaldehyde Solution

9.1.1 Pipette 1 mL of formaldehyde standard solution into an iodine flask. Into another flask pipette 1 mL of distilled water; this is the blank.

9.1.2 Add 10 mL of 1% sodium bisulfite and 1 mL of 1% starch solution to each flask.

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9.1.3 Titrate with 0.1 N iodine to a dark blue color.

9.1.4 Destroy the excess iodine with 0.05 N sodium thiosulfate.

9.1.5 Add 0.01 N iodine until a faint blue end point is reached. The excess inorganic bisulfite is now completely oxidized to sulfate, and the solution is ready for the assay of the formaldehyde-bisulfite addition product.

9.1.6 Chill the flask in an ice bath and add 25 mL of chilled buffer solution. Using a microburette, titrate the liberated sulfite with 0.01 N iodine to a faint blue end point. The amount of iodine added in this step must be accurately measured and recorded.

9.1.7 Since 1 mL of 0.01 N I_2 solution is equivalent to 0.15 mg of formaldehyde, the concentration C_s of the standard formaldehyde solution (in mg/mL) is given by the equation:

$$C_s = V_{I_2} \times N_{I_2} \times 15$$

where:

V_{I_2} = volume (in mL) of 0.01 N I_2 solution used to titrate the liberated sulfite, corrected for the blank.

N_{I_2} = the exact normality of the 0.01 NI_2 solution.

9.2 Prepare standards covering the range of 0.3 to 20 µg/mL by adding aliquots of the standardized formaldehyde solution onto 100 mg portions of impregnated charcoal. These portions of charcoal can be obtained from unused charcoal tubes if bulk charcoal is not available.

9.3 Allow the standards to sit for at least an hour, and proceed as in Section 8.3.2.

9.4 From peak heights or areas, construct a standard curve. With each set of samples analyzed, a complete calibration curve should be constructed using newly prepared standards.

10. Calculations

10.1 From the calibration curve, read the concentration of each sample in µg/mL. Multiply by the volume of desorbing

solution to obtain the total µg of formaldehyde per sample. Correct for the blank if necessary.

10.2 The concentration of formaldehyde (C_m) in the air sample may be expressed in mg/m^3.

$$C_m = \frac{W\ (\mu g)}{V\ (l)}$$

where:

W = weight of formaldehyde in the air sample
V = volume of air sampled

10.3 The concentration may also be expressed in terms of parts per million by volume (C):

$$C = mg/m^3 \times \frac{24.45}{M.W.} \times \frac{760}{P} \times \frac{T+273}{298}$$

where: 24.45 = molar volume (l/mole) at 25°C and 760 mm Hg
M.W. = molecular weight of formaldehyde (30.03)
P = pressure in mm Hg of air sampled
T = temperature in °C of air sampled

11. References

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59.

HEXAVALENT CHROMIUM

Measurements Research Branch

Analytical Method

Analyte:	Chromate Ion	Method No.:	P&CAM 319
Matrix	Air	Range:	0.5 - 10 $\mu g/mg^3$
Procedure:	Filter collection, extraction, colorimetry	Precision:	0.029 (analytical)
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

This method expands the diphenylcarbazide method (Refs. 11.1, 11.2) from acid- or water-soluble to <u>total</u> <u>hexavalent</u> chromium (Cr(VI)).

A known volume of air is drawn through a polyvinyl chloride (PVC) filter. The filter is extracted with hot, 3% sodium carbonate-2% sodium hydroxide solution to dissolve all Cr(VI) and to protect it from reduction to trivalent chromium. The extract is acidified with sulfuric acid and analyzed by diphenylcarbazide colorimetry at 540 nm.

2. Working Range, Sensitivity, and Detection Limit

2.1 The working range is 0.5 to 10 µg Cr(VI)/m^3 in a 600-L air sample. This corresponds to 0.3 to 6 µg Cr(VI)/sample, dissolved in 25 mL. The samples may be diluted for larger amounts of Cr(VI). For smaller amounts, larger air samples must be taken.

2.2 The sensitivity (0.0044 Absorbance) and detection limit are approximately 0.05 µg Cr(VI)/m^3 for a 600-L air sample, using a final volume of 25 mL and a 5-cm optical cell.

3. Interferences

3.1 Iron (III) and vanadium (V) give yellow diphenylcarbazide complexes, with color intensities equal to 0.04 µg Cr(VI) given by 200 µg Fe (III) or 4 µg V (V). The vanadium complex is unstable, and samples containing vanadium in less than a 10-fold excess by weight over Cr(VI) may be determined accurately by

allowing the solution to stand for 10 minutes after addition of the diphenylcarbazide. For samples containing large amounts of iron or vanadium, these elements are removed from the sample by extraction at pH 4 with 8-quinolinol in chloroform (Ref. 11.4).

3.2 Mercury (I or II) reacts slowly with diphenylcarbazide to give a violet-blue precipitate. Addition of sodium chloride before color development eliminates this interference (Ref. 11.4).

3.3 Nitrates cause fading of the color; this can be eliminated by buffering to pH 2 with sodium dihydrogen phosphate (Ref. 11.5).

3.4 Chromium (III), when present at 100 μg/sample, has no effect on the determination of 0.5 μg Cr(VI).

4. Precision and Accuracy

4.1 The precision of the analytical method, using PVC filters spiked with 0.3, 0.6, and 1.2 μg Cr(VI) as potassium dichromate solution, was 3.4%, 2.0%, and 3.2% relative standard deviation (RSD), respectively.

4.2 A collection efficiency of 0.945 was determined for 100 $\mu g/m^3$ Cr(VI) as chromic acid mist using 5-μm pore size PVC filters (Ref. 11.2).

4.3 Recoveries of Cr(VI) determined by adding weighed amounts of the pure compounds to PVC filters and extracting were (mean % recovery ± standard deviation): barium chromate ($BaCrO_4$), 99.8 ± 4.6; calcium chromate ($CaCrO_4$), 99.5 ± 7.3; lead chromate ($PbCrO_4$), 98.5 ± 2.6; and potassium dichromate ($K_2Cr_2O_7$), 95.1 ± 2.9.

5. Advantages and Disadvantages

5.1 The method is simple, rapid, and is specific for Cr(VI) in the presence of Cr(III) or other reducing substances such as iron.

5.2 The method prevents loss of hexavalent chromium by maintaining alkaline conditions during extraction of the samples.

5.3 Water-insoluble and water-soluble hexavalent chromium compounds are soluble in the alkaline extraction medium used.

6. Apparatus

6.1 The apparatus for the collection of the personal air samples is:

6.1.1 Filter holder, 3-piece cassette, polystyrene, 37-mm diameter.

6.1.2 Shrinkable cellulose band.

6.1.3 Polyvinyl chloride (PVC) filter, 5.0-μm pore size, 37-mm diameter, supported by a backup pad. (NOTE: Cellulose ester filters are unacceptable because they may react with Cr(VI). Gelman VM-1 or equivalent are acceptable.)

6.1.4 Personal sampling pump, calibrated in line with a representative filter to an accuracy of ± 5% at the recommended flow rate (1.5 to 2.5 L/min).

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.1.8 Bottles, glass, screw cap (30-mL scintillation vials are adequate).

6.1.9 Tweezers, polypropylene or polytetrafluoroethylene.

6.2 Spectrophotometer, for use at 540 nm with 5-cm cells.

6.3 Cuvettes, matched, 5-cm path length.

6.4 Filtration apparatus, vacuum, with PVC filter, 5-μm pore size.

6.5 Beakers, borosilicate, 50-mL, with watch glass covers.

6.6 Volumetric flasks, 25-mL, 100-mL, and 1-L.

6.7 Hot plate, 120-140°C.

6.8 Micropipettes, 20-μL and other convenient sizes.

7. Reagents

All reagents should be analytical reagent grade, and "distilled" water means double-distilled or deionized.

7.1 Sulfuric acid, H_2SO_4, concentrated (98%).

7.2 Sulfuric acid, 6 N. Add 167.0 mL concentrated sulfuric acid (7.1) slowly to distilled water in a 1-L volumetric flask and dilute to the mark with distilled water.

7.3 Sulfuric acid, 0.2 N. Add 5.5 mL of concentrated sulfuric acid (7.1) to distilled water in a 1-L volumetric flask and dilute to the mark with distilled water.

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7.4 Sodium carbonate, Na_2CO_3, anhydrous.

7.5 Sodium hydroxide, NaOH.

7.6 Potassium chromate, K_2CrO_4, or potassium dichromate, $K_2Cr_2O_7$.

7.7 Filter extraction solution. Dissolve 20.0 g of sodium hydroxide and 30.0 g of sodium carbonate in distilled water in a 1-L volumetric flask and dilute to the mark with distilled water. Store the solution in a tightly capped polyethylene bottle and prepare it fresh monthly.

7.8 Diphenylcarbazide. Dissolve 0.50 g of sym-diphenylcarbazide in a mixture of 100 mL of acetone and 100 mL of distilled water. Store in an opaque bottle in the refrigerator. The solution is stable for up to 1 month.

7.9 Cr(VI) stock standard (1000 μg/mL). Dissolve 3.735 g potassium chromate or 2.829 g potassium dichromate in distilled water and dilute to the mark in a 1-L volumetric flask. Store in a polyethylene bottle, and prepare it fresh every 6 months.

7.10 Cr(VI) working standard (10 μg/mL). Dilute 1 mL of the Cr(VI) stock standard to 100 mL with distilled water. Prepare the solution fresh daily.

8. Procedure

8.1 Cleaning of Equipment. Glassware, including screw-cap bottles, should be washed in hot water with detergent and rinsed with, in order, tap water, dilute (5%) nitric acid, and distilled water. Under no circumstances should chromic acid cleaning solution be used.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the PVC filter and the backup pad in the cassette filter holder and press together firmly to insure that a seal is made around the edge of the filter. Apply a shrinkable cellulose band around the assembled cassette.

8.2.2 Remove the cassette plugs and attach the cassette to the personal sampling pump by means of flexible tubing. Clip the cassette face down to the worker's lapel. The sampled air should not pass through any hose or tubing before entering the cassette.

8.2.3 Take the sample at an accurately known flow rate in the range 1.5 to 2.5 L/min. A sample size of 600 L is recommended. Check the pump during operation to assure proper functioning. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 Remove the PVC filter from the cassette within 1 hour of completion of sampling and place it in a screw-cap bottle. Handle the filter only with plastic tweezers. Discard the backup pad.

8.2.5 With each batch of 10 samples or less, submit a blank filter from the same batch used for sampling.

8.3 Analysis of Samples

8.3.1 Remove the PVC filter from the bottle, place it in a 50-mL beaker, and add 5.0 mL of filter extraction solution (7.7). Cover the beaker with a watch glass and heat it near the boiling point on a hot plate, with occasional swirling, for 30 to 45 min. Do not allow the solution to evaporate to dryness, because hexavalent chromium may be lost due to reaction with the PVC filter. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.

8.3.2 Cool the solution and transfer it quantitatively, with distilled water rinses, to a 25-mL volumetric flask, keeping the total volume about 20 mL. (Note: If the solution is cloudy, it should be filtered first through a PVC filter in a vacuum filtration apparatus (6.4), using distilled water rinses).

8.3.3 Add 1.90 mL of 6 N sulfuric acid to the volumetric flask and swirl to mix. Caution: carbon dioxide will be evolved, causing increased pressure in the flask. Let the solution sit for several minutes, until vigorous gas evolution ceases, and then dilute to the mark with distilled water.

8.3.4 Add 0.5 mL of diphenylcarbazide solution (7.8) and invert several times to mix thoroughly. Then pour out about one-half of the contents of the flask, stopper the flask, and shake it vigorously several times, removing the stopper each time to relieve pressure. (NOTE: This step releases excess carbon dioxide, which would otherwise cause high and erratic readings.)

8.3.5 Transfer the solution to a 5-cm cell and read the absorbance at 540 nm. Zero the spectrophotometer with a

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reagent blank. Intensely colored solutions may be diluted with 0.2 N sulfuric acid and the resulting absorbance multiplied by the appropriate dilution factor.

9. Calibration and Standardization

9.1 To 25-mL volumetric flasks, add 20, 40, 60, 80, and 100-µL volumes of Cr(VI) working standard (7.10) and dilute to the mark with 0.20 N sulfuric acid (7.3) to produce solutions containing 0.2, 0.4, 0.6, 0.8, and 1.0 µg Cr(VI). Add 0.5 mL diphenylcarbazide solution (7.8), mix, and read the absorbance of each solution in a 5-cm cell at 540 nm.

9.2 Draw a calibration curve by plotting the absorbance of the standards vs. amount of Cr(VI), in micrograms/25 mL.

10. Calculations

10.1 Subtract the absorbance of the sample blank from the absorbance of each sample.

10.2 From the calibration curve (9.2) determine the micrograms of Cr(VI) in each sample.

10.3 Express the concentration of Cr(VI) in the air sample as

$$C = \frac{W}{V}$$

where: C = concentration of Cr(VI), $\mu g/m^3$
W = weight of Cr(VI) in the sample, µg
V = volume of air sampled, m^3

NOTE: For personal sampling pumps with rotameters, the air volume should be corrected

$$V_{corr} = Q \times t \sqrt{\frac{P_1 T_2}{P_2 T_1}}$$

where: Q = sample flow rate, L/min
t = sampling time, min
P_1 = pressure (mm Hg) of atmosphere when pump was calibrated
P_2 = pressure (mm Hg) of atmosphere sampled
T_1 = temperature (K) of atmosphere when pump was calibrated
T_2 = temperature (K) of atmosphere sampled.

11. References

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PARTICULATE ARSENICALS

Measurements Research Branch
Analytical Method

Analyte:	Particulate Arsenicals (See Table 1)	Method No:	P&CAM 320
Matrix:	Air	Range:	5-20 µg/cu m (as As)
Procedure:	Filter collection, extraction, ion chromatography, hydride generation, quartz furnace/AAS	Precision:	14.4-4.7% Depending on concentration and species. (See Section 4.1)
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 Particulate arsenicals are collected on a 37-mm polytetrafluoroethylene (PTFE) polyethylene backed membrane filter at 1.5 Lpm.

1.2 The arsenicals are extracted ultrasonically from the filter in aqueous carbonate/bicarbonate/borate buffer.

1.3 The arsenical species are separated using an anion-exchange chromatographic column. Hydrides of each species are generated and quantitated by AAS detection using quartz furnace atomization.

2. Working Range, Sensitivity, and Detection Limit

2.1 The optimum analytical working range for each arsenical is given in Table 1. The range is defined as the linear region of the calibration curve above which an analytical precision better than 10% is obtained under the conditions recommended in this procedure. The corresponding ranges in air are also presented in Table 1 and are based on a 300-L air sample. Since the sensitivity is dependent on the exact volume of the sample injection loop, the upper limit of the working range can be increased by using higher concentration standards which are injected via loops of smaller volume. This method was tested over the range of 5-20 µg/cu m using a 300-L air sample.

2.2 The analytical sensitivity obtained for each arsenical species under the conditions recommended in this procedure is presented in Table 1. The sensitivity is defined as the concentration that

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will produce a signal of 1% absorption. The values for the sensitivity will vary depending on the volume of the sample injection loop and the instrumentation.

2.3 The detection limits for the individual arsenical analytes in air and in solution, are given in Table 1. These are the concentrations which produce a signal equivalent to two times the base line noise for aqueous solutions analyzed under the recommended conditions.

3. Interferences

3.1 Any arsenic compound which, under the same experimental conditions, has the same retention time as the organoarsenical of interest is an interference. For the arsenic compounds which were studied the only known interference is inorganic arsenic (III) which interferes with the determination of dimethylarsenic acid. This problem can be eliminated by altering chromatographic conditions as described in Section 8.3.2.

3.2 Any ion present in the sample matrix at a high enough level which can alter the ionic strength of the eluent may interfere with the ion chromatographic separation of the arsenicals.

4. Precision and Accuracy

4.1 The analytical precision obtained under the conditions recommended in this procedure is presented in Table 1. The precision of the combined sampling and analytical method was tested using filters loaded in a dynamic aerosol generation/sampling system with particulates of the three organoarsenical compounds. The concentration levels tested for each species were 5, 10, and 20 micrograms arsenic per cubic meter of air. Depending on the concentration and species, the relative standard deviation was determined to range from 14.4% at the lowest level to 4.7% at the highest level.

4.2 The collection efficiency of the method for organoarsenicals in the range of 5-20 µg/cu m using a 300-L sample was found to be greater than 99%. The collection efficiency of the method for inorganic arsenic was not determined.

4.3 The accuracy of the combined sampling and analytical method was tested at the same time as the precision by analyzing additional aerosol samples from each set using Neutron Activation (NAA) and X-ray Fluorescence (XRF) analyses. Since NAA and XRF techniques provide only the total elemental arsenic, the total arsenic obtained from the IC-AAS analysis was used for comparison. The accuracy ranged from 90-120% of the values obtained by NAA and XRF.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids.

5.2 Particulate arsenicals can be speciated and quantified by this method.

5.3 The effluent from the IC column is continuously monitored by the AAS detection system. Therefore, it is not necessary to take chromatographic fractions of the sample for analysis.

5.4 Although it is not required, the method can be fully automated to increase analytical precision.

5.5 This method has been developed for use at extremely low levels where normally insignificant errors can be a major problem. Extreme care in all stages of the analysis must be taken.

6. Apparatus

6.1 Apparatus for the Collection of Personal Air Samples

6.1.1 Filter holder, 3-piece cassette, polystyrene, 37-mm diameter.

6.1.2 PTFE polyethylene backed membrane filters, 1.0-μm pore size, 37-mm diameter, Millipore Type FA or equivalent, supported by cellulose backup pad.

6.1.3 Personal sampling pump which is calibrated with a representative filter unit to an accuracy of ±5% of the recommended flow rate of 1.5 Lpm.

6.1.4 Thermometer

6.1.5 Manometer

6.1.6 Stopwatch

6.1.7 Tweezers

6.2 Apparatus for the Ion Chromatographic (IC) Separation System

6.2.1 Ion-exchange chromatograph modified such that the suppressor column and the electric conductivity detector are bypassed and the effluent from the analytical column, via microbore Teflon tubing (Dionex, 0.3-mm I.D. x 0.6-mm O.D.) is fed directly into the arsine generation system (see Figure 1).

6.2.2 Plastic syringe, 10-mL with male Luer fitting.

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6.3 Apparatus for Arsine Generation System

6.3.1 Proportioning pump (Technicon or equivalent).

6.3.2 Flow-rated pump tubes (Technicon or equivalent): 2.00 cc/min and 0.80 cc/min.

6.3.3 Glass manifold mixing coils, 5-turn and 20-turn, 1.5-mm I.D. x 3-mm O.D. (Technicon or equivalent).

6.3.4 Three glass "T" Connectors, 1.5-mm I.D. x 3.5-mm O.D (Technicon or equivalent).

6.3.5 Gas-liquid separator. See Figure 2 for specifications.

6.3.6 Expansion chamber. See Figure 2 for specifications.

6.3.7 Approximately 2½ feet of PTFE tubing, ¼" O.D.

6.3.8 Three PTFE swagelok fittings ¼" I.D.

6.3.9 Rotometer, 100-900 cc/min range.

6.3.10 Argon gas.

6.4 Apparatus for the AAS Detection System

6.4.1 Atomic absorption spectrophotometer having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the UV region and a direct readout in absorbance units. The spectrophotometer must be equipped with the following accessories.

6.4.2 Arsenic Electrodeless Discharge Lamp and EDL power supply.

6.4.3 Quartz Furnace Atomization Cell. The cell is a 16-cm long and 13-mm I.D. windowless quartz tube, with an 18-cm long and 4-mm diameter inlet tube fused in the center (Figure 3). The cell is carefully wound with Nichrome heating wire (resistance 4.28 ohms/ft) with a spacing of approximately 2-3 mm between turns. The cell is thermally insulated by wrapping the heating wire with several layers of asbestos tape. The terminals are connected by a service cord to a Variac transformer. The complete cell is mounted safely on the flat surface of a single slot AAS burner head assembly. Alignment of the cell in the optical path is accomplished by using the burner alignment controls.

6.5 Assorted Glassware

6.5.1 Beakers, 50-mL.

6.5.2 Flasks, volumetric, assorted sizes.

6.5.3 Pipets, delivery, assorted sizes.

7. Reagents

All reagents used should be ACS Reagent Grade or better.

7.1 Deionized water.

7.2 Sodium carbonate, Na_2CO_3.

7.3 Sodium bicarbonate, $NaHCO_3$.

7.4 Sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$.

7.5 Hydrochloric acid, HCl.

7.6 Potassium persulfate, $K_2S_2O_8$.

7.7 Sodium borohydride, $NaBH_4$.

7.8 Potassium hydroxide, KOH (pellets).

7.9 Monomethylarsonic acid. Reference purity available from the Ansul Company (Weslaco, Texas).

7.10 Dimethylarsenic acid (cacodylic acid). Reference purity available from the Ansul Company (Weslaco, Texas).

7.11 p-Aminophenylarsonic acid. Reference purity available from Matheson Coleman and Bell (MC/B).

7.12 Arsenic trioxide, As_2O_3.

7.13 Arsenic pentoxide, As_2O_5.

7.14 Potassium persulfate solution, saturated in 15% HCl (by volume).

7.15 One percent sodium borohydride (w/v) in 0.2% potassium hydroxide (w/v) solution. Add 5 g sodium borohydride, 1 g potassium hydroxide to deionized water and dilute to 500 mL.

7.16 Monomethylarsonic acid stock standard (1000 µg/mL As). Dissolve 0.9341 g $CH_3AsO_3H_2$ in deionized water and dilute to 500 mL.

7.17 Dimethylarsenic acid stock standard (1000 µg/mL As). Dissolve 0.9210 g $(CH_3)_2AsO_2H$ in deionized water and dilute to 500 mL.

7.18 p-Aminophenylarsonic acid stock standard (1000 µg/mL As). Dissolve 1.4485 g p-$H_2NC_6H_4AsO_3H_2$ in 5 mL of 1 N NaOH and dilute to 500 mL with deionized water. Protect from light.

7.19 Arsenic trioxide stock standard (1000 µg/mL As). Dissolve 0.6602 g As_2O_3 in 5 mL of 1 N NaOH and dilute to 500 mL with deionized water.

7.20 Arsenic pentoxide stock standard (1000 µg/mL As). Dissolve 0.7669 g As_2O_5 in 5 mL of 1 N NaOH and dilute to 500 mL with deionized water.

7.21 Eluent A (0.0024 M $NaHCO_3$/0.0019 M Na_2CO_3/0.001 M $Na_2B_4O_7 \cdot 10H_2O$). Dissolve 0.8067 g $NaHCO_3$, 0.8055 g Na_2CO_3, and 1.5257 g $Na_2B_4O_7 \cdot 10H_2O$ in 4 liters of deionized water.

7.22 Eluent B (0.005 M $Na_2B_4O_7$). Dissolve 7.6284 g $Na_2B_4O_7 \cdot 10H_2O$ in 4 liters of deionized water.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should be soaked initially in mild detergent solution to remove any residual grease or chemicals, then rinsed with deionized water.

8.1.2 After initial cleaning, glassware must be rinsed in 10% nitric acid and then rinsed thoroughly with deionized water, and then dried.

8.2 Collection and Shipping of Samples

8.2.1 Each personal sampling pump must be calibrated with a representative filter cassette in-line to assure accurately known sample flows.

8.2.2 Assemble the filter cassette as follows: First, place a cellulose backup pad in place in the rear section of the three-piece filter cassette holder. On top of this place a PTFE filter (Section 6.1.2) and then put the center retaining ring and front section of the cassette in place. Close firmly to insure that the center ring seals the edge of the filter.

8.2.3 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.2.4 Collect the sample at 1.5 liters per minute. The air being sampled should not pass through any hose or tubing before entering the filter cassette. A sample size of 300-L is recommended.

8.2.5 Since it is possible for a filter to become plugged by heavy particulate loading, the pump rotometer should be observed frequently, and the sampling should be terminated if there is any evidence of a problem.

8.2.6 Terminate sampling at the predetermined time and note sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.2.7 Carefully record the sample identity and all relevant sampling data.

8.2.8 With each batch of ten samples, submit one "filter blank" from the same lot of filters which was used for sample collection. No air is drawn through the blank filters.

8.2.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Preparation of Samples

1. For each sample, pipette 25.0 mL of eluent A buffer solution (Section 7.22) into a clean 50 mL beaker.

2. Open the filter holder. Carefully remove the PTFE membrane filter with the aid of a pair of clean tweezers and transfer the filter into the beaker, placing the exposed side in direct contact with the surface of the buffer solution. Seal the beaker with parafilm.

3. Agitate the contents of the beaker for 30 minutes in an ultrasonic water bath. After sonication the sample extracts are ready for analysis.

4. If the extracts will not be analyzed immediately, they should be stored in a refrigerator ($\sim 4^{\circ}C$) until analysis.

8.3.2 Analysis by Ion Chromatography/AAS Detection (IC-AAS)

The complete analytical system is illustrated in Figure 1. Although it is not required, it would be preferable to use a fully automated IC system to increase precision.

As discussed in Section 3.0, arsenic (III) interferes with the determination of dimethylarsenic acid. This problem is eliminated by performing two separate analyses on each

sample utilizing two eluent buffer systems (A and B) of different ionic strength. Eluent A allows the separation of monomethylarsonic acid, p-aminophenylarsonic acid, and arsenic (V). If arsenic (III) is not present in the sample, dimethylarsenic acid is also effectively determined. Eluent B is a lower ionic strength buffer and is used only to resolve dimethylarsenic acid from arsenic (III). With this eluent the other arsenical species have very long retention times and will accumulate on the column, tying up active resin sites. Therefore the column must be flushed with Eluent A after ∿ 10-15 samples have been analyzed, and the column reequilibrated for 1 hour with Eluent B before further analysis.

1. Analytical Operating Conditions

IC Parameters

a) Pre-column: 3x150 mm Anion

b) Separator column: 3x150 mm Anion

c) Column temperature: Ambient

d) Flow rate: 2.6 mL/min

e) System pressure: 600 psi

f) Injection volume: ∿ 0.8 mL (variable)

g) Eluent A for analysis of:

- Unresolved dimethylarsenic acid/arsenic (III)
- Monomethylarsonic acid
- p-Aminophenylarsonic acid
- Arsenic (V)

h) Eluent B for analysis of:

- Dimethylarsenic acid
- Arsenic (III)

Arsine Generation Parameters

a) Saturated persulfate - HCl solution: 0.8 cc/min

b) $NaBH_4$ - KOH solution: 2.0 cc/min

c) Argon carrier gas: 300 cc/min

AAS Parameters

a) Quartz Furnace temperature: 800°C

b) Arsenic EDL: 8 watts (or as recommended by the manufacturer)

c) Wavelength: 193.7 nm

d) Slit width: 0.7 nm (or as recommended by the manufacturer)

e) D_2 background correction: None

f) Signal: Absorbance

g) Scale Expansion: 3x

h) Recorder: 10 mv f.s.

i) Chart speed: 1 cm/min

2. System Setup

AAS Detection System

a) The AAS instrumental parameters must be adjusted to optimum.

b) The quartz cell must be properly aligned in the optical path to maximize the amount of light passing through it.

c) The quartz cell is gradually heated to the desired temperature (800°C) by increasing in small increments the voltage with the Variac transformer. The temperature inside the furnace is monitored with a thermocouple.

IC System

a) To achieve reproducible chromatographic resolution it is critical to allow the IC column to equilibrate by pumping the particular eluent to be used for at least one hour before analysis. This can be done before connecting the IC effluent to the arsine generation manifold.

b) The IC effluent is fed directly into the arsine generation manifold using microbore tubing. A length of tubing no more than 18" should be sufficient. It is important not to introduce any crimps in the microbore tubing.

Arsine Generation System

a) The gaseous arsines which are formed are first separated from solution using the gas-liquid separator illustrated in Figure 2 and then transferred with argon carrier gas through PTFE tubing to the heated quartz furnace.

3. Sample Analysis

Before analysis of samples, the analytical system is allowed to equilibrate until a steady base line is reached on the recorder.

a) Using a 10-mL plastic syringe, inject a standard onto the chromatograph. Record the sample identity and instrumental conditions. It is preferable to push a sample volume of three times the injection loop volume through the injection loop to thoroughly rinse the loop of previous sample contamination. Also, the plastic syringe should be rinsed with deionized water between samples.

b) Identify the component peaks. Typical retention times are:

Eluent System A:

- Dimethylarsenic acid/arsenic (III)	1 min
- Monomethylarsonic acid	2 min
- p-Aminophenylarsonic acid	4 min
- Arsenic (V)	7.5 min

Eluent System B:

- Dimethylarsenic acid	1.5 min
- Arsenic (III)	2.0 min

If the chromatographic resolution needs to be optimized, adjust the eluent concentration accordingly.

c) For each standard and sample measure the height or area of each peak.

9. Calibration and Standardization

9.1 Prepare a 1.0 µg/mL mixed analyte intermediate standard solution from the individual 1000 µg/mL stock standard solutions prepared in Sections 7.17-7.21. Dilute with Eluent A (Section 7.22).

9.2 Prepare working standards of 10, 20, 40, 60, and 80 ng/mL by diluting 1, 2, 4, 6, and 8 mL of the 1.0 µg/mL intermediate standard to 100 mL with Eluent A. These standard solutions should be prepared fresh daily.

9.3 This series of standards is analyzed under the same IC-AAS conditions and during the same time period as the unknown samples to monitor the performance of the analytical system.

9.4 Prepare at least one blank and analyze it at the same time as the standards and samples.

9.5 With each set of samples analyzed, a complete calibration curve for each arsenic species should be constructed using the standards prepared in 9.2. This is achieved by plotting the peak heights against the corresponding concentrations.

10. Calculations

10.1 From the calibration curves obtained in Section 9.5 calculate for each sample the amount of arsenic for each species in µg.

10.2 In the event that a filter blank is found, a correction for the blank must be made for each sample.

$$W = S - B$$

where

W = net sample weight (µg)

S = weight found in sample filter (µg)

B = weight found in blank filter (µg)

10.3 For personal sampling pumps with rotometers only, the following volume correction should be made.

$$V = f \times t \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{\frac{1}{2}}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 Calculate the arsenical concentrations (C) in the air sample (µg/cu m) using the formula:

$$C = \frac{W}{V}$$

11. References

11.1 Ricci, G., Shepard, S., Hester, N., and Colovos, G.: "The Development of a Method for the Determination of Organoarsenicals in Air". NIOSH Contract #210-77-0134.

11.2 Ricci, G., Shepard, S., Hester, N., and Colovos, G: "Suitability of Various Filtering Media for the Collection and Determination of Organoarsenicals in Air,: to be published.

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Stan Shepard, MTS
Norman Hester, Ph.D.
George Colovos, Ph.D
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Environmental Monitoring and
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NIOSH Contract No. 210-77-0134

Table 1. Sensitivity, detection limit, and working range data for analysis of particulate arsenicals using the recommended procedure.

Arsenical	Sensitivity ng/mL/1%A	Detection Limit (as As)		Range* (as As)		Analytical Precision %RSD
		300-L Air Sample $\mu g/m^3$	Solution ng/mL	300-L Air Sample $\mu g/m^3$	Solution ng/mL	
Dimethylarsenic Acid	1.3	0.62	7	1.7 - 6.7	20 - 80	11.2 - 1.6
Arsenic (III)	2.1	0.71	8	1.7 - 6.7	20 - 80	11.2 - 1.3
Monomethylarsonic Acid	2.1	0.72	9	1.7 - 6.7	20 - 80	8.1 - 4.4
p-Aminophenylarsonic Acid	6.1	0.64	8	1.7 - 6.7	20 - 80	6.0 - 3.0
Arsenic (V)	13.0	0.46	6	1.7 - 6.7	20 - 80	10.8 - 1.0

* The upper limit of the range can be increased by using higher concentration standards which are injected via loops of smaller volume. Although not tested with air samples, the useful range can be extended from 5 $\mu g/m^3$ down to 1.7 $\mu g/m^3$ based upon the analytical solution range.

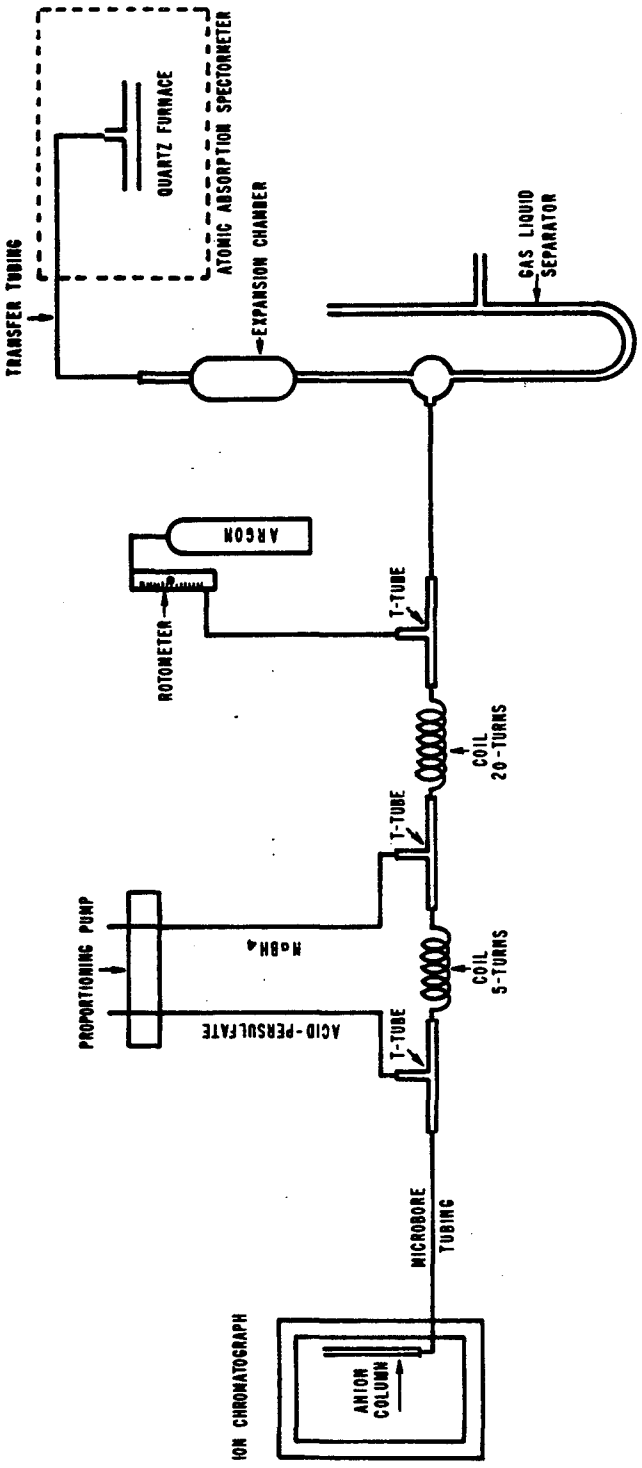

Figure 1. IC/AAS analytical system.

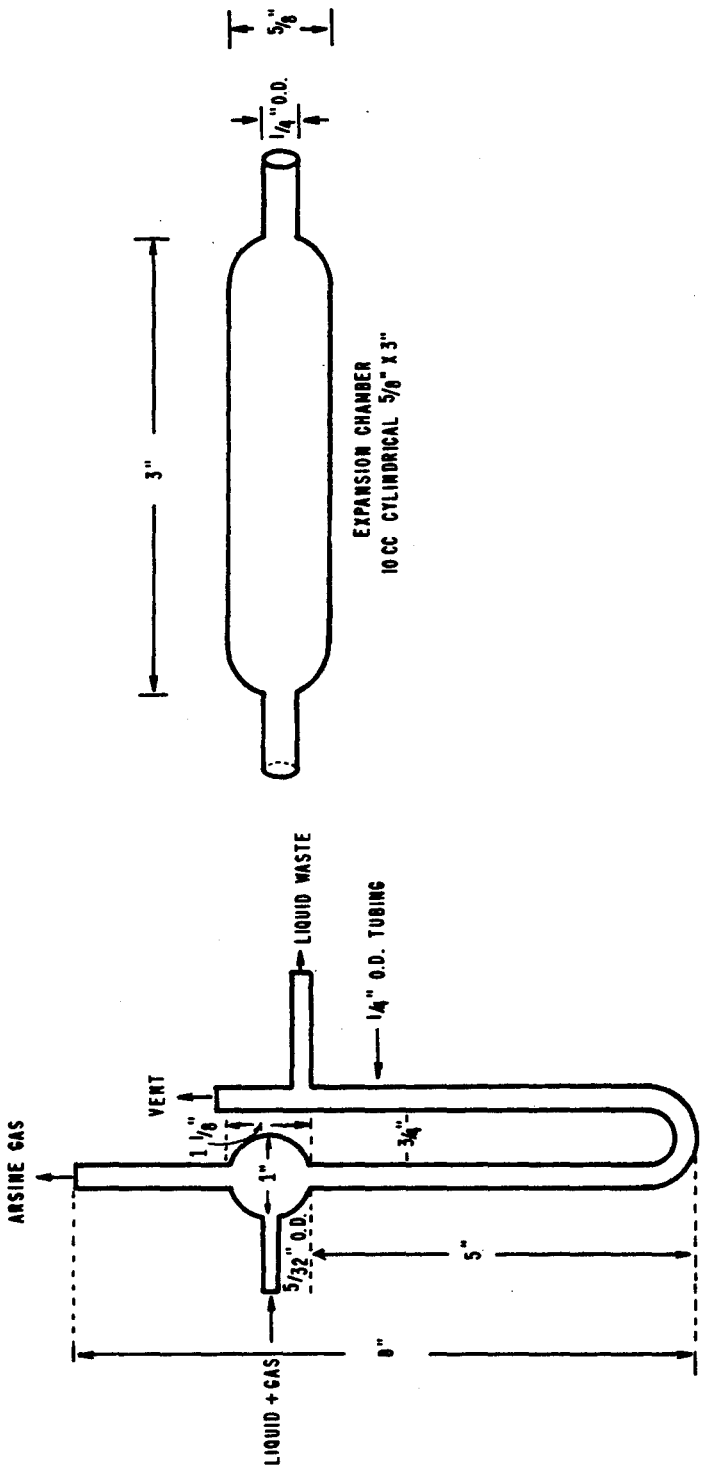

Figure 2. Gas-liquid separator and expansion chamber.

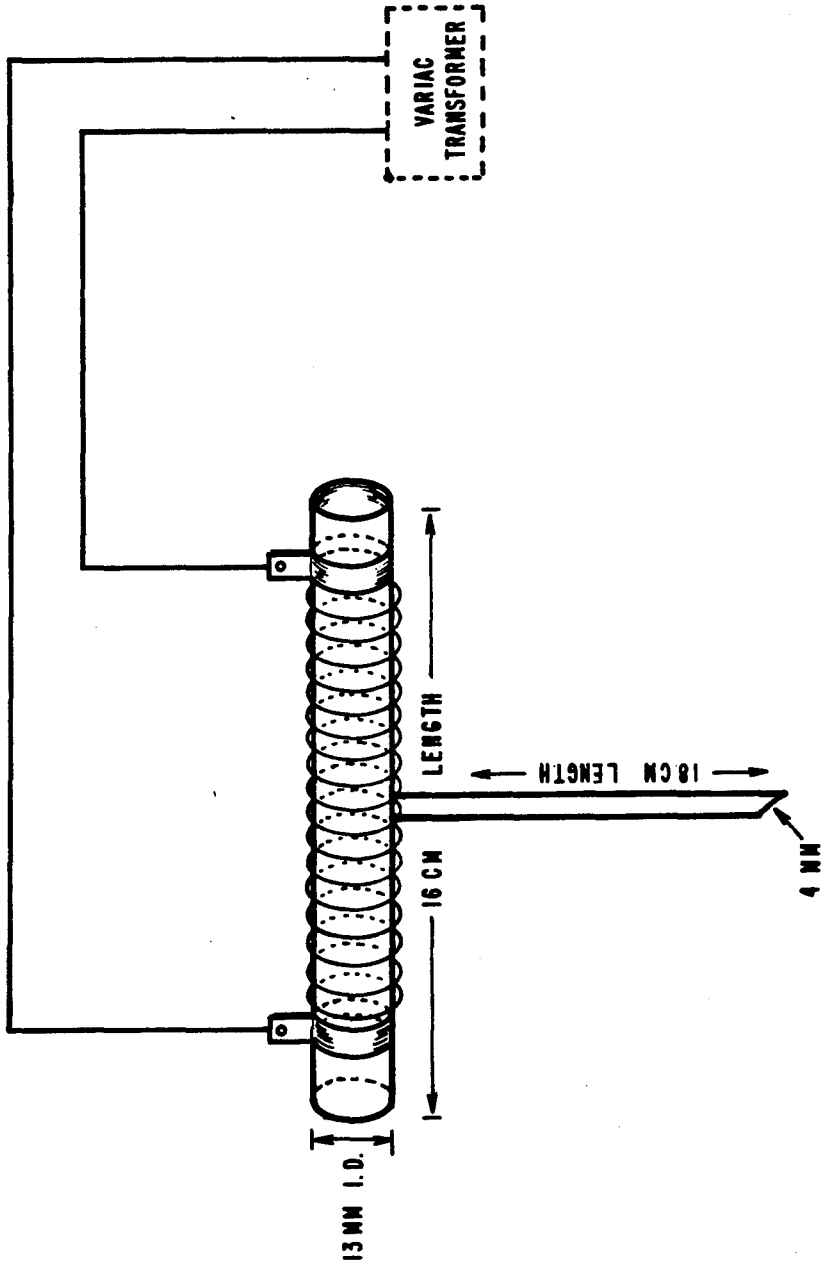

Figure 3. Quartz furnace atomization cell.

1,2-DICHLOROPROPANE

Measurements Research Branch

Analytical Method

Analyte:	1,2-Dichloropropane	Method No.:	P&CAM 321
Matrix:	Air	Range:	0.124 to 128 mg/m^3 in 3 L of air
Procedure:	Adsorption on charcoal, desorption with 15% (v/v) acetone in cyclohexane, GC with electrolytic conductivity detection	Precision:	0.064
Date Issued:	6/15/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 A known volume of air is drawn through a tube containing petroleum-based charcoal to trap the 1,2-dichloropropane present.

1.2 The charcoal in the tube is transferred to a small vial where the 1,2-dichloropropane is desorbed with 15% (v/v) acetone in cyclohexane.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph equipped with a Hall electrolytic conductivity detector.

1.4 The height of the resulting peak is determined and compared with the peak heights obtained from the injection of standards.

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2. Working Range, Sensitivity, and Detection Limit

2.1 The sampling and analytical method was tested with nominal sample loadings of 0.37 to 384 µg of 1,2-dichloropropane per charcoal tube. The samples were collected from atmospheres containing 1,2-dichloropropane in the range of 0.124 to 128 mg/m^3 at 25 to 28 °C and at a relative humidity of 90% or greater.

2.2 With the Hall detector set on a conductivity of 10 and an attenuation of 32, the analytical sensitivity corresponded to a response of 0.5% of full scale deflection for each nanogram of 1,2-dichloropropane injected.

2.3 The lowest analytically quantifiable level (LAQL) for this method was found to be less than 0.5 µg of 1,2-dichloropropane per sorbent sample. (Sorbent samples were extracted with 1 mL of the solvent.) From the tests with the total sampling and analytical method cited in Section 2.1, it appeared that the LAQL was less than 0.36 µg; however, desorption efficiency tests were not performed at this level. The instrumental detection limit was about 0.1 µg of 1,2-dichloropropane in 1 mL of the extraction solvent; the relative standard deviation of replicate determinations at this level was 8%.

3. Interferences

3.1 If the possibility of interference exists, separation conditions (column packing, temperature, carrier flow, detector, etc.) must be changed to circumvent the problem. In some cases, capillary column gas chromatography may be necessary.

3.2 The gas chromatographic operating conditions described below in Section 8.3.3 for the packed column—3% Carbowax 1500 on 80/100-mesh Chromosorb W HP—were found to separate 2,2-dichloropropane; 1,3-dichloropropane; trans- and cis-1,3-dichloro-1-propene; trichloroethylene; and tetrachloroethylene from 1,2-dichloropropene. These compounds are among those most likely to be collected along with 1,2-dichloropropane in air (see Reference 11.1). One other compound that may also occur in air samples with 1,2-dichloropropane is 1,2-dichloroethane. It was found that this compound could not be resolved from 1,2-dichloropropane with the packed Carbowax column; however, the two compounds were resolved on a Carbowax 20M glass capillary column, 30 m by 0.25 mm i.d. (see Reference 11.1).

3.3 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of 1,2-dichloropropane.

3.4 Any substance that has the same retention time as 1,2-dichloropropane with the gas chromatographic operating conditions described in this method is an interferent. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for replicate measurements was 6.4% for seventeen sorbent samples challenged with 0.124 to 128 mg/m^3 of 1,2-dichloropropane in air. The pooled relative standard deviation for the analytical method was 3.1% for eighteen sorbent samples spiked with 0.522 to 522 µg of 1,2-dichloropropane.

4.2 A total hydrocarbon analyzer was used to independently monitor the concentration of 1,2-DCP in test atmospheres. The determinations with sorbent sampling gave values averaging 100% of those found with the monitor over the range of the method.

4.3 The breakthrough volume of the sorbent tube was found to be about 20 L with sampling rates of 0.07 to 0.17 L/min at 1,2-dichloropropane concentrations of 62 to 85 mg/m^3 and at a relative humidity greater than 90%. The breakthrough volume was reduced to about 6 L at much higher concentration levels, 738 to 865 mg/m^3. Elevation of the sampling temperature to 40 °C at these higher concentration levels did not significantly change the capacity.

4.4 Samples of 1,2-dichloropropane (about 0.37-µg quantities) sorbed from test atmospheres with the charcoal sorbent tubes were found to be stable at 25 °C for at least 7 d. Samples of 1,2-dichloropropane (0.5-µg quantities) were found to be stable on charcoal samples for 26 d at 25 °C in sealed vials. These samples were prepared by spiking solutions of the analyte onto the charcoal; they were stored in the dark in both tests.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential interferences are avoided by the gas chromatographic procedure. The samples are analyzed by means of quick instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the charcoal tube. When the sample value obtained for the backup section of the tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage the analyte may migrate throughout the tube; however, there was no observed migration of 0.37-μg quantities of sorbed analyte after storage for 7 d at 25 °C in sealed sorbent tubes.

5.3 Another disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of accurate performance (±5%) at 0.05 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Sorbent tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d., flame sealed at both ends. Each tube contains two sections of a specially prepared 20/40-mesh petroleum-based charcoal—a 100-mg sorbing section and a 50 mg backup section. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated with a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 2 in. H_2O at a sampling rate of 0.2 L/min. This type of tube is available from SKC, Inc. (Eighty-Four, PA); its catalog number is 226-65.

6.3 Gas chromatograph equipped with a Hall eleytrolytic conductivity detector (Tracor Model 700).

6.4 Nickel GC column (2 mm i.d. by 3 m long) packed with 3% Carbowax 1500 on 60/80-mesh Chromosorb W HP.

6.5 Vials, 1 mL, with serum caps containing Teflon-lined silicone rubber septa.

6.6 Microliter syringes, 10 μL and convenient sizes for making dilutions.

6.7 Pipets, 1.00 mL and convenient sizes for making dilutions.

6.8 Ultrasonic bath.

7. Reagents

7.1 Acetone, "distilled in glass".

7.2 Cyclohexane, "distilled in glass".

7.3 1,2-Dichloropropane, b.p. of 95 to 96 °C, reagent grade (Aldrich Chemical Co.).

7.4 High purity nitrogen for GC carrier gas.

7.5 Prepurified hydrogen for Hall detector.

7.6 Electrolyte solution for Hall detector: 50% (v/v) 2-propanol and distilled, deionized water.

8. Precedure

8.1 Cleaning of Equipment. All nondisposal glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, distilled water, acetone, and cyclohexane (in that order).

8.2 Collection of Shipping of Samples

8.2.1 Immediately before sampling, break the ends of the tubes to provide an opening that is at least 2 mm (one-half the internal diameter of the tube).

8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of sorbent is the backup layer and is positioned nearer the sampling pump.

8.2.3 Place the sorbent tube in a vertical position during sampling to prevent channeling through the tube.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.2.5 Measure and report the flow rate and time or volume sampled. The sample is taken at 0.05 to 0.2 L/min. The maximum volume sampled should not exceed 4.0 L at 0.2 or 0.5 L/min.

8.2.6 The temperature and pressure of the air being sampled are measured and reported.

8.2.7 Immediately after sampling, seal the two ends of the tube with Teflon tape and plastic caps. Store the tube in the dark.

8.2.8 For every ten samples taken, process one sorbent tube not exposed to 1,2-dichloropropane in the same manner as the samples (break, seal, and transport). Do not sample air through this tube. The tube should be labeled as a blank.

8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

8.2.10 Ship nine to twelve unopened sorbent tubes so that desorption efficiency studies can be performed on the same type and lot of charcoal used for sampling.

8.2.11 Log and immediately refrigerate samples as soon as they are received at the laboratory. During refrigeration, store the tubes in an airtight container to prevent contamination by the diffusion of chemicals through the plastic end caps.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the sorbent tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer each section of sorbent to a 1-mL vial. Discard the metal spring. Place the glass wool plug into the vial containing the 100-mg sorbent section and the foam plugs into the vial with the backup section.

8.3.2 Desorption of Samples. After the two sections of a tube are transferred to small vials, pipet 1.00 mL of the solvent (15% (v/v) acetone in cyclohexane) into each of the two vials. Crimp a serum cap into place immediately after the solvent has been added. Extract the sealed sorbent samples by ultrasonification for 30 min at room temperature.

8.3.3 GC Conditions

- Carrier gas, 25 mL/min.
- Injection port temperature, 150 °C.
- Column temperature, 50 °C.
- Hall detectors parameters:

  furnace temperature, 840 °C.
  electrolyte flow rate, 0.9 mL/min.
  hydrogen gas flow rate, 50 mL/min.

8.3.4 Injection. Inject a 5-µL aliquot of a sample extract or standard into the gas chromatograph by the solvent flush technique. Use 1 µL of the mixed solvent as the solvent flush. Maintain a 1-µL air gap between the solvent flush and the 5-µL aliquot.

8.3.5 Measurement of Peak Height. The product of peak height and attenuator setting is linear over the concentration range of about 0.1 to 350 µg/mL. The peak height is multiplied by the attenuator setting necessary to keep the peak on scale. Results are read from a standard curve prepared as discussed in Section 9. If peak heights indicate an apparent concentration above 100 ng/mL, dilute the sample solution appropriately for reanalysis.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of the petroleum-based charcoal. Also for a given batch of charcoal, the desorption efficiency may vary with the weight of contaminant adsorbed. In laboratory tests, the petroleum-based charcoal gave an average desorption efficiency of 0.954 with a RSD of 3.1% for loadings of 1,2-dichloropropane in the range of 0.522 to 522 µg on 100-mg beds of sorbent material.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third should be an intermediate level. Dissolve the analyte in 15% (v/v) acetone in cyclohexane to prepare stock solutions. The concentrations should be such that no more than 5 µL of a stock solution will be injected onto the sorbent. Place 100 mg of the sorbent in a small vial and cap the vial. Inject an aliquot of the appropriate stock solution into the sorbent bed. Allow each vial to stand overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 1.00 mL of the solvent. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of 1,2-dichloropropane found in a sample versus the desorption efficiency.

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9. Calibration and Standardization

9.1 Prepare a stock standard solution by diluting 3.00 mL (3.47 g) of 1,2-dichloropropane to 100 mL with 15% (v/v) acetone in cyclohexane. By serial dilutions with the solvent, prepare a series of working standards varying in concentration over the range of 100 ng/mL to 350 µg/mL. Follow the dilution shceme presented below:

Initial concn, µg/mL	Aliquot volume, mL	Final diluted volume, mL	Final concn, µg/mL
34,700	1	100	347
347	7	10	243
347	3	10	104
347	1	10	34.7
347	1	50	6.95
34.7	3	100	1.04
1.04	5	10	0.520
1.04	1	10	0.104

The standard solutions are stable indefinitely at room temperature if kept in airtight containers.

9.2 Determine the working standards under the same GC conditions and during the same time period as the samples. Alternate the determination of standards and samples. Establish a standard curve by plotting the concentrations of the standards in µg/mL versus peak heights. Since 1-mL aliquots of solvent are employed to extract sorbent samples, µg/mL is equivalent to µg/sample.

10. Calculations

10.1 Read the sample weight in µg from the standard curve.

10.2 Blank corrections are not expected to be necessary, but if the analysis shows a blank correction is needed, the correction is:

$$W_F = W_s - W_b$$

where: W_F = corrected amount (µg) on the front section of the sorbent tube.

W_s = amount (µg) found on the front section of the sorbent tube.

W_b = amount (µg) found on the front section of the blank sorbent tube.

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (μg) in the front section.

W_F = amount (μg) after blank correction.

D = desorption efficiency corresponding to the weight W_F.

Calculate the corrected amount on the backup section, M_B, similarly.

10.4 Express the concentration, C, of 1,2-dichloropropane in the air sampled in mg/m^3, which is numerically equal to μg/L.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = corrected amount (μg) of 1,2-dichloropropane found on front section.

M_B = corrected amount (μg) of 1,2-dichloropropane found on backup section.

V = volume (L) of air sampled.

10.5 If desired, the results may be expressed in ppb at 25 °C (298 K) and 760 torr.

$$c(ppb) = C(ng/L) \times \frac{24.45}{112.99} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.

T = temperature (°C) of air sampled.

24.45 = molar volume (L/mol) at 25 °C and 760 torr.

112.99 = molecular weight (g/mol) of 1,2-dichloropropane.

11. References

11.1 "Research Report for 1,2-Dichloropropane"; NIOSH Contract No. 210-78-0012; Southern Research Institute, Birmingham, Alabama.

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11.2 Taylor, D. G.; Kupel, R. E.; Bryant, J. M., "Documentation of the NIOSH Validation Tests"; National Institute for Occupational Safety and Health; Cincinnati, Ohio, April 1977. DHEW (NIOSH) Publication No. 77-185.

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TRIMELLITIC ANHYDRIDE

Measurement Support Branch

Analytical Method

Analyte:	Trimellitic Anhydride*	Method No:	P&CAM 322
Matrix:	Air	Range :	0.048 - 0.24 mg/m^3
Procedure:	Filter collection, extraction derivatization, GC-FID	Precision:	0.087
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Trimellitic anhydride (TMA) is collected from air on a PVC-copolymer membrane filter. The filter is extracted with methanol and the methanol volume is reduced by evaporation. Boron trifluoride/methanol is added to the extract to derivatize the anhydride. The mixture is heated at 97°C for 20 minutes during which the anhydride is converted to its trimethyl ester. After cooling the boron trifluoride is complexed and precipitated with a pyridine/pentane/ether mixture. An aliquot of the mixture is injected and analyzed by a gas chromatograph equipped with flame ionization detector. The concentration of unknown samples is determined from a calibration curve.

2. Working Range, Sensitivity and Detection Limit

2.1 The working range is from 0.048 - 0.24 mg/m^3 for a 400-L air sample corresponding to 19.2 - 96/µg sample.

2.2 The detection limit was not determined, but it is estimated to be on the order of 2 µg per 5 µL injection at 8 x 10 attenuation using F.I.D.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.

*1,2,4-Benzenetricarboxylic acid-1,2-anhydride

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3.2 Any compound that has the same retention time as the trimethyl ester of trimellitic anhydride at the operating conditions described in this method is an interference. The interference may be eliminated by changing the operating conditions of the chromatograph, e.g. by changing the temperature programming or carrier gas flow-rate.

3.3 This method will not differentiate between trimellitic anhydride and trimellitic acid. Under derivatization both compounds will form the same trimethyl ester (trimethyl trimellitate).

4. Precision and Accuracy

The analytical pooled relative standard deviation (RSD) is 8.7% determined from 15 TMA spiked PVC-copolymer filters over the range of 19.2-96 µg/filter. The average recovery is 103.3%. Calibration standards (n=21) exhibited an RSD of 7.6%.

5. Advantages and Disadvantages

5.1 The method offers a one step derivatization procedure in which the anhydride directly converts into its corresponding trimethyl ester.

5.2 The method has a low detection limit, 2 µg.

5.3 Trimellitic anhydride recoveries are quantitative with acceptable precision.

5.4 After derivatization, samples are stable for at least two days. The retention time of the ester is approximately 7.5 minutes.

5.5 The method may be used as a general method for other organic anhydrides and carboxylic acids.

5.6 See Section 3.3.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Polyvinyl chloride-copolymer membrane filters, 0.8 µm in pore size, 37-mm in diameter, Gelman DM-800 or equivalent.

6.1.2 Plastic three piece 37-mm filter holders (cassettes). The filter is supported in the cassette by a cellulose backup pad.

6.1.3 A personal air sampling pump capable of operating at 1.5 to 2.0 liters per minute.

6.1.4 A thermometer, barometer and a stopwatch.

6.2 Analytical Equipment

6.2.1 Gas chromatograph equipped with a flame ionization detector (FID) and glass-lined injection port.

6.2.2 A stainless-steel column, 9' (274 cm), 2-mm I.D. packed with 60/80 mesh Tenax-GC (Applied Science Labs., Inc., State College, PA.) or equivalent porous polymer packing. No liquid stationary phase is needed.

6.2.3 A strip-chart recorder, 1mV full scale.

6.2.4 Test tubes, glass 13 x 100-mm size with Telfon lined screw caps. Rubber lined caps produce extraneous peaks.

6.2.5 Glass syringe, 10 µL.

6.2.6 Pipettes, 10 µL, 25 µL, 50 µL, variable 50-250 µL and 0.25-5 mL.

6.2.7 Volumetric flask, 250 mL.

6.2.8 Beakers, 50 mL and 250 mL.

6.2.9 Hot plate, variable heat settings.

6.2.10 Watch glasses to fit on 50 mL beakers.

6.2.11 Ultrasonic bath.

6.2.12 Air evaporator/concentrator (6 syringe manifold block for reducing the methanol volume in the test tubes).

6.2.13 High temperature GC injection septa (350°C).

6.2.14 Analytical balance, to ± 0.01 mg.

6.2.15 Tweezers, flexible tubing, applicator stick, weighing paper.

7. Reagents

Whenever possible, reagents used should be ACS reagent grade or better.

7.1 Methanol.

7.2 Pentane.

7.3 Diethyl ether.

7.4 Boron trifluoride/methanol, 14% w/v mixture (commercially available from GC supplier).

7.5 Pyridine.

7.6 Pyridine mixture. Prepare a 7:3 pyridine/pentane mixture in a screw-cap tube.

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7.7 Trimellitic anhydride (1,2,4-Benzenetricarboxylic anhydride).

7.8 Laboratory compressed-air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PVC-copolymer membrane filter is supported by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the filter does not lie flat on the backup pad and the spacer ring does not fit snugly into the bottom of the filter holder, sample leakage will occur around the filter. Remove the cassette plugs. Use a piece of flexible tubing to connect the filter holder to the pump.

8.3.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 400 liters is recommended. Sample at a flow rate of 1.7 liters per minute for 4 hours. The flow rate should be known with an accuracy of at least $\pm$ 5%. A high volume air sample may also be submitted along with the other personal samples for qualitative GC work.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is unavailable, record the elevation. Replace filter plugs.

8.3.6 Blank. With each batch of ten samples submit at least one filter from the same lot of filters which was used for sample collection and which is subjected to the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.7 Shipping. The filter cassettes should be plugged and shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Extraction

Place a field or a spiked filter sample in a 50-mL beaker and add 3 mL methanol. Put a watch-glass on the beaker and place beaker on a hot plate (65°C) for one minute. Remove beaker and place it in the ultrasonic bath for one minute (watch-glass is still on the beaker to prevent sample loss and water contamination of the sample during ultrasonication).

Rinse the bottom of the watch glass with 1 mL methanol and collect the rinse in the beaker. Lift the filter with tweezers above the methanol level and rinse both sides of the filter slowly with two 3-mL aliquots of methanol, collecting the rinse in the same beaker. Roll and squeeze the filter with tweezers against the inside wall of the beaker to remove methanol retained by the filter, then discard the filter.

Place the beaker on the hot plate (55°C) and reduce the methanol level to less than 5 mL. Transfer the methanol extract to a test tube. Rinse the beaker two or three times with small amounts of methanol and combine the rinsings in the test tube. Evaporate the methanol in the test tube to near dryness (about 10 µL) by blowing warm air over the surface with the use of the evaporator block. For comparison, 10 µL methanol may be added to an empty test tube to observe the amount of 10 µL. The sample is now ready for derivatization.

8.4.2 Derivatization

To each sample or standard tube that contains an anhydride sample, add 125 µL BF_3/methanol. Screw the cap tightly and place the tube in a water bath (97°C) for 20 minutes. Remove tube and let it cool to room temperature. Add the following solvents to the tube: 50 µL diethyl ether, 50 µL pentane, and 50 µL of the pyridine mixture. Between solvent additions screw the cap on each tube to prevent evaporation of the solvents. Shake tube mildly between additions. (With the pyridine addition a white precipitate forms, which is a complex of BF_3· pyridine.) After a few minutes the white material precipitates and the sample is ready for analysis. No centrifuging is necessary.

8.4.3 Gas Chromatographic Conditions

Column:	See Section 6.2.2
Column Temperature Program:	250°C for 2 minutes, then 16°/min to 310°C, hold for 4 min. at 310°C

Injection Temperature:	315°C
Detector Temperature:	325°C
Helium Flow Rate:	35 mL/min
Hydrogen Flow Rate:	53 mL/min
Air Flow Rate	550 mL/min
Detector:	FID, Attenuation 16 x 10 and 32 x 10
Injection Volume:	5 µL
Retention Time:	7.5 minutes

8.5 Filter Recovery Determination

8.5.1 Spiking Solution. Prepare a stock solution of 0.01 M trimellitic anhydride (1.92 µg / µL) by dissolving 0.4803 g TMA in a 250 mL volumetric flask containing methanol and making up the remaining volume with methanol.

8.5.2 Spike six PVC-copolymer filters for each level using pipettes. Use 10, 25, and 50 µL volumes of the spiking solution to get 19.2, 48, and 96 µg TMA on each filter respectively. When each filter is dry, follow Section 8.4 to analyze the sample.

8.5.3 Percent recovery (R, extraction efficiency) is determined as follows:

$$R = \frac{W_r}{W_s} \times 100$$

where: W_r = micrograms recovered

W_s = micrograms spiked

Convert peak area to micrograms from the equation of the calibration curve.

9. Calibration and Standardization

9.1 Using the 0.01 M TMA solution from 8.5.1, prepare 6 calibration standards per level by pipetting 10, 25, and 50 µL into test tubes. This is equivalent to 19.2, 48, and 96 µg TMA per each level. Be sure to screw the caps on the tubes between additions. Follow Section 8.4.2 to derivatize the standards.

9.2 Since the total volume in each tube after extraction is different- 285, 300, and 325 µL for 19.2, 48, and 96 µg level respectively - a correction for the areas must be made. Use the factors of 1.053 and 1.14 to multiply the areas of the standards at the 48 and 96 µg levels respectively.

9.3 Prepare a plot of the corrected areas of the standards versus concentration of TMA. Do statistical analysis of "least squares" to determine the equation of the calibration curve.

9.4 Suggestion: It was found, after the method was completed, that since no sample loss occurred even when the sample was completely evaporated, that one may eliminate the correction factors and the evaporation of field samples to 10 µL by completely evaporating to dryness standards and field samples and carrying out the normal procedure from there on.

10. Calculations

10.1 The concentration of unknown TMA samples can be determined graphically from the plot of peak areas of the standards versus concentration.

10.2 The concentration of unknown TMA samples may also be determined from the equation of line obtained from "least squares" statistical analysis

$$C = \frac{A - Y}{M}$$

where: C = concentration of TMA in µg/sample

A = peak area of the sample

Y = line intercept value (from least squares)

M = line slope value (from least squares).

10.3 For personal pumps with rotameters only, the following correction for air volumes sampled should be made:

$$\text{Corrected volume} = F \times T \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{\frac{1}{2}}$$

where: F = sample flow rate

T = sampling time

P_1 = pressure during calibration of sampling pump in mm Hg

P_2 = pressure of air sampled in mm Hg

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T_1 = temperature during calibration of sampling pump (^oK)

T_2 = temperature of air sampled (^oK)

10.4 The concentration of trimellitic anhydride in air (C_A) can be expressed in mg/m^3

$$C_A = \frac{W}{V}$$

where: W = weight of field sample in µg

V = volume of air sampled in liters

11. References

11.1 Snell, F.D., and L.S. Ettre, Encyclopedia of Industrial Chemical Analysis, 17, 171, (1968).

11.2 NIOSH Current Intelligence Bulletin # 21, "Trimellitic Anhydride", Publication No. 78-121.

11.3 Biondi, P.A., and M. Cagnasso, Journal of Chromatography, 109, 389 (1975).

John Palassis

Measurement Services Section

TITANIUM DIBORIDE

Measurement Support Branch

Analytical Method

Analyte:	Titanium Diboride	Method No.:	P&CAM 323
Matrix:	Air	Range:	0.1 to 4 mg/m^3
Procedure:	Filter collection, redeposition, X-ray diffraction	Precision:	0.138 (Analytical)
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

1. Synopsis

1.1 A known volume of air is drawn through a membrane filter to trap airborne dust.

1.2 The filters are ashed and the residue redeposited on silver membrane filters.

1.3 The filter samples are scanned by X-ray diffraction to determine the presence of titanium diboride and other phases which may cause matrix interference.

1.4 The mass of titanium diboride present is determined by measuring the diffraction peak intensity for the analyte and for the silver filter. The mass is calculated from calibration data.

2. Working Range, Sensitivity, and Detection Limit

2.1 The range of the method is from 0.1 to 4 mg/m^3 for a 500-L sample corresponding to 50-2000 µg per sample. The range of the method for samples containing titanium diboride and other compounds is dependent on the amount of interfering compounds and X-ray absorbing substances present in the sample.

2.2 The detection limit of titanium diboride is 20 µg on a 25-mm silver filter; however, quantitative measurements cannot be made at this level.

3. Interferences

3.1 Using copper Kα X-ray radiation, boron carbide, titanium dioxide (rutile) and the silver secondary peak interfere with the primary titanium diboride peak. Since matrix absorption corrections must be

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made with a silver membrane filter, the titanium diboride secondary peak is consequently used as the analytical peak.

3.2 The analytical peak may also have a small interference with the secondary boron carbide peak, only if boron carbide is present in large amounts.

3.3 Silver chloride found as an impurity in the silver filters may interfere with the tertiary titanium diboride peak.

3.4 The presence of phase interference can be verified by X-ray diffraction analysis. If interferences are present, analytical measurements are made using a different titanium diboride peak with a commensurate decrease in sensitivity and precision.

3.5 The presence of specific elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

3.6 The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and correction must be made. (See Sections 10.3 and 10.4).

4. Precision and Accuracy

4.1 The pooled relative standard deviation in the range of 50-2000 µg titanium diboride was 0.138.

4.2 The average recovery of titanium diboride from filters, after ashing, at the 50, 600, and 2000 µg levels was 94%.

5. Advantages and Disadvantages

5.1 The X-ray diffraction method is specific and can determine titanium diboride in the presence of other titanium compounds. The method is non-destructive of the analyte and the ashing step aids in eliminating organic and other volatile compounds that may interfere.

5.2 The method can be adapted to automation for analysis of routine samples.

5.3 The equipment is relatively expensive.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Polyvinyl chloride (PVC) membrane filters, 5-µm in pore size, 37-mm in diameter, MSA FWS-B or equivalent.

6.1.2 Plastic three piece 37-mm filter holders (cassettes). The filter is supported in the cassette by a cellulose backup pad.

6.1.3 Ten-mm nylon cyclone for collecting the respirable fraction.

6.1.4 A personal air sampling pump capable of operating at 1.5 to 2.0 liters/min. The pump must be calibrated to ± 5% at the recommended flow rate with a representative filter holder and filter in the line.

6.1.5 Thermometer, barometer, stopwatch.

6.2 X-ray diffraction equipment with a copper target X-ray tube. The equipment should be optimized for intensity rather than resolution.

6.3 Silver membrane filters, 25-mm diameter and 0.45-μm pore size: Selas Flotronics, Spring House, Pennsylvania, 19477.

6.4 Filtration apparatus (Gelman No. 1107 or equivalent) and side arm vacuum flask.

6.5 Volumetric Flask, 1-liter.

6.6 Reagent bottles with ground glass stoppers, 1-liter.

6.7 Low temperature radio frequency plasma asher.

6.8 Pyrex beakers, 50 mL, and watch glasses to fit over the beakers.

6.9 Instrument calibration reference specimen, mica, Arkansas stone (alpha quartz) or other stable standard.

6.10 Filter storage cassettes.

6.11 Forceps, applicator stick.

6.12 Polyethlene wash bottle.

6.13 Analytical balance to ± 0.01 mg, and weighing paper.

6.14 Ultrasonic bath or probe.

6.15 Sonic sifter with assorted sieves including a 10-μm sieve.

6.16 Assortment of pipettes, 2-25 mL.

6.17 X-ray diffraction filter holders.

6.18 Magnetic stirrer.

7. Reagents

The analytical reagents should be ACS reagent grade or equivalent.

7.1 Titanium diboride, < 10 μm particle size.

7.2 Glue (Canada-balsam) for attaching silver filters to filter holders.

7.3 Isopropanol.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water, distilled water, and isopropanol.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PVC membrane filter is supported by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the filter does not lie flat on the backup pad and the spacer ring does not fit snugly into the bottom of the filter holder, sample leakage will occur around the filter. Remove the cassette plugs. Attach the cyclone to the filter holder. Use a piece of flexible tubing to connect the filter holder to the pump.

8.3.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 500 liters is recommended. Sample at a flow rate of 1.7 liters per minute for 5 hours. The flow rate should be known with an accuracy of at least ± 5%. A high volume respirable air-sample or a rafter settled dust sample in a glass vial must also be submitted along with the other personal samples.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is unavailable, record the elevation. Replace filter plugs.

8.3.6 Blank. With each batch of ten samples submit at least one filter from the same lot of filters which was used for sample collection and which is subjected to the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.7 Shipping. The filter cassettes should be plugged and shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Obtain a qualitative X-ray diffraction scan (broad 2θ) of the bulk dust sample to determine the presence of titanium diboride and any matrix interference. The expected diffraction peaks are:

	Peak Angles	
	2-Theta Primary	2-Theta Secondary
Titanium diboride	44.64	34.22
Silver	38.12	44.28

8.4.2 Low Temperature Ashing of Samples. Using forceps, place filter samples in 50 mL beakers, mark beakers for identification and situate within the sample compartment of the low temperature asher so that the sample exposure to the plasma is optimized. The samples should be ashed for 2 hours at 400 watts RF power and at an oxygen pressure of 0.5 - 1.0 mm Hg using the techniques recommended in the instrument manual. After ashing add 15 mL of isopropanol to each beaker.

8.4.3 Ultrasonically agitate the beaker contents for 3 minutes, having a watch glass over the beaker.

8.4.4 Rinse the underside of the watch glass with isopropanol collecting the rinsings in the beaker. Place a silver filter in the filtration apparatus and attach the funnel. Pour several milliliters of isopropanol on the filter. With no suction, very little isopropanol will penetrate the filter. Pour the suspension from the beaker into the funnel, washing the beaker several times with isopropanol from the wash bottle. Apply a vacuum to the filter flask so the suspension is filtered rapidly. Do not wash the funnel walls. Leave the vacuum on for sufficient time to produce a dry filter. Disassemble the filter funnel, slowly release the vacuum, and remove the filter with forceps.

8.4.5 Attach the silver filter, using an applicator stick and glue, to a sample holder and insert in the diffractometer.

8.4.6 Analyze the most intense diffraction peak of titanium diboride that is free from matrix interference by step scanning the peak and integrating the counts. The experimental conditions used in this method were:

	Titanium Diboride	Silver
Scanning range	33.50 - 34.80° 2θ	37.03 -39.03° 2θ
Scanning time	10 sec./0.02° 2θ	0.5 sec./0.02° 2θ

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Measure the background on each side of the peak for one half the time used for peak scanning, and add the counts from each side for a total (average) background. The position of the background must be determined for each set of samples. The net count or intensity, I_t, is the difference between the peak integrated count and the total background count.

8.4.7 Determine the net count, I_{Ag}, of the appropriate silver peak following the procedure of 8.4.6. Scan times should be shorter for silver filters but should be consistent throughout the method.

8.4.8 After each unknown is scanned, determine the net count I_r^o, of the reference specimen. Determine normalized intensities, $\hat{I}$, for each peak by dividing the peak intensity by that of the reference specimen. Examples for the titanium diboride and silver peaks are:

$$\hat{I}_t = \frac{I_t}{I_r^o}$$

$$\hat{I}_{Ag} = \frac{I_{Ag}}{I_r^o}$$

8.4.9 Remove the silver filter from the filter holder and remount with the reverse side (clean side) exposed to the X-ray beam. Determine the net count for the silver peak, I_{Ag}^o, (Section 8.4.7). Normalize the measured intensities (Section 8.4.8),

$$\hat{I}_{Ag}^o = \frac{I_{Ag}^o}{I_r^o}$$

and record $\hat{I}_{Ag}^o$. This value will vary slightly from filter to filter.

9. Calibration and Standardization

9.1 Preparation of Titanium Diboride Standards

9.1.1 Wet sieve the titanium diboride in isopropanol through a 10-μm sieve, or dry sieve using the sonic sifter with 75-10 μm sieves.

9.1.2 Prepare two suspensions of titanium diboride in isopropanol by weighing approximately 10- and 100 mg of the dry titanium diboride to the nearest 0.01 mg in 50 mL beakers. Proceed with 9.1.3-9.1.6 for each beaker.

9.1.3 Measure 1.0 L of isopropanol in a volumetric flask. Add approximately 30 mL of isopropanol from the 1-L volumetric flask to

the beaker and ultrasonically agitate the suspension for five minutes.

9.1.4 Add approximately one half of the remaining isopropanol from the 1-L volumetric flask to the 1-L storage bottle. Place a magnet stirrer in the storage bottle and stir the isopropanol.

9.1.5 When the ultrasonic agitation is complete, quantitatively transfer the suspension from the beaker to the storage bottle. Rinse the beaker with several aliquots of the remaining isopropanol and add all rinsings to the storage bottle.

9.1.6 Add the remaining isopropanol to the bottle and continue stirring for thirty minutes.

9.1.7 Prepare a series of standard filters using the 10 and 100 mg/L suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range.

9.1.8 Mount a silver filter on the filtration apparatus. Place several mL of isopropanol in the filter funnel. Vigorously handshake the suspension and immediately withdraw an aliquot 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. Resume the procedure after shaking the suspension. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the suspension. As soon as the pipet has drained, apply the vacuum and rapidly filter the suspension. Leave the vacuum on for sufficient time to dry the filter. Do not wash down the sides of the funnel after the deposit is in place, since this will rearrange the material on the filter. Transfer the filter to the sample mount that is to be used in the diffractometer.

9.2 Perform step scans on the standards and reference specimen using the same conditions as those used for the samples. Using the procedure of Sec. 8.4.8, determine and record the normalized intensity, I_t^o, for each peak measured.

10. Calculations

10.1 Calculate the exact weights of titanium diboride deposited on each standard filter from the concentrations of the standard suspensions and aliquot volumes. Record the weight, w, of each standard. Prepare a calibration curve by plotting I_t^o as a function of w. Poor reproducibility (>20% RSD) at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line for low weights and curvature at high weights should be ignored when determining the line of best fit.

10.2 Determine the initial slope, m, of the linear calibration curve in counts/μg. The intercept, b, of the line with $\hat{I}^{o}_{t}$ axis should be approximately zero. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an inpurity is included in the measured peak.

10.3 Using the normalized intensities, $\hat{I}_{Ag}$, for the silver peaks of each sample (Sec. 8.4.8), and the $\hat{I}^{o}_{Ag}$ calculated for the clean side of the silver filter, calculate the transmittance, T, of each sample as follows.

$$T = \frac{\hat{I}_{Ag}}{\hat{I}^{o}_{Ag}}$$

10.4 Determine the correction factor, f(T), for each sample according to the formula (or use Table I)

$$f(T) = \frac{-R \ln T}{1-T^{R}}$$

where R is

$$R = \frac{\sin\theta_{Ag}}{\sin\theta_{t}}$$

and θ_{Ag} and θ_{t} are the angles θ (not 2θ) of the silver and titanium diboride peaks. Table I lists f(T) values for T values from 0.5 to 1.0 for a common $2\theta_{t}$ and $2\theta_{Ag}$ combination.

10.5 Calculate the weight, w, in micrograms of the titanium diboride in each sample:

$$w = \left[\frac{\hat{I}_{t}-b}{m}\right] x \left[f(T)\right]$$

If the blank contains an appreciable amount of titanium diboride, that amount should be subtracted from each field sample.

10.6 For personal sampling pumps with rotameters only, the following correction should be made

$$V = f \cdot t \left[\frac{P_1 \quad T_2}{P_2 \quad T_1}\right]^{1/2}$$

where: V = corrected air volume (L)
f = sample flow rate (Lpm)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg).

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (^oK)

T_2 = temperature of air sampled (^oK)

10.7 Calculate the airborne concentration, C, of titanium diboride in micrograms per cubic meter.

$$C = \frac{w}{V}$$

11. References

NIOSH Manual of Analytical Methods, 2nd Edition, Volume 5, P&CAM 259, "Free Silica in Airborne Dust".

John Palassis
Measurement Services Section

TABLE I

Matrix Absorption Correction Factors

Titanium Diboride (34.22°)/Silver Peak (38.12°), Degrees 2θ

T	f(T)	T	f(T)
1.00	1.0000	0.75	1.1681
0.99	1.0056	0.74	1.1764
0.98	1.0113	0.73	1.1848
0.97	1.0170	0.72	1.1934
0.96	1.0228	0.71	1.2021
0.95	1.0287	0.70	1.2110
0.94	1.0347	0.69	1.2200
0.93	1.0408	0.68	1.2293
0.92	1.0470	0.67	1.2387
0.91	1.0533	0.66	1.2483
0.90	1.0596	0.65	1.2581
0.89	1.0661	0.64	1.2680
0.88	1.0726	0.63	1.2782
0.87	1.0793	0.62	1.2887
0.86	1.0860	0.61	1.2993
0.85	1.0929	0.60	1.3101
0.84	1.0999	0.59	1.3212
0.83	1.1070	0.58	1.3326
0.82	1.1142	0.57	1.3442
0.81	1.1215	0.56	1.3561
0.80	1.1289	0.55	1.3682
0.79	1.1365	0.54	1.3807
0.78	1.1442	0.53	1.3934
0.77	1.1521	0.52	1.4064
0.76	1.1600	0.51	1.4198
		0.50	1.4335

T = Sample transmittance (see Section 10.3)

f(T) = Sample correction factor (see Section 10.4)

BORON CARBIDE

Measurement Support Branch

Analytical Method

Analyte:	Boron Carbide	Method No.:	P&CAM 324
Matrix:	Air	Range:	0.2 to 4 mg/m^3
Procedure:	Filter collection, redeposition, X-ray diffraction		
Date Issued:	8/29/80	Precision:	0.04 (Analytical)
Date Revised:		Classification:	E (Proposed)

1. Synopsis

   1.1 A known volume of air is drawn through a membrane filter to trap airborne dust.

   1.2 The filters are ashed and the residue redeposited on silver membrane filters.

   1.3 The filter samples are scanned by X-ray diffraction to determine the presence of boron carbide and other phases which may cause matrix interference.

   1.4 The mass of boron carbide present is determined by measuring the diffraction peak intensity for the analyte and for the silver filter. The mass is calculated from calibration data.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The range of the method is from 0.2 to 4 mg/m^3 for a 500-L sample corresponding to 100-2000 µg per sample. The range of the method for samples containing boron carbide and other compounds is dependent on the amount of interfering compounds and X-ray absorbing substances present in the sample.

   2.2 The detection limit of boron carbide is 50 µg on a 25-mm silver filter; however, quantitative measurements cannot be made at this level.

3. Interferences

   3.1 Using copper Kα X-ray radiation, titanium dioxide (anatase) and the primary silver peak interfere with the primary boron carbide peak; therefore, no measurements can be done with either the primary boron carbide or silver peak. The secondary boron carbide peak is chosen

as the analytical peak if no interferences are present.

3.2 A small interference may show up in the analytical peak from the secondary titanium diboride peak, if titanium diboride is present in a high concentration. The primary peak of titanium diboride will interfere with the secondary silver peak.

3.3 If niobium oxide is present it will interfere with the tertiary boron carbide peak.

3.4 Silver chloride, found as an impurity in the silver filter, may interfere with some low-intensity boron carbide peaks.

3.5 The presence of phase interference can be verified by X-ray diffraction analysis. If interferences are present, analytical measurements are made using a different boron carbide peak with a commensurate decrease in sensitivity and precision.

3.6 The presence of specific elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

3.7 The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and corrections must be made (see Sections 10.3 and 10.4).

4. Precision and Accuracy

4.1 The pooled relative standard deviation for the secondary analytical boron carbide peak in the range of 100-2000 µg was 4.0% determined from calibration curve standards (n=24). Additional boron carbide peaks - less intense than the analytical peak - indicated a 5.9% RSD for the $23.54^{\circ}2\theta$ angle (n=18) and 2.7% RSD for the $22.11^{\circ}2\theta$ angle (n=21) determined using the calibration curve standards.

4.2 A recovery study of boron carbide from ashed filters indicated that boron carbide at the 600 µg level can be recovered with 92% efficiency.

5. Advantages and Disadvantages

5.1 The X-ray diffraction method is specific and can determine boron carbide in the presence of different matrices. The method is non-destructive of the analyte and the ashing step aids in eliminating organic and other volatile compounds that may interfere.

5.2 The method can be adapted to automation for analysis of routine samples.

5.3 The equipment is relatively expensive.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Polyvinyl chloride (PVC) membrane filters, 5 µm in pore size, 37-mm in diameter, MSA FWS-B or equivalent.

6.1.2 Plastic three piece 37-mm filter holders (cassettes). The filter is supported in the cassette by a cellulose backup pad.

6.1.3 Ten-mm nylon cyclone for collecting the respirable fraction.

6.1.4 A personal air sampling pump capable of operating at 1.5 to 2.0 liters/min. The pump must be calibrated to ± 5% at the recommended flow rate with a representative filter holder and filter in the line.

6.1.5 Thermometer, barometer, stopwatch.

6.2 X-ray diffraction equipment with a copper target X-ray tube. The equipment should be optimized for intensity rather than resolution.

6.3 Silver membrane filters, 25-mm diameter and 0.45-µm in pore size: Selas Flotronics, Spring House, Pennsylvania, 19477.

6.4 Filtration apparatus (Gelman No. 1107 or equivalent) and side arm vacuum flask.

6.5 Volumetric Flask, 1-liter.

6.6 Reagent bottles with ground glass stoppers, 1-liter.

6.7 Low temperature radiofrequency plasma asher.

6.8 Pyrex beakers, 50 mL, and watch glasses to fit over the beakers.

6.9 Instrument calibration reference specimen, mica, Arkansas stone (alpha quartz) or other stable standard.

6.10 Filter storage cassettes.

6.11 Forceps, applicator stick.

6.12 Polyethylene wash bottle.

6.13 Analytical balance to ± 0.01 mg, and weighing paper.

6.14 Ultrasonic bath or probe.

6.15 Sonic sifter with assorted sieves including a 10 µm sieve.

6.16 Assortment of pipettes, 2-25 mL.

6.17 X-ray diffraction filter holders.

6.18 Magnetic stirrer.

7. Reagents

The analytical reagents should be ACS reagent grade or equivalent.

7.1 Boron carbide, < 10 μm particle size.

7.2 Glue (Canada-balsam) for attaching silver filters to filter holders.

7.3 Isopropanol.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water, distilled water, and isopropanol.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The PVC membrane filter is supported by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the filter does not lie flat on the backup pad and the spacer ring does not fit snugly into the bottom of the filter holder, sample leakage will occur around the filter. Remove the cassette plugs. Attach the cyclone to the filter holder. Use a piece of flexible tubing to connect the filter holder to the pump.

8.3.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.3 A sample size of 500 liters is recommended. Sample at a flow rate of 1.7 liters per minute for 5 hours. The flow rate should be known with an accuracy of at least ± 5%. A high volume respirable air-sample or a rafter settled dust sample in a glass vial must also be submitted along with the other personal samples.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently,and

the sampling should be terminated at any evidence of a problem.

8.3.5 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is unavailable, record the elevation. Replace filter plugs.

8.3.6 Blank. With each batch of ten samples submit at least one filter from the same lot of filters which was used for sample collection and which is subjected to the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.7 Shipping. The filter cassettes should be plugged and shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Obtain a qualitative X-ray diffraction scan (broad 2θ) of the bulk dust sample to determine the presence of boron carbide and any matrix interference. The expected diffraction peaks are:

	Peak Angles	
	2-Theta Primary	2-Theta Secondary
Boron Carbide	37.80	34.91
Silver	38.12	44.28

8.4.2 Low Temperature Ashing of Samples. Using forceps, place filter samples in 50 mL beakers, mark beakers for identification and situate within the sample compartment of the low temperature asher so that the sample exposure to the plasma is optimized. The samples should be ashed for 2 hours at 400 watts RF power and at an oxygen pressure of 0.5-1.0 mm Hg using the techniques recommended in the instrument manual. After ashing, add 15 mL of isopropanol to each beaker.

8.4.3 Ultrasonically agitate the beaker contents for 3 minutes, having a watch glass over the beaker.

8.4.4 Rinse the underside of the watch glass with isopropanol, collecting the rinsings in the beaker. Place a silver filter in the filtration apparatus and attach the funnel. Pour several milliliters of isopropanol on the filter. With no suction, very little isopropanol will penetrate the filter. Pour the suspension from the beaker into the funnel, washing the beaker several times with isopropanol from the wash bottle. Apply a vacuum to the filter flask so the suspension is filtered rapidly. Do not wash the funnel walls. Leave the vacuum on for sufficient time to produce a dry filter. Disassemble

the filter funnel, slowly release the vacuum, and remove the filter with forceps.

8.4.5 Attach the silver filter using an applicator stick and glue to a sample holder and insert in the diffractometer.

8.4.6 Analyze the most intense diffraction peak of boron carbide that is free from matrix interference by step scanning the peak and integrating the counts. The experimental conditions used in this method were:

	Boron Carbide	Silver
Scanning range	34.40 - 35.50°2θ	43.30 - 44.80°2θ
Scanning time	10 sec/0.02°2θ	0.5 sec/0.02°2θ

Measure the background on each side of the peak for one half the time used for peak scanning, and add the counts from each side for a total (average) background. The position of the background must be determined for each set of samples. The net count or intensity, I_c, is the difference between the peak integrated count and the total background count.

8.4.7 Determine the net count, I_{Ag}, of the appropriate silver peak following the procedure of 8.4.6. Scan times should be shorter for silver filters but should be consistent throughout the method.

8.4.8 After each unknown is scanned, determine the net count I_r^o, of the reference specimen. Determine normalized intensities $\hat{I}$, for each peak by dividing the peak intensity by that of the reference specimen. Examples for the boron carbide and silver peaks are:

$$\hat{I}_c = \frac{I_c}{I_r^o}$$

$$\hat{I}_{Ag} = \frac{I_{Ag}}{I_r^o}$$

8.4.9 Remove the silver filter from the filter holder and remount with the reverse side (clean side) exposed to the X-ray beam. Determine the net count for the silver peak, I_{Ag}^o, (Section 8.4.7). Normalize the measured intensities (Section 8.4.8),

$$\hat{I}_{Ag}^o = \frac{I_{Ag}^o}{I_r^o}$$

and record $\hat{I}_{Ag}^o$. This value will vary slightly from filter to filter.

9. Calibration and Standardization

9.1 Preparation of Boron Carbide Standards

9.1.1 Wet sieve the boron carbide with isopropanol through a 10-μm sieve, or dry sieve using the sonic sifter with 75-10 μm sieves.

9.1.2 Prepare two suspension of boron carbide in isopropanol by weighing approximately 10- and 100 mg of the dry boron carbide to the nearest 0.01 mg in 50 mL beakers. Proceed with 9.1.3 -9.1.6 for each beaker.

9.1.3 Measure 1.0 L of isopropanol in a volumetric flask. Add approximately 30 mL of isopropanol from the 1-L volumetric flask to the beaker and ultrasonically agitate the suspension for five minutes.

9.1.4 Add approximately one half of the remaining isopropanol from the 1-L volumetric flask to the 1-L storage bottle. Place a magnetic stirrer in the storage bottle and stir the isopropanol.

9.1.5 When the ultrasonic agitation is complete, quantitatively transfer the suspension from the beaker to the storage bottle. Rinse the beaker with several aliquots of the remaining isopropanol and add all rinsings to the storage bottle.

9.1.6 Add the remaining isopropanol to the bottle and continue stirring for thirty minutes.

9.1.7 Prepare a series of standard filters using the 10 and 100 mg/L suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range.

9.1.8 Mount a silver filter on the filtration apparatus. Place several mL of isopropanol in the filter funnel. Vigorously handshake the suspension and immediately withdraw an aliquot 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. Resume the procedure after shaking the suspension. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the suspension. As soon as the pipet has drained, apply the vacuum and rapidly filter the suspension. Leave the vacuum on for sufficient time to dry the filter. Do not wash down the sides of the funnel after the deposit is in place, since this will rearrange the material on the filter. Transfer the filter to the sample mount that is to be used in the diffractometer.

9.2 Perform step scans on the standards and reference specimen using the same conditions as those used for the samples. Using the procedure of Sec. 8.4.8, determine and record the normalized intensity, $\hat{I}_c^o$, for each peak measured.

10. Calculations

10.1 Calculate the exact weights of boron carbide deposited on each standard filter from the concentrations of the standard suspensions and aliquot volumes. Record the weight, w, of each standard. Prepare a calibration curve by plotting $\hat{I}_c^o$ as a function of w. Poor reproducibility (>20% RSD) at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line for low weights and curvature at high weights should be ignored when determining the line of best fit.

10.2 Determine the initial slope, m, of the linear calibration curve in counts/µg. The intercept, b, of the line with the $\hat{I}_c^o$ axis should be approximately zero. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from 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.

10.3 Using the normalized intensities, $\hat{I}_{Ag}$, for the silver peaks of each sample (Sec. 8.4.8), and the $\hat{I}_{Ag}^o$ calculated for the clean side of the silver filter, calculate the transmittance, T, of each sample as follows:

$$T = \frac{\hat{I}_{Ag}}{\hat{I}_{Ag}^o}$$

10.4 Determine the correction factor, f(T), for each sample according to the formula (or use Table I)

$$f(T) = \frac{-R \ln T}{1-T^R}$$

where R is

$$R = \frac{\sin\theta_{Ag}}{\sin\theta_c}$$

and θ_{Ag} and θ_c are the angles θ (not 2θ) of the silver and boron carbide peaks. Table I lists f(T) values for T values from 0.5 to 1.0 for common $2\theta_c$ and $2\theta_{Ag}$ combinations.

10.5 Calculate the weight, w, in micrograms of the boron carbide in each sample:

$$w = \left[\frac{\hat{I}_c - b}{m}\right] x \left[f(T)\right]$$

If the blank contains an appreciable amount of boron carbide, that amount should be subtracted from each field sample.

10.6 For personal sampling pumps with rotameters only, the following correction should be made

$$V = f \cdot t \sqrt{\frac{P_1 \quad T_2}{P_2 \quad T_1}}$$

where: V = corrected air volume (L)
f = sample flow rate (Lpm)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (^{o}K)
T_2 = temperature of air sampled (^{o}K)

10.7 Calculate the airborne concentration, C, of boron carbide in micrograms per cubic meter.

$$C = \frac{W}{V}$$

11. References

Niosh Manual of Analytical Methods, 2nd Edition, Volume 5, P&CAM 259, "Free Silica in Airborne Dust".

John Palassis
Measurement Services Section

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TABLE I

Matrix Absorption Correction Factors Boron Carbide/Silver Peak, Degrees 2θ

Boron Carbide	34.91	23.54	22.11		34.91	23.54	21.11
Silver	44.28	44.28	44.28		44.28	44.28	44.28
T	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)
1.00	1.0000	1.0000	1.0000				
0.99	1.0063	1.0093	1.0099	0.74	1.2011	1.3038	1.3249
0.98	1.0127	1.0188	1.0200	0.73	1.2107	1.3187	1.3409
0.97	1.0193	1.0284	1.0302	0.72	1.2205	1.3340	1.3573
0.96	1.0259	1.0382	1.0407	0.71	1.2305	1.3495	1.3740
0.95	1.0326	1.0481	1.0513	0.70	1.2407	1.3654	1.3911
0.94	1.0394	1.0582	1.0620	0.69	1.2512	1.3816	1.4086
0.93	1.0463	1.0685	1.0730	0.68	1.2618	1.3982	1.4264
0.92	1.0533	1.0790	1.0842	0.67	1.2726	1.4152	1.4447
0.91	1.0604	1.0897	1.0955	0.66	1.2836	1.4325	1.4633
0.90	1.0676	1.1005	1.1071	0.65	1.2949	1.4502	1.4824
0.89	1.0750	1.1115	1.1189	0.64	1.3064	1.4683	1.5019
0.88	1.0825	1.1227	1.1309	0.63	1.3182	1.4868	1.5218
0.87	1.0900	1.1342	1.1431	0.62	1.3302	1.5058	1.5423
0.86	1.0977	1.1458	1.1555	0.61	1.3425	1.5252	1.5632
0.85	1.1056	1.1576	1.1682	0.60	1.3550	1.5450	1.5846
0.84	1.1135	1.1697	1.1811	0.59	1.3678	1.5654	1.6066
0.83	1.1216	1.1820	1.1943	0.58	1.3809	1.5862	1.6290
0.82	1.1298	1.1945	1.2077	0.57	1.3944	1.6076	1.6521
0.81	1.1382	1.2073	1.2213	0.56	1.4081	1.6295	1.6757
0.80	1.1467	1.2203	1.2353	0.55	1.4221	1.6519	1.7000
0.79	1.1554	1.2335	1.2495	0.54	1.4365	1.6750	1.7249
0.78	1.1642	1.2470	1.2640	0.53	1.4513	1.6986	1.7504
0.77	1.1732	1.2608	1.2787	0.52	1.4664	1.7229	1.7766
0.76	1.1823	1.2749	1.2938	0.51	1.4819	1.7478	1.8036
0.75	1.1916	1.2892	1.3092	0.50	1.4979	1.7734	1.8312

T = Sample transmittance (See Section 10.3)
f (T) = Sample correction factor (See Section 10.4)

BENZIDINE-, o-TOLIDINE- AND o-DIANISIDINE-BASED DYES

Measurements Research Branch

Analytical Method

Analyte:	Benzidine o-Tolidine o-Dianisidine	Method No.:	P&CAM 325
		Range:	20-600 $\mu g/m^3$ (See Table 1)
Matrix:	Air		
		Precision:	0.045-0.104 (Analytical)
Procedure:	Filter collection, sodium hydrosulfite reduction, HPLC-UV		
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Benzidine- and benzidine congener-based dyes are collected from air on a filter and extracted with water. To an aliquot of this solution is added a phosphate buffer solution containing sodium hydrosulfite. This reagent reductively cleaves all azo linkages in the dye and releases any benzidine or benzidine congener present. Benzidine and benzidine congeners are then quantitated in the resulting solution by high performance liquid chromatography with UV detection.

2. Working Range, Sensitivity and Detection Limit

2.1 The range for the dyes used to validate this method are given in Table 1. Dye formulations consist of the actual dye material and a diluent. The data were obtained using specific formulations, but have been corrected to reflect the amount of pure dye in the formulation.

2.2 A 10-µL injection of a 0.38-µg/mL benzidine solution resulted in a peak whose height was 9% of full scale on a 10 millivolt recorder. The amplifier of the liquid chromatograph detector was set on the 0.02 AUFS range. This corresponds to a 4.737×10^{-4} AU/ng sensitivity. The same injection sizes for a 0.77-µg/mL o-tolidine solution (9% full scale) and 0.56-µg/mL o-dianisidine solution (3.5% full scale) produced sensitivities of 2.353×10^{-4} AU/ng and 1.25×10^{-4} AU/ng, respectively.

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2.3 The measurement limit for benzidine in 10-µL injections was approximately 3.8 ng, corresponding to an air concentration of 3.0 µg/m^3 for 500-L of air sampled. For o-dianisidine and o-tolidine in 10-µL injections, the measurement limits were 7.7 ng and 5.6 ng, respectively.

3. Interferences

Aniline, azobenzene, p-aminophenol, p-phenylenediamine and p-nitroaniline were found not to interfere in the analysis of benzidine, o-dianisidine and o-tolidine on a mole-to-mole ratio.

4. Precision and Accuracy

4.1 The relative standard deviation of the analytical measurement for the dyes tested varies from the ranges shown in Table 1. If samples are not analyzed within seven days, relative standard deviation of the analysis grows larger. The overall standard deviation will be larger due to errors associated with sample collection.

4.2 The efficiency of recovery and reduction of samples stored up to seven days was 0.85 or greater for all four dyes evaluated with this method. Since the method cannot differentiate among various benzidine- or benzidine congener-based dyes, recovery efficiency correction factors cannot be applied unless a single dye is present and its identity is known (see Section 8.4).

5. Advantages and Disadvantages

5.1 The major advantages are the specificity and sensitivity of the method for dyes based on benzidine and its congeners, o-tolidine and o-dianisidine.

5.2 The equipment required for analysis is relatively expensive.

5.3 The method does not differentiate between free benzidine and its congeners present in the collected sample and benzidine and its congeners derived from the dye.

5.4 Samples should be analyzed within seven days.

6. Apparatus

6.1 Sampling equipment, consisting of filter unit (Millipore 5.0-µm Mitex (Teflon) filter or equivalent, 37-mm diameter with backup pad, in a three-piece plastic cassette filter holder) and personal sampling pump capable of sampling at 2 L/min. The pump must be calibrated with a representative filter in line, using a

soap bubble flowmeter or wet- or dry-test meter and its flow rate must be known accurately to within ± 5%.

6.2 High pressure liquid chromatograph equipped with a detector capable of UV detection at 280 nm.

6.3 Waters Model RCM 100 Radial Compression Module with a Waters Radial Pak A (packed with octadecylsilylated silica of 10-μm particle diameter) or equivalent column. A system such as this is necessary because a highly efficient system is required to resolve aniline and benzidine. A filter between the injector and column should not be used, because this dead volume causes a loss in resolving power of the chromatographic column.

6.4 A syringe or autosampler for HPLC injection.

6.5 An electronic integrator or other suitable method for peak area measurement.

6.6 Microliter syringes in suitable sizes for preparation of standard solutions.

6.7 Volumetric flasks in convenient sizes for preparation of standard solutions.

6.8 Vials, 4-mL, with screw caps.

6.9 Volumetric pipette, 1-mL.

6.10 Tweezers.

6.11 Beakers, 50-mL.

6.12 Ultrasonic water bath.

7. Reagents

Whenever possible, reagents used should be ACS reagent grade or better.

7.1 Water, deionized and distilled.

7.2 Methanol, HPLC grade.

7.3 Benzidine. Prepare a 1.56-mg/mL stock solution of benzidine in methanol. This solution is stable for one month when stored in a refrigerator.

7.4 o-Tolidine. Prepare a 1.53-mg/mL stock solution of o-tolidine in methanol. This solution is stable for one month when stored in a refrigerator.

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7.5 o-Dianisidine. Prepare a 0.56-mg/mL stock solution of o-dianisidine in methanol. This solution is stable for one month when stored in a refrigerator.

7.6 Disodium hydrogen phosphate.

7.7 Potassium dihydrogen phosphate.

7.8 Sodium hydrosulfite.

7.9 HPLC mobile phase buffer. Add 3.390 g of potassium dihydrogen phosphate and 3.530 g of disodium hydrogen phosphate to a 1000-mL volumetric flask. Bring to volume with distilled water. Filter through a 0.22-μm mixed cellulose ester membrane filter and degas before use. This buffer should be freshly prepared before each day's analyses.

7.10 Reduction buffer solution. Add 1.179 g of potassium dihydrogen phosphate and 4.300 g of disodium hydrogen phosphate to a 1000-mL volumetric flask. Bring to volume with distilled water and filter prior to use. This solution should be freshly prepared before each day's analyses.

7.11 Reduction solution. Add 100 mg of sodium hydrosulfite to a 10-mL volumetric flask. Bring to volume using the reduction buffer solution described in 7.10. The solution should be prepared immediately before the reduction of the dye samples, since the sodium hydrosulfite is not stable in aqueous solution for any length of time.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water and dried.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the three-piece cassette filter holder and close firmly. The filter is supported by a backup pad. Secure the cassette holder together with tape or shrinkable band.

8.2.2 Remove the cassette plugs and attach the outlet of the filter cassette to the personal sampling pump inlet with flexible tubing.

8.2.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.4 A sample size of 500 L is recommended. Sample at a flow rate of 1.5 - 2.0 L/min. The flow rate should be known with an accuracy of 5%.

8.2.5 Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for a filter to become plugged by heavy particulate loading, the pump rotameter should be observed frequently and sampling should be terminated at any evidence of a problem.

8.2.6 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.2.7 After sampling, disconnect the filter. Cap the inlet and outlet of the filter cassette with plugs. Label the cassette.

8.2.8 With each batch or partial batch of ten samples, submit a blank filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this filter as the blank.

8.2.9 The cassettes should be shipped in a suitable container designed to prevent damage in transit. The samples should be shipped to the laboratory and analyzed as soon as possible (preferably within seven days). Cassettes should be stored in the dark until analysis.

8.2.10 A bulk sample of each of the dyes believed to be present in the area samples should be submitted separately with the filters.

8.3 Analysis of Samples

8.3.1 Remove the filter from the cassette with clean tweezers and place it face up in a 50-mL beaker. (The beaker should be of sufficient diameter to allow the filter lie flat in the bottom.)

8.3.2 Add 1 mL of water to the filter and swirl so that all the filter area is washed by the water.

8.3.3 Add a second mL of water to the beaker and shake as described in 8.3.2. The filter is then turned sample side down and the beaker placed in an ultrasonic bath

for 15 min. If an ultrasonic bath is not available, the beaker should be left to stand for 0.5 hr with occasional shaking.

8.3.4 Add a 1-mL aliquot of the sample solution to a 4-mL vial. Add 1 mL of the freshly prepared reducing solution (Section 7.9). Cap the vial and allow to stand for at least one hour or until the change in solution color is completed. Shake the vial occasionally during this period.

8.3.5 HPLC conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature:	Ambient
Column Pressure:	500 psi
Flow Rate:	1 mL/min
Mobile Phase:	60% methanol and 40% phosphate buffer (see Section 7.7)
Detector:	UV at 280 nm
Sample Size:	10 microliters
Capacity Ratio (k'):	benzidine - 0.344
	o-tolidine - 1.47
	o-dianisidine - 1.28

8.3.6 Inject a 10-µL aliquot of the reduced sample. Duplicate injections should compare within 3%. Rinse the syringe before injection of another sample.

8.3.7 Measure the area of the sample peak with an electronic integrator or some other suitable form of area measurement. Read the results from a standard curve prepared as discussed below.

8.4 Determination of Recovery Efficiency

8.4.1 If only a single dye is known to be present in the filter sample, recovery efficiency can be determined using a bulk sample of the dye. A solution of a known concentration of this dye is prepared. Known volumes of this solution are spiked onto filters and allowed to dry in a dessicator for one day. The filters should be spiked at several different levels and then analyzed by the procedure outlined in Section 8.3. On the day of analysis of the filters, the same volume of dye solution which was spiked on to the filters is mixed with 2 mL of water. This solution is the equivalent of the solution prepared from the filter samples in step 8.3.3 and can be analyzed by going on to step 8.3.4. The results of these analyses will give an amount of benzidine or

benzidine congener found on the spiked filter and in the liquid sample. Any difference in these two values will be due to recovery losses or gains. The recovery efficiency is calculated by the following equation:

$$RE = \frac{W_S}{W_L}$$

where: W_S = weight of benzidine or benzidine congener found on the spiked filter
W_L = weight of benzidine or benzidine congener found in the liquid sample
RE = recovery efficiency

The recovery efficiency may be dependent on the amount of dye collected on the filter. Plot the recovery efficiency versus weight of benzidine or benzidine congener found. Use this curve in Section 10.3 to correct for recovery losses.

9. Calibration and Standardization

A series of standards, varying in concentration, are prepared and analyzed under the same LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/4 mL versus peak area.

9.1 From the stock standard solution (Section 7.10) appropriate aliquots are withdrawn and dilutions are made in methanol. Prepare at least 5 working standards to cover the ranges of interest (0.38 to 16 µg/mL, benzidine; 0.77 to 15.3 µg/mL, o-tolidine; 0.56 to 11.7 µg/mL, o-dianisidine). This range is based on a 500-L air sample. A single standard solution should contain benzidine, o-tolidine and o-dianisidine at varying levels of concentration (e.g., benzidine - high concentration; o-tolidine - medium concentration; o-dianisidine - low concentration).

9.2 Analyze samples as per Section 8.3.

9.3 Prepare a standard calibration curve by plotting concentration of benzidine congener in µg/4 mL versus peak area.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume correction is needed because the standard curve is based on µg/4 mL volume and the sample and standard injection volumes are identical.

10.2 A correction for the blank should be made if necessary.

$$W_c = W_s - W_b$$

where: W_c = corrected weight in µg
W_s = µg found in sample filter
W_b = µg found in blank filter.

10.3 Read the recovery efficiency from the curve (see Section 8.4) for the amount of benzidine or benzidine congener found on the filter. This amount can then be corrected for recovery losses by the following equation:

$$W_{rc} = \frac{W_c}{RE}$$

where: W_{rc} = weight in µg, recovery corrected
W_c = weight in µg, blank corrected from Section 10.2
RE = recovery efficiency from Section 8.4.

10.4 For personal sampling pump with rotameters only, the following volume correction should be made.

$$V_c = f \times t \left[\frac{P_1}{P_2} \times \frac{T_2}{T_1}\right]^{1/2}$$

where: V_c = corrected air volume (L)
f = flow rate sampled (L/min)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (^oK)
T_2 = temperature of air sampled (^oK).

10.5 The concentration of benzidine or benzidine congener from the dyes in the air sample can be expressed in mg/m^3 (µg/L = mg/m^3)

$$mg/m^3 = \frac{W_c}{V_c}$$

where: W_c = corrected weight (µg) (from Section 10.2)
V_c = corrected air volume (liters).

11. References

11.1 Kirk Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 3, pp. 404-408, J. Wiley & Sons, New York, 1967.

11.2 Kennedy, E. R., and M. J. Seymour, "Development of an Analytical Method for Benzidine-Based Dyes," presented at the Second Annual Chemical Conference of the North American Continent, Las Vegas, Nevada, August 1980.

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Table 1

Dyes For Which the Method Has Been Tested

Dye[a]	Range µg/4 mL	Range µg/m³[b]	Precision[c]
C.I. Direct Red 28[d]	27.3 - 273.4	54.6 - 546.8	0.04
C.I. Direct Blue 6[d]	15.0 - 300.0	30.0 - 600.0	0.06
C.I. Direct Brown 95[d]	24.3 - 242.6	48.6 - 485.2	0.07
C.I. Direct Black 38[e]	12.5 - 250.0	25.0 - 500.0	0.05
C.I. Direct Red 2[e]	16.7 - 334.2	33.4 - 668.4	0.09
C.I. Direct Blue 8[e]	10.2 - 204.0	20.4 - 408.0	0.10

[a]Dye is listed by its Colour Index (C.I.) name.

[b]The atmospheric concentrations were calculated assuming a collection volume of 0.5 M^3 (2 L/min for 4.17 hours).

[c]These relative standard deviations represent the analytical precision only.

[d]These compounds were reduced using a reduction buffer composed of 11.79 g potassium phosphate and 43.00 g sodium phosphate/L of solution. HPLC flow rate was 2 mL/min for analyses. Other conditions were as described in the method.

[e]These compounds were reduced using conditions described in the method.

TOLUENE-2,4-DIISOCYANATE

Measurements Research Branch

Analytical Method

Analyte:	A urea derivative of 2,4-TDI	Method No.:	P&CAM 326
Matrix:	Air	Range:	0.017 to 0.58 mg/m^3
Procedure:	Collection and derivatization on coated glass wool, HPLC	Precision:	0.060
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

1. Synopsis

1.1 A known volume of air is drawn through a glass tube containing two sections of glass wool coated with a reagent, N-p-nitrobenzyl-N-propylamine. 2,4-TDI reacts with the reagent to form N,N"-(4-methyl-1,3-phenylene)bis[N'-[(4-nitrophenyl)methyl]-N'-propylurea] (2,4-TDIU) as a derivative.

1.2 The sections of coated glass wool are treated with dichloromethane.

1.3 The dichloromethane solutions are analyzed by high pressure liquid chromatography (HPLC) with an ultraviolet detector set at 254 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 The range useful for quantitation of the urea derivative (2,4-TDIU) in solution is equivalent to 1 to greater than 250 μg 2,4-TDI/mL. 2,4-TDI in air at concentrations ranging from 0.017 to 0.58 mg/m^3 can be quantified for 60-liter air samples. The capacity of the sampling tube for 2,4-TDI is at least 35 μg.

2.2 At a sensitivity of 0.02 absorbance unit for full scale deflection, analyses of 1.01-μg quantities of 2,4-TDIU (equivalent to

0.313-μg quantities of 2,4-TDI) in 50-μL portions of solution gave rise to peaks with an average deflection of 73% of full scale.

2.3 The detection limit of 2,4-TDIU in solution is equivalent to approximately 0.24 μg of 2,4-TDI/mL. The calculated detection limit for 2,4-TDI in a 60-liter air sample is 0.004 mg/m^3.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 N-p-Nitrobenzyl-N-propylamine on glass wool is unstable in the presence of light and is unstable to a lesser extent during storage at room temperature in the dark. Interference during HPLC analysis can result if sampling tubes are exposed to light for an excessive period or are stored at room temperature in the dark for an excessive period. Four sections of coated glass wool in glass tubes which had been exposed to light for 25 hours in a fume hood illuminated by fluorescent lighting gave rise to peaks which corresponded to an average of approximately 0.7 μg of 2,4-TDI per section of coated glass wool. Analysis of sections of coated glass wool stored 7 days at room temperature in the dark in three experiments resulted in average signals which corresponded to approximately 0.3, 0.5 and 0.5 μg of 2,4-TDI. Ten sections of coated glass wool stored at -21°C for 28 days gave rise to no peaks which corresponded to 2,4-TDI.

3.3 Any compound which has the same retention time as that of 2,4-TDIU and is detected under the HPLC conditions described for this method is an interference.

3.4 The following compounds would not interfere with the analysis of 2,4-TDI in this method: 2,6-TDI, hexamethylene diisocyanate (HDI), and 2,4-diaminotoluene. Diphenylmethane-4,4'-diisocyanate (MDI) would cause little or no interference. The peak resolution, R_s, for 2,4-TDIU and the corresponding urea derivative of MDI (MDIU) is approximately 1.5.

4. Precision and Accuracy

4.1 The relative standard deviation for the total sampling and analytical method in the range 0.039 to 0.53 mg/m^3 was 0.060. This value includes an assumed pump error of 0.05.

4.2 The accuracy of this method has not been determined conclusively. Analytical method recoveries after application of 2,4-TDI from the vapor phase were essentially quantitative at the following levels of 2,4-TDI: 1, 2, 10 and 20 µg.

4.3 2,4-TDIU in sampling tubes has been found to be stable at room temperature.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and convenient for personal sampling.

5.2 The analytical method is specific for 2,4-TDI.

5.3 The performance of a Partisil 10 HPLC column used in the evaluation of this method was satisfactory after the analysis of more than 420 front sections and more than 150 back sections of coated glass wool during a period of more than one year.

5.4 Disadvantages of this method are: (a) a time limitation of 7 days or less for storage of sampling tubes at room temperature in the dark, (b) a need to protect sampling tubes from light and (c) a need to wash the HPLC column when N-p-nitrobenzyl-N-propylamine causes a large detector response (see Sections 3.2 and 8.3.6).

6. Apparatus

6.1 Sampling Equipment

6.1.1 Sampling Tubes. Each sampling tube consists of a glass tube approximately 4 cm long with an 8-mm o.d. and a 6-mm i.d. containing two sections of glass wool coated with N-p-nitrobenzyl-N-propylamine (see Section 6.1.2). The front section of coated glass wool is 7 mm long and is located near one end (the inlet) of the tube. The back section is 5 mm long and is in contact with the front section. Insert the front section into the tube and compress it tightly to the desired length. If the portion of coated glass wool is an insufficient quantity for the desired length, insert another portion of coated glass wool and force it to a position between the previously inserted portion and the inside wall of the tube. Then insert the back section and compress it tightly to the desired length. Seal the ends of the tube with plastic caps. The sampling tubes may be stored at -21°C in the dark for at least 4 weeks. Limit the period of storage of

sampling tubes at room temperature in the dark to 7 days or less. Protect the sampling tubes from light (see Section 3.2).

6.1.2 Reagent Coated Glass Wool. Place 300 mg (0.0013 mole) of N-p-nitrobenzyl-N-propylamine hydrochloride into a 125-mL separatory funnel. Add 25 mL of deionized water and shake the mixture until all of the hydrochloride has dissolved. Cause free amine to separate from the aqueous phase by adding 15 mL of 1 N NaOH solution and shaking the mixture. Extract the N-p-nitrobenzyl-N-propylamine with 50 mL of hexane. Pipet 40.0 mL of the hexane solution into a clean, dry 50-mL beaker wrapped in aluminum foil and containing 1.82 g of silanized glass wool. Push the wet glass wool against the wall of the beaker with a clean glass tube connected with flexible tubing to a cylinder of nitrogen. Under dim light, evaporate hexane from the beaker with the aid of a stream of nitrogen. Knead the glass wool to produce a uniform coating and continue evaporating hexane until the coated 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 sampling tubes.

6.1.3 Glass tubes with right-angle bends, approximately 4.5 cm long, with a 6-mm i.d. and an 8-mm o.d. Each tube has one right-angle bend. Wrap each tube with black tape. These glass tubes can be attached to the inlets of sampling tubes with rubber sleeves to help protect coated glass wool from bright light.

6.1.4 Rubber Sleeves. The rubber sleeves should consist of opaque rubber tubing. Some of these rubber sleeves may be fitted over the sampling tubes to help protect coated glass wool from light. Other rubber sleeves may be used to attach glass tubes with right-angle bends to sampling tubes (see Section 6.1.3).

6.1.5 Calibrated Personal Sampling Pump. The personal sampling pump should be calibrated for the recommended flow rate of 1 liter per minute with a representative sampling tube in line.

6.1.6 Stopwatch.

6.2 High pressure liquid chromatograph equipped with an ultraviolet detector set at 254 nm.

6.3 HPLC column, 25-cm x 4.6-mm i.d., packed with Partisil 10.

6.4 Frits, 0.5-micrometer pore diameter, for use in front of the packing in the HPLC column.

6.5 Partisil 10 or other silica packing for use in replacing lost packing from HPLC column (see Section 8.3.7).

6.6 Syringes, 100-µL.

6.7 Glass vials, 1-mL, with caps lined with polytetrafluoroethylene.

6.8 U-Tube, glass, with glass stopcocks.

6.9 Volumetric flasks, 5-mL and other convenient sizes.

6.10 Tweezers.

6.11 Glass rod.

6.12 Pipet, 1-mL.

7. Reagents

7.1 Toluene-2,4-diisocyanate (2,4-TDI).

7.2 N-p-Nitrobenzyl-N-propylamine hydrochloride.

7.3 2,4-TDIU. Mix 1.03 g (0.00446 mole) of N-p-nitrobenzyl-N-propylamine hydrochloride with 25 mL of deionized water in a 125-mL separatory funnel. Add 15 mL of 1 N NaOH and shake the mixture. Extract the N-p-nitrobenzyl-N-propylamine with 50 mL of toluene and separate the layers. Add a solution of 262 µL (0.32 g, 0.00184 mole) of 2,4-TDI in 30 mL of toluene to the solution of N-p-nitrobenzyl-N-propylamine. Collect the precipitate by filtration and purify the product by dissolving it in a small volume of dichloromethane and precipitating it with hexane. Dry the product in vacuo. Melting point = 136-139°C. (Reference 11.1)

7.4 Dichloromethane, distilled in glass.

7.5 2-Propanol, distilled in glass.

7.6 Di-n-butylamine, high purity.

7.7 Tetrahydrofuran, high purity.

7.8 Bromocresol purple indicator solution.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and deionized water. Glass tubing used for sampling tubes (Section 6.1.1) and for glass tubes with right-angle bends (Section 6.1.3) should be cleaned with dichloromethane and dried in an oven.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the plastic caps from the ends of the sampling tube. Protect the sampling tube from bright light. Attach a glass tube with a right-angle bend (Section 6.1.3) to the inlet of the sampling tube with a rubber sleeve (Section 6.1.4). Fit an additional rubber sleeve over the sampling tube.

8.2.2 In each set of sampling tubes consisting of twenty or fewer sampling tubes, label four of the sampling tubes as "blanks." The "blank" sampling tubes and corresponding tubes used in actual air sampling should contain coated glass wool from the same batch (Section 6.1.2).

8.2.3 Handle the "blank" sampling tubes and the other sampling tubes under the same conditions of temperature and light exposure. Do not uncap and do not draw air through the "blank" sampling tubes.

8.2.4 Connect the sampling tube to a calibrated personal sampling pump with flexible tubing.

8.2.5 Sample at a flow rate of 1 liter/minute for 60 minutes. The flow rate should be known with an accuracy of $\pm 5\%$.

8.2.6 Record pertinent data in regard to sampling including sampling times and initial and final air temperatures. If atmospheric pressure data are not available, record the elevation.

8.2.7 After sampling, seal the uncapped sampling tubes with plastic caps and store these tubes and the "blank" sampling tubes in the dark and, if practical, at -21°C until analyses are performed. If the sampling tubes must be stored at room temperature, limit the total storage time at room temperature to 7 days or less. Consider any

storage time at room temperature before the collection of air samples as part of the total storage time at room temperature. The sampling tubes may be stored at -21°C in the dark for at least 4 weeks.

8.2.8 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a cap lined with polytetrafluoroethylene.

8.2.9 Do not transport a bulk sample with the sampling tubes in the same container.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the plastic caps from the sampling tube. Expel the front section of coated glass wool from the sampling tube by pushing against the back section with tweezers or a glass rod and transfer the section to a 1-mL glass vial. Transfer the back section to another 1-mL glass vial. Force the sections of coated glass wool to the bottom of each vial and add 1.00 mL of dichloromethane to each vial with a pipet. Seal each vial tightly with a cap lined with polytetrafluoroethylene. Shake each vial vigorously for approximately 1 minute.

8.3.2 HPLC Conditions. The operating conditions for high pressure liquid chromatography are:

Column Dimensions:	25 cm x 4.6 mm i.d.
Column Packing:	Partisil 10
Column Temperature:	Room temperature
Mobile Phase:	2:98 2-propanol-dichloromethane (v/v)
Flow Rate:	2.0 mL/minute
Detector:	UV (254 nm)
Injection Volume:	50 µL
Column Efficiency:	Approximately 460 theoretical plates for 2,4-TDIU

Compound*	Approximate Adjusted Retention Volume (V_R')	Approximate Capacity Factor (k')
2,4-TDIU	5 mL	2.3
MDIU	2.8 mL	1.3
2,6-TDIU	18.4 mL	8.4
HDIU	>30 mL	>13.6

*MDIU, 2,6-TDIU and HDIU are the corresponding urea derivatives of diphenylmethane-4,4'-diisocyanate (MDI), toluene-2,6-diisocyanate (2,6-TDI), and hexamethylene diisocyanate (HDI), respectively.

NOTE: If HPLC conditions are employed which are different from those mentioned in this section, "blank" sampling tubes should be analyzed after storage of such tubes and after exposure of such tubes to light to help determine possibilities of interference.

8.3.3 Inject a 50-µL aliquot of sample solution into the liquid chromatograph and determine the size of the peak corresponding to 2,4-TDIU.

8.3.4 If the concentration of 2,4-TDIU is above the lower quantitation limit, reanalyze the sample solution with two standards at concentrations above and below that of 2,4-TDIU in the sample solution (see Section 9.2). Precede and follow an injection of the sample solution with an injection of a standard solution.

8.3.5 Analyze the "blank" samples with the field samples.

8.3.6 After an aliquot of a sample solution has been injected into the liquid chromatograph, N-p-nitrobenzyl-N-propylamine may emerge eventually from the HPLC column and cause a large response in the detector. The period of time from the injection of an aliquot of sample solution to the time N-p-nitrobenzyl-N-propylamine would begin to emerge from the column may differ from one Partisil 10 column to another. Wash the column periodically to remove N-p-nitrobenzyl-N-propylamine by pumping 100% 2-propanol through the column at 2 mL/minute for 1 minute or longer. Then pump 2:98 2-propanol-dichloromethane (v/v) at 2 mL/minute through the column for at least 14 minutes before the next injection.

8.3.7 Change the frit in front of the column packing when pressure becomes excessive (see Section 6.4). If a small quantity of packing is lost, replace the lost packing with fresh Partisil 10 or other silica packing.

8.3.8 Measure peak heights or peak areas.

8.3.9 Construct a calibration curve for each sample based on the two adjacent standards (see Section 8.3.4).

8.4 Determination of Analytical Method Recovery

8.4.1 Significance of Determination. The determination of analytical method recovery may provide information which would aid in correcting for bias (if any) in the analytical method. Sample recoveries should be determined in the range of interest and should be quantitative or nearly quantitative (see Section 4.2).

8.4.2 Procedure. Connect a U-tube to the inlet of a sampling tube with a short piece of tubing in order that exposure of 2,4-TDI vapor to the tubing will be minimal. Connect the outlet of the sampling tube to a pump capable of drawing air at 1 liter/minute. Add an appropriate quantity of 2,4-TDI in 5 μL of dichloromethane solution to the U-tube, replace the stopcock, and immediately turn on the pump. Allow the pump to operate for 20 minutes. Make additional applications of the same quantity of 2,4-TDI in dichloromethane for four additional sampling tubes. Analyze the sampling tubes with standards and three "blank" sampling tubes. Perform this procedure at two or more levels of 2,4-TDI. The levels should span the range of interest.

The analytical method recovery equals the average quantity of 2,4-TDIU found in the samples corrected for the average blank and divided by the quantity of 2,4-TDIU equivalent to the quantity of 2,4-TDI applied.

9. Calibration and Standardization

9.1 Determinations of Purity of 2,4-TDI. Perform determinations by Method 1. If desirable, perform determinations by Method 2, also, and compare results. If the purity of the 2,4-TDI is questionable or unsatisfactory, purify some 2,4-TDI by distillation.

9.1.1 Method 1. Place a front section of coated glass wool from a sampling tube into a 1-mL glass vial and add 1.00 mL of dichloromethane. Seal the vial tightly with a rubber cap lined with polytetrafluoroethylene. Add approximately 20 μg of 2,4-TDI in 5 μL of dichloromethane solution with a syringe. Allow the mixture to stand for 5 minutes. Then shake the vial vigorously for 1 minute. Prepare several samples in this manner. Analyze the samples with 2,4-TDIU standards in dichloromethane solution. Analyze a few "blank" solutions. "Blank" values should be zero. Assume reaction yields are quantitative

and calculate the percent purity, P, of 2,4-TDI with respect to each sample according to the following equation:

$$P = \frac{G}{U} \times 0.310 \times 100$$

where:

G = Quantity of 2,4-TDIU found in sample
U = Theoretical quantity of 2,4-TDI added to the dichloromethane solution if the 2,4-TDI were 100% pure
0.310 = A value based on the division of the molecular weight of 2,4-TDI (174.16) by the molecular weight of 2,4-TDIU (562.63)

Find the average percent purity.

9.1.2 Method 2. Dissolve 480 µL (0.00283 mole) of di-n-butylamine in 10 mL of tetrahydrofuran. Add 100 µL of 2,4-TDI [density = 1.22 g/mL at 25°C (Reference 11.2)] and allow at least 6 minutes for reaction to take place. Add a few drops of bromocresol purple indicator solution and titrate the excess di-n-butylamine to a yellow end point with 0.05 M HCl. Analyze two additional samples of 2,4-TDI in this manner. If all impurities in the 2,4-TDI were chemically inert under these conditions, the percent purity, P', of 2,4-TDI may be found by use of the following equation:

$$P' = \frac{0.5[B - (VM)]}{W} \times 100$$

where:

B = Total molar quantity of di-n-butylamine before reaction
V = Volume of HCl expressed on a liter basis
M = Concentration of HCl expressed in molarity
W = Molar quantity of 2,4-TDI if 100% pure

Find the average percent purity for the three samples.

9.2 Construction of Calibration Curve. A calibration curve may be an aid in selecting standards to be analyzed with samples. Prepare 5 mL of a dichloromethane solution containing 50 mg of 2,4-TDIU. Dilute aliquots of this solution with dichloromethane to prepare a series of standard solutions with concentrations in the range 0.6 to 160 µg 2,4-TDIU/mL. Analyze 50-µL aliquots of the standard solutions under HPLC conditions indicated in Section 8.3.2. Construct a curve of peak height or peak area versus concentration of 2,4-TDIU.

10. Calculations

10.1 Determine the quantity of 2,4-TDIU found on the front section of coated glass wool from the appropriate calibration curve from Section 8.3.9.

10.2 Determine the quantity of 2,4-TDIU found on the back section of coated glass wool.

10.3 Correct the quantities of 2,4-TDIU for corresponding "blank" values.

10.4 Add the corrected quantities of 2,4-TDIU found on the front and back sections to find the total corrected quantity (Q) of 2,4-TDIU in the sampling tube.

10.5 Calculate the concentration of 2,4-TDI in the air sample in µg/liter (C) according to the following equation where V is the volume of air sampled in liters and 0.310 is a value based on the division of the molecular weight of 2,4-TDI (174.16) by the molecular weight of 2,4-TDIU (562.63):

$$C = \frac{Q}{V} \times 0.310$$

Concentrations in µg/liter and mg/m^3 are numerically the same.

11. References

11.1 Hastings Vogt, C. R., C. Y. Ko and T. R. Ryan, "Simple Ureas Derived from Diisocyanates and Their Liquid Chromatography on a 5-cm Column," J. Chromatogr., 134, 451-458 (1977).

11.2 Hawley, G. G., The Condensed Chemical Dictionary, ninth ed., Van Nostrand Reinhold Company, New York (1977), p. 868.

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HIPPURIC ACID IN URINE

Biological Support Branch

Analytical Method

Analyte:	Hippuric Acid	Method No.:	P&CAM 327
Matrix:	Urine	Range:	0.005-0.5 g/L
Procedure:	Spectrophotometric	Precision:	0.06
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

1. Synopsis

   1.1 Hippuric acid in urine reacts with benzenesulfonyl chloride in pyridine water solution to produce a colored product.

   1.2 Ethanol is added after 30 minutes at room temperature, the samples centrifuged to remove any turbidity, and the sample read in a spectrophotometer at 410 nm using ethanol as a blank.

2. Working Range, Sensitivity and Detection Limit

   2.1 The working range of the procedure is from 0.005-0.5 g/L of hippuric acid. The working range can be expanded by appropriate dilution of standards or samples.

   2.2 The minimum quality detected is 0.002 g/L of hippuric acid.

3. Interferences

   3.1 This method should not be used if the individual has ingested aspirin or has had exposure to styrene, xylene or salicyclic acid because metabolites of these compounds will react and produce a colored product.

   3.2 If ingestion of aspirin or exposure to xylene, salicyclic acid or styrene is expected, a method employing chromatographic separation should be used.

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4. Precision and Accuracy

4.1 The percent relative standard deviation is 6% over the working range of the method.

4.2 Accuracy has not been evaluated. Control populations should be evaluated to establish normals.

5. Advantages and Disadvantages

5.1 The principal advantage is that the method is direct, requires no extractions or purifications, and can be carried out with easily obtainable general laboratory equipment.

5.2 The principal disadvantage is that the method also measaures meta- and p-methyl hippuric acid, a metabolite of meta- and p-xylene, and salicyluric acid, a metabolite of salicylic acid or aspirin. Since hippuric acid is a reported metabolite of styrene, the method cannot be used when styrene is present. The lack of absolute specificity makes the method unsatisfactory when exposures to xylene, salicylic acid or aspirin is suspected.

6. Apparatus

6.1 Spectrophotometer with a 1-cm light path cell capable of reading a wavelength of 410 nm with a band width not exceeding 10 nm.

6.2 Centrifuge tubes, 15-mL Pyrex, conical.

6.3 Centrifuge capable of delivering 1500-2000X gravity with 15-mL conical centrifuge tubes.

6.4 Pipets, serological, 0.5-mL, 1-mL and 5-mL Pyrex and pipet bulb for use with organic reagents.

6.5 Vibration mixer (vortex).

6.6 Volumetric flasks with glass stopper, 100-mL size.

6.7 Urinometer.

7. Reagents

The reagents described must be made up using ACS reagent grade chemicals.

7.1 Hippuric acid stock standard (0.5 mg/mL): Dissolve 50 mg hippuric acid in water and dilute to 100 mL in a glass-stoppered volumetric flask (stable for one month at room temperature).

7.2 Benzenesulfonyl chloride: Use as it comes from the bottle (stable at room temperature).

7.3 Pyridine, reagent grade.

7.4 Thymol, USP for use as a urine preservative.

7.5 Ethanol, absolute, reagent grade.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Glassware should be cleaned with detergent or cleaning solution, rinsed thoroughly with distilled water, and oven dried.

8.2 Collection and Shipping of Samples

8.2.1 A "spot" urine sample of about 100 mL is collected following two days of suspected exposure. The sample should be taken at the end of the second day.

8.2.2 Samples should be collected in polyethylene bottles, and, if not analyzed the same day, frozen in a -20°C freezer until analysis can be done.

8.2.3 Urine should be preserved with a few crystals of thymol.

8.2.4 Samples are stable one day at 20°C and up to two months at -20°C.

8.3 Analysis of Samples

8.3.1 Dilute one part urine with four parts of distilled water.

8.3.2 Pipet 0.5 mL urine into a glass centrifuge tube.

8.3.3 Add 0.5 mL pyridine to the tube and mix by tapping with a finger.

8.3.4 Add 0.2 mL of benzenesulfonyl chloride and mix for about five seconds with a vibration mixer.

8.3.5 The colored solution is allowed to stand for 30 minutes at room temperature (20-30°C), diluted to 5.0 mL with ethanol and mixed on the vibration mixer.

8.3.6 The tube is then centrifuged at 1500-2000X gravity for five minutes to remove slight turbidity.

8.3.7 Absorbance of the solution is then determined in a spectrophotometer at 410 nm in a 1-cm curvette using ethanol to zero the instrument.

8.3.8 A hippuric acid standard (0.1 mg/mL) and water blank are treated in the same manner.

8.3.9 The specific gravity of the urine sample is taken and used in the calculations.

8.3.10 Individuals with high exposure to toluene may have to have their urine samples diluted one to ten insted of one to five as in 8.3.1 prior to analysis. The appropriate dilution factor is used in the calculations.

9. Calibration and Standardization

9.1 A standard curve is set up using dilutions of the 0.5 mg/mL stock hippuric acid solutions. Solutions should be made up to cover the working range of 0.005-0.5 mg/mL hippuric acid.

9.2 The standards are treated exactly like urine sample as in 8.3.

10. Calculations

10.1 A standard curve is prepared as in Section 9 and the concentration of hippuric acid in the standard is plotted against the absorbance at 410 nm.

10.2 The concentration of hippuric acid in the urine specimen, Cu, is determined from the standard curve or calculated as follows:

$$C_u = \frac{C_S \; A_u \; D}{A_S}$$

where C_S = the concentration of hippuric acid in the standard
A_u = the absorbance of the urine specimen
D = the dilution factor of the urine (generally 5)
A_S = the absorbance of the standard

10.3 Standard reporting units are in g/L.

10.4 The specific gravity is measured and the hippuric acid concentration is corrected as shown

$$C = \frac{24 \; C_u}{S}$$

where S = the last two digits of the specific gravity of the urine specimen (e.g., 1.021).

10.5 The normal range reported by Tomukuni for 20 healthy adult males was 0.44 ± 0.20 mg/mL (mean ± standard deviation) which corresponds to 0.44 ± 0.20 g/L.

11. References

11.1 Tomokuni, K. and M. Ogata. Direct Colorimetric Determination of Hippuric Acid in Urine. Clin. Chem. 18, 349-351 (1972).

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δ-AMINOLEVULINIC ACID DEHYDRATASE (ALAD) IN BLOOD

Biological Support Branch

Analytical Method

Analyte:	Porphobilinogen	Method No.:	P&CAM 328
Matrix:	Heparinized blood	Range:	10-60 units/mL RBC (red blood cells)
Procedure:	Enzymatic, spectrophotometric	Precision:	0.05
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

1. Synopsis

   1.1 Lead in small quantities is known to inhibit the enzyme δ-aminolevulinic dehydratase which converts δ-aminolevulinic acid to porphobilinogen (ALA → PBG).

   1.2 The rate of formation of PBG is measured in a whole blood hemolysate incubated with ALA. The amount of PBG is measured by condensation with Ehrlich's reagent and spectrophotometric measurement of the red color at 555 nm.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The range of the procedure is from 10-60 units per mL of packed red blood cells.

   2.2 This assay should only be used to assess low level lead exposure because of the extreme sensitivity of the enzyme.

3. Interferences

   3.1 Various groups have investigated inhibition of ALAD in vitro by minerals such as zinc, tin, mercury, cadmium, and silver. Others have studied the influence of succinylacetone, EDTA, and other specific organics. While many of these substances do inhibit ALAD in vitro, it is usually under conditions which are not normally encountered in the workplace.

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4. Precision and Accuracy

4.1 Precision is 5% relative standard deviation.

5. Advantages and Disadvantages

5.1 The compound measured (PBG) is a product of an enzymatic reaction, and any endogenous (PBG) is readily blanked out.

5.2 This method estimates ALAD in whole blood, whereas other methods have used washed erythrocytes. There is no reported difference between venous and capillary blood.

5.3 This method is very sensitive to low level lead exposures.

5.4 This enzyme is subject to instability under certain conditions (see 8.2.4) and, therefore, might reflect false positives.

5.5 Chronic exposures are not distinguishable from acute exposures using this method.

5.6 Even under optimum conditions, samples should be analyzed within 48 hours of collection.

6. Apparatus

6.1 Spectrophotometer with a 1-cm light path capable of reading a 2.0 mL sample at 555 nm.

6.2 Centrifuge, microhematocrit.

6.3 Reader, microhematocrit.

6.4 Tubes, microhematocrit.

6.5 Centrifuge, clinical, table top.

6.6 Water bath, $37^{\circ} \pm 1^{\circ}C$.

6.7 Tubes, 15-mL conical centrifuge.

6.8 Mixer, vortex.

6.9 Pipets, TD, 1-mL.

6.10 Pipets, TC, 200- L.

6.11 Pipets, 2.0-mL graduated serological.

6.12 Bulbs, pipet.

6.13 Balance, analytical.

6.14 Meter, pH.

6.15 Test tubes, disposable, 5-mL.

7. Reagents

7.1 Phosphate-citrate buffer, 0.01 M/L: Dissolve 6.703 g dibasic sodium phosphate ($Na_2HPO_4 7H_2O$) in 100 mL of distilled water. Dissolve 5.25 g citric acid in 100 mL of distilled water. Adjust the pH of the phosphate solution to 6.65 by adding citric acid solution. Store at 4°C.

7.2 δ-Aminolevulinic acid (ALA) solution, 0.01 M/L: Dissolve 16.8 mg δ-ALA HCl (Sigma Chemical Co., St. Louis, Missouri) in 10 mL phosphate citrate buffer. Prepare a fresh solution daily.

7.3 Ehrlich's reagent: Dissolve 1.0 g p-dimethylaminobenzaldehyde in 30 mL glacial acetic acid. Add 10 mL 70% perchloric acid and dilute to 50 mL with glacial acetic acid. This solution is stable for six hours. Caution - perchloric acid.

7.4 Trichloroacetic acid, 10% containing $HgCl_2$: Dissolve 10.0 g trichloroacetic acid in 50 mL distilled water. Add 2.7 g $HgCl_2$ and dilute to 100 mL with distilled water. Store at room temperature.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Glassware should be cleaned with detergent or cleaning solution, rinsed thoroughly with tap and distilled water, and oven dried. Store in a dust-free cabinet.

8.2 Collection and Shipping of Samples

8.2.1 Samples of venous whole blood should be collected in vacuum tubes containing heparin. Hemolysis should be avoided.

8.2.2 Samples should be kept at 4°C until analysis. Samples must not be frozen nor kept at any temperature above 20°C.

8.2.3 Samples can be shipped conveniently in polyfoam packers containing bagged ice or refrigerant.

8.2.4 Samples must be analyzed within 48 hours of collection.

8.3 Analysis of Samples

8.3.1 Add 1.3 mL distilled water to two small centrifuge tubes labeled "blank" and "sample."

8.3.2 Transfer 200 µL of well-mixed whole blood from the collection tube with a disposable capillary micropipet (TC) to each of the tubes taking care to rinse out the pipets with the water in the tubes.

8.3.3 Add 1.0 mL of ALA reagent to all tubes and mix.

8.3.4 Add 1.0 mL of trichloroacetic acid to the blank tube. Only one blank is usually needed per group of samples.

8.3.5 Incubate all tubes at 37°C for one hour in a water bath.

8.3.6 After one hour, add 1.0 mL of trichloroacetic acid to all sample tubes and remove from the water bath.

8.3.7 Mix all tubes on the vortex mixer and centrifuge at 1500-2000 RPM for ten minutes. Read the absorbance at 555 nm using the blank to zero the instrument. Complete all readings within 15 minutes.

8.3.8 Using care not to disturb the precipitate, transfer 1.0 mL of the supernatant to a clean test tube.

8.3.9 Add 1.0 mL of fresh Ehrlich's reagent to each tube and mix. Let stand for 10 minutes. Read the absorbance at 555 nm using the blank to zero the instrument. Complete all readings within 15 minutes.

8.3.10 Fill microhematocrit tubes with well-mixed whole blood and centrifuge them for five minutes. Determine the hematocrit by using the hematocrit reader.

9. Calibration and Standardization

9.1 This assay does not make use of chemical standards. The product of the reaction, porphobilinogen, has a known extinction coefficient. It is, therefore, possible to calculate, from absorbance, the quantity of PBG produced under the specified conditions.

9.2 Since the standardization is based on extinction coefficient, it is imperative that the optical system be correctly calibrated for both wavelength and photometric accuracy.

9.3 The results are expressed as units of enzyme/mL packed red blood cells at 37°C. A unit is defined as the amount of enzyme activity required to produce 1 μ mole of PBG in one minute at 37°C.

9.4 Samples having an absorbance difference between blank and sample of 1 or more should be diluted 1:2 and rerun with an appropriate blank.

10. Calculations

10.1 Enzyme units/mL RBC at 37°C are calculated as follows:

$$(A_t - A_o) \times \frac{100}{H} \times f = \text{units/mL RBC}$$

where A_t = the absorbance of the sample at 60 minutes, read on a spectrophotometer which is adjusted to read zero absorbance using blank solution

A_o = the absorbance at time zero

f = factor for dilution blood dilution - (blood volume x time) times 1/absorptivity of PBG x 2

H = hematocrit

$$f = \frac{3.50 \times 2}{0.2 \times 60} \times \frac{1}{0.036} \times 2 = 32.4$$

In its most simplified form, the equation for final calculation is:

$$\frac{(A)(100)(32.4)}{H} = \text{units ALAD/mL RBC at } 37^{\circ}C$$

10.2 According to Weissberg, et al. (Reference 11.1), the expected blood lead/ALAD relationship is as follows:

Blood Lead	mean ALAD + SD
30 μg/100 mL	32.26 ± 11.12
30-44 μg/100 mL	25.82 ± 9.11
45-55 μg/100 mL	18.00 ± 5.48
60 μg/100 mL	12.26 ± 3.53

11. References

11.1 Weissberg, J. B., Lipschutz, F. and Oski, F. A. δ-Aminolevulinic acid dehydratase activity in circulating blood cells. New Eng. J. Med., 284, 565-569 (1971).

11.2 Bonsignore, D., Calissano, P. and Cartesegna, C. Un semplice metodo per la determinazione della δ-aminolevulinico-deidrasi mel sangue. Comportamento cell "enzima nell" intossicazione saturina. Med Lavoro, 56, 199-205 (1965)(in Italian).

11.3 Burch, H. B. and Siegel, A. L. Improved method for measurement of δ-aminolevulinic acid dehydratase activity in human erythrocytes. Clinical Chem., 17, 1039-1041 (1971).

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POLYCHLORINATED BIPHENYLS IN BLOOD SERUM

Biological Support Branch

Analytical Method

Analyte:	Polychlorinated Biphenyls	Method No.:	P&CAM 329
		Range:	30-10,000 ng/mL
Matrix:	Blood serum	Precision:	0.14
Procedure:	Extraction, gas-liquid chromatography with electron capture detector		
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

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1. Synopsis

   1.1 Mixtures of the various isomers of polychlorinated biphenyls (PCB) are extracted from serum with a 1:1 (v/v) mixture of ethyl ether and n-hexane.

   1.2 The serum extract is treated with a 2% (w/v) solution of methanolic potassium hydroxide to convert the pesticide DDT to its metabolite DDE.

   1.3 The PCB's in the methanolic potassium hydroxide solution are extracted into n-hexane.

   1.4 The PCB's in the hexane are separated from co-extractable material by silica gel column chromatography.

   1.5 The hexane extract is concentrated and analyzed for PCB by gas-liquid chromatography using an electron capture detector.

2. Working Range, Sensitivity and Detection Limit

   2.1 The working range is from 30-10,000 ng/mL when using a 5-mL serum sample. This range can be increased by using more serum.

2.2 The absolute sensitivity of the electron capture detector is 50 pg/injection.

2.3 The detection limit is estimated to be 26 ng/mL based on 5-mL serum sample.

3. Interferences

3.1 Many pesticides and their metabolites interfere with PCB analysis. The most common are the DDT metabolites p,p'-DDE and o,p'-DDE.

4. Precision and Accuracy

4.1 Ninety serum samples spiked with mixtures of Aroclor 1242 and 1254 over a range of 25-500 ng/mL showed an average relative standard deviation of 14%.

4.2 The overall recovery of PCB through all of the extraction, concentration, saponification, clean-up and gas chromatography steps exceeds 80% throughout the working range.

5. Advantages and Disadvantages

5.1 The method is technically complex with many steps. There are many steps where sample loss or contamination can occur.

5.2 Quantitation is difficult because it is based on peak patterns in standards which are rarely identical with peak patterns in serum.

5.3 The procedure makes some erroneous assumptions.

5.3.1 There is no metabolism of PCB in the human body, therefore, patterns for standards equal patterns for samples.

5.3.2 The electron capture detector responds equally to all possible isomers of polychlorinated biphenyls.

5.3.3 All isomers are extracted with equal efficiency.

5.3.4 Other chlorinated hydrocarbon pesticides are not present in significant quantities compared to amounts of PCB present.

6. Apparatus

6.1 Organic-free 16 x 150-mm culture tubes with Teflon-lined screw caps.

6.2 Rotary mixer, variable speed.

6.3 Centrifuge, bench top.

6.4 Kuderna-Danish concentrator tubes, 25-mL (Kontes, Vineland, New Jersey).

6.5 Ebullators (Kontes, Vineland, New Jersey).

6.6 Micro-Synder columns (Kontes, Vineland, New Jersey).

6.7 Tube heater (Kontes, Vineland, New Jersey).

6.8 Chromatography column, 7 mm i.d. x 200 mm with a 50-mL reservoir and Teflon stopcock.

6.9 Syringes, 10- µL, glass.

6.10 Graduated cylinder, 25-mL, glass.

6.11 Gas chromatographic column, glass, 6' x 1/4" (4 mm i.d.), packed with 1.5% OV-17, 1.95% QF-1 on 80/100 mesh Supelcoport .

6.12 Gas-liquid chromatograph equipped with an electron capture detector.

7. Reagents

7.1 Methanol, hexane, ethyl ether, and acetone, pesticide grade.

7.2 Potassium hydroxide, analytical grade.

7.3 Ultrapure water.

7.4 Mixture of PCB's designated as Aroclor 1016, 1242, 1221, 1232, 1248, 1254, 1260, and 1262. Stock solutions are prepared using at least 10 mg of each dissolved in a convenient volume of n-hexane.

7.5 Silica gel (Woelm), activity grade I.

7.6 Sodium sulfate, anhydrous, analytical grade.

8. Procedure

8.1 Cleaning of Glassware

8.1.1 All glassware, including syringes and blood tubes, must be free of all organics which will produce a response in the electron capture detector.

8.1.2 Wash in detergent-tap water followed with tap water rinses.

8.1.3 Soak in chromic acid followed with tap and distilled water rinses.

8.1.4 Rinse three times with acetone and three times with n-hexane.

8.2 Collection and Shipping of Samples

8.2.1 Blood must be collected in all glass syringes with stainless steel needles (no plastic syringes).

8.2.2 Immediately after collection, the blood is transferred to a clean centrifuge tube, permitted to clot, and centrifuged to separate the serum from the clot.

8.2.3 The serum is transferred to a clean 16 x 150 mm culture tube with a Teflon-lined screw cap.

8.2.4 The serum is sent to the laboratory for analysis in insulated containers with an internal temperature of 4°C (used in bagged refrigerant).

8.2.5 The serum is kept frozen until analysis.

8.3 Analysis of Samples

8.3.1 Extraction

1. Pipet 5 mL of serum into a clean 16 x 150 mm culture tube which contains 4 mL of methanol.

2. Cap the tube and mix the contents on a rotary mixer (50-55 rpm) for four minutes.

3. Add 5 mL of hexane-ethyl ether (1:1 v/v).

4. Mix on the rotary mixer (50-55 rpm) for 15 minutes.

5. Centrifuge at 2000 rpm for two to five minutes.

6. The upper solvent layer is transferred by pipet into a 25-mL Kuderna Danish concentrator tube.

7. Steps 3 through 6 are repeated twice and the extracts are combined in the concentrator tube.

8. The extract is concentrated to 0.5 mL under a slow stream of dry organic-free nitrogen.

8.3.2 Saponification

1. Add 2 mL of a 2% (w/v) solution of methanolic potassium hydroxide to the concentrator tube with an ebullator.

2. Attach a micro-Synder column and bring the contents to a gentle boil by use of the tube heater and reduce the volume to 0.3 mL. If a precipitate forms, add a few drops of methanolic potassium hydroxide solution and warm gently over steam until it dissolves.

3. Cool the solution slightly and add 2 mL of methanol water (1:1 v/v).

4. When the solution reaches room temperature, add 2 mL of n-hexane.

5. Stopper the tube and shake vigorously.

6. A small amount of glass wool is matted into the bottom of a 7 mm i.d. x 200 mm chromatographic column with a 50-mL reservoir and Teflon stopcock.

7. Three grams of silica gel are mixed with 50 mL of hexane, and the suspension is poured into the column.

8. The suspension is allowed to settle and topped with 5-7 g of sodium sulfate.

9. Wash the column with 20 mL of hexane and as the hexane settles into the sodium sulfate bed, add the concentrated saponified extract.

10. A 25-mL graduated cylinder is placed below the chromatographic column.

11. Rinse the concentrator tube and the micro-Synder column with 1 mL of hexane.

12. As the saponified extract enters the sodium sulfate layer, add the concentrator tube and micro-Synder column rinses to the chromatographic column.

13. As the rinses settle in the sodium sulfate layer, add 25 mL of hexane.

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14. Collect 25 mL of eluate from the column in the graduated cylinder.

15. Rinse down the walls of the graduated cylinder with 2 mL of hexane.

16. Concentrate to 1 mL and analyze by gas-liquid chromatography.

8.3.4 Analysis by Gas-Liquid Chromatography

1. All analyses are done on a gas-liquid chromatograph equipped with an electron capture detector.

2. The instrument parameters are:

injector	200°C
column	190°C
manifold	250°C
detector	300°C

The carrier gas is 5% methane in Argon with a flowrate of 75 mL/min.

3. Five µL of each extract is injected. Depending upon the type of Aroclor, the elution time may vary from a few minutes to approximately one hour.

9. Calibration and Standards

9.1 Five µL of each working standard is injected.

9.2 Retention time and baseline values for each chromatogram are calculated.

9.3 An average retention time is calculated for each peak of an Aroclor standard of interest based upon three multiple injections.

9.4 A 5% retention window or a retention time $\pm$ 2.5% is established. Any peak present in this window will be accepted as a true peak.

9.5 A standard curve is prepared by plotting the total peak height versus concentration or the amount of Aroclor injected.

10. Calculations

10.1 The concentration of Aroclor or PCB (C) in ng/mL is calculated as follows:

$$C = \frac{H_u \; C_S \; S_V \; E_V}{H_S}$$

where H_u = the sum of peak heights attributed to PCB in the serum sample
H_S = the sum of PCB peak heights of the standard
S_V = the volume of blood serum analyzed
C_S = the concentration of the standard in ng/mL
E_V = the total volume of the extract.

10.2 Concentrations of PCB (C) can also be calculated from the standard curve as follows:

$$C = \frac{C_g \; E_V}{S_V}$$

11. References

11.1 Analysis of PCB in Blood Samples, NIOSH Contract 210-78-0107-0000, Environmental Science and Engineering, Inc., Gainesville, Florida (1978).

11.2 Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples, U.S. EPA, Environmental Toxicology Division, Research Triangle Park, North Carolina (1974).

11.3 Manual of Analytical Quality Control for Pesticides in Human and Environmental Media, U.S. EPA, Environmental Toxicology Division, Research Triangle Park, North Carolina (1976).

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PHENOL IN URINE

Biological Support Branch

Analytical Method

Analyte:	Phenol	Method No.:	P&CAM 330
Matrix:	Urine	Range:	2.0-300 μg/mL
Procedure:	Acid hydrolysis ether extraction gas chromatography, FID	Precision:	0.128
Date Issued:	8/29/80		
Date Revised:		Classification:	B (Accepted)

1. Synopsis

A known volume of urine is hydrolyzed and then phenol and other metabolites are extracted into an organic solvent. The extracted phenol and metabolites are released from the solvent matrix by the temperature of the injection port, separated by gas chromatography and detected by a flame ionization detector. An internal standard is added prior to the sample injection.

2. Working Range, Sensitivity and Detection Limit

2.1 The working range is from 2.0-300 μg phenol/mL urine.

2.2 The flame ionization detector has a linear response for up to 300 μg of phenol/mL of urine.

2.3 The detection limit of this analytical procedure is 0.5 μg of phenol/mL of urine.

3. Interferences

3.1 o-Phenyl phenol and any compound which has the same retention time and detector response as phenol under the GC operating conditions described in this method can interfere. However, this type of interference can be overcome by changing the operating conditions of the instrument.

3.2 Water in the extractant can be detrimental to the packing in the GC column and will cause plugging.

3.3 Any substance ingested or normally present in a worker which contains benzene or can be metabolized to phenol will produce a false positive urine phenol.

3.4 Workers exposed to phenol will excrete urinary phenol which will give false positives for exposure to benzene.

3.5 Extremely dilute urine can lead to misleading results (see 10.2).

4. Precision and Accuracy

4.1 Precision (relative standard deviation) for 10 replicate control urine samples was 12.8% (corrected to a specific gravity of 1.024) and 14.7% without correction.

4.2 Absolute recoveries calculated from data were found to range from 90% for samples containing 100-200 μg phenol/mL of urine to 95% for samples containing 2-100 μg phenol/mL of urine when extracted with either diethyl ether or diisopropyl ether (see 5.5).

5. Advantages and Disadvantages

5.1 The procedure has high specificity and provides for rapid determination of phenol.

5.2 It differentiates phenol and its conjugates from ortho-, meta- and para-cresols in urine.

5.3 This method can also be used for measuring different organic solvents such as cresol, nitrobenzene, etc. Interferences are minimal and most of those which do occur can be eliminated by altering chromatographic conditions. (The procedure has not been thoroughly evaluated for other solvents, only for phenol.)

5.4 The ether extract containing phenol is subject to evaporation, and precautions should be aken to minimize evaporation. This can be accomplished by keeping the extractant under refrigeration until injection into the gas chromatograph.

5.5 The widely-used colorimetric method described by Buchwald yields 50% higher phenol concentrations on normal urine than those obtained in this method. The colorimetric method is not specific and responds to other urine phenols such as the cresols.

6. Apparatus

6.1 Gas chromatograph equipped with a flame ionization detector.

6.2 A mechanical or electronic integrator for determining peak areas or a recorder for determining peak heights.

6.3 Glass column (6 ft. x 1/4 in., i.d. 2 mm) packed with stabilized 2% diethylene glycol adipate (DEGA) on Anakron (60/70 mesh).

6.4 Small glass-stoppered graduate centrifuge tubes (15 mL) or equivalent.

6.5 Microliter syringes, 10 µL and other convenient sizes for making standards.

6.6 Volumetric flasks, 100 mL or convenient sizes for making standards.

6.7 Micro disposable glass pipets for use with organic solvents (SMI or equivalent).

6.8 Water bath for maintaining 95°C temperature.

6.9 Urometer or hydrometer for measuring specific gravity of urine.

6.10 Vortex mixer.

6.11 Small polyethylene screw cap bottles, 100 mL.

6.12 Culture tubes, disposable (10 x 75 mm).

7. Reagents

All reagents should be of analytical or spectroquality grade.

7.1 Diethyl ether (ether), or diisopropyl ether.

7.2 HCl, concentrated, or perchloric acid, 70%.

7.3 Sodium sulfate, anhydrous.

7.4 Thymol, urine preservative.

7.5 Nitrobenzene (internal standard): Dissolve approximately 30 mg of nitrobenzene into 50 mL of distilled water.

7.6 Phenol.

7.7 Acetone.

7.8 Ice.

7.9 Helium, prepurified, grade A.

7.10 Dry hydrogen.

7.11 Air, filtered, compressed.

7.12 Stock standard: Dissolve approximately 200 mg of phenol into 100 mL of distilled water.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 All glassware used for the laboratory analysis should be detergent washed and rinsed with tap water followed by a chronic acid treatment and thoroughly rinsed with distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Urine samples are collected in small polyethylene screw cap bottles and a few crystals of thymol are added for preservation.

8.2.2 The urine must be kept in ice or under refrigeration during transport to the laboratory.

8.2.3 If analysis is to be postponed for more than a week, the urine should be frozen and preferably shipped that way, packed in dry ice in polyethylene shipping containers.

8.3 Analysis of Samples

8.3.1 The specific gravity of the urine is determined to see if the sample has a specific gravity less than 1.010; if it is lower, the sample must be rejected and another one obtained.

8.3.2 Pipet 5 mL of urine into a 15-mL, glass-stoppered centrifuge tube.

8.3.3 Add 1 mL of concentrated HCl (perchloric acid is also acceptable), mix by vortex and transfer the lightly stoppered centrifuge tube to a water bath (95°C) and hydrolyze for 1.5 hours. Afterwards, remove the tube and allow to cool to room temperature.

8.3.4 Add 10 µL nitrobenzene (internal standard) and adjust the volume in the centrifuge tube to 10 mL with distilled water.

8.3.5 Pipet 2 mL diethyl ether (diisopropyl ether is also acceptable) into the tube and shake vigorously for one minute to extract the phenol and other metabolites. Allow the phases to separate (placing the centrifuge tube in a freezer decreases phase separation time).

8.3.6 Transfer approximately 0.5 mL of the clear ether solvent to a small culture tube that contains a few milligrams of sodium sulfate and mix.

8.3.7 To avoid evaporation and concentration of sample (diethyl ether or diisopropyl ether), mark solvent height on the culture tube an maintain the volume. Keep the sample in an ice bath until ready to inject into the gas chromatograph.

8.3.8 The parameters of the gas chromatograph are as follows:

Helium carrier gas flow:	40 mL/min
Hydrogen gas flow to detector:	30 mL/min
Airflow to detector:	300 mL/min
Injector temperature:	200°C
Manifold temperature:	200°C
Column temperature conditions:	Isothermal at 130°C for four minutes and then rapidly programmed to 190°C to bake out other urinary compounds before the next sample injection.
Retention time:	3.5 min

8.3.9 Inject 5 µL of the extractant into the gas chromatograph using the solvent flush injection technique. The 10 µL syringe is first flushed with ether to wet the barrel and plunger. Three µL of solvent are first drawn into the syringe, then the plunger is pulled back about 0.3 µL to separate the solvent flush from the sample. The needle is then immersed in the sample, and a 5 µL aliquot is withdrawn, taking into consideration the volume of the needle (approximately 0.8 µL). After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle.

8.3.10 The area of the sample peak is measured by an electronic integrator or by some other suitable form of area measurement device and compared to the area of the internal standard. A standard curve based on peak heights can also be used.

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9. Calibration and Standardization

9.1 Prepare a series of phenol in urine standards varying from no additions of phenol to 200 µg phenol/mL of urine by diluting the phenol stock standard (see 7.12) to an appropriate volume in urine.

9.2 The spiked urine samples serve as standards and are analyzed under the same gas chromatography.

9.3 Ten µL of nitrobenzene (internal standard, 0.60 mg/mL) are added to each spiked urine sample prior to sample injection into the gas chromatograph.

9.4 The calibration curve is established by plotting phenol concentration (µg/mL) versus the ratio of the peak areas of phenol per peak areas of nitrobenzene.

NOTE: In the above calibration, peak area values are used. This results in the highest accuracy, especially if an integrator is used, for obtaining the peak area values. However, the peak height may be used instead of area for the quantitative evaluation. When using peak heights, it is very important to keep in mind that the slightest change in column temperature and carrier gas flow rate can effect the peak heights more than the peak areas.

10. Calculations

10.1 The concentration of phenol in urine can be determined from the standard curve or calculated as shown below

$$C = \frac{A\ C_{IS}}{A_{IS}}$$

where C = the concentration of phenol in urine expressed as µg phenol/mL of urine
C_{IS} = the concentration of the internal standard expressed as µg nitrobenzene/mL
A = the area of the urine phenol peak
A_{IS} = the area of the internal standard peak.

10.2 Urine specimens that have a specific gravity less than 1.010 and greater than 1.038 will produce misleading data. The phenol concentration of the urine (C) can be adjusted to a "normalized" specific gravity of 1.024 as shown

$$C_{sg} = \frac{24\ C}{SG}$$

where C_{sg} = the "corrected" phenol concentration normalized to a specific gravity of 1.024
SG = the last two digits of the urine specimens specific gravity (i.e., 1.018).

10.3 Phenol in urine specimens can also be reported using a creatinine correction. For this correction to be valid, urine creatinine must be determined by a separate method and the concentration of creatinine must exceed 0.4 g/L. The concentration of phenol in urine, corrected for creatinine excretion (C_c), expressed as mg phenol/g creatinine is as follows

$$C_c = \frac{C_1}{C_{cre}}$$

where C_1 = the urine phenol concentration expressed as mg phenol/L of urine
C_{cre} = the concentration of creatinine in urine expressed as g creatinine/L of urine.

10.4 Normal ranges found in this laboratory are 3.1-5.8 mg/L corrected to a specific gravity of 1.024 and 1.5-2.8 mg phenol/g creatinine. It must be emphasized that laboratories should establish their own normal ranges using urines from personnel not exposed to benzene, phenol or excessive amounts of dietary sodium benzoate (used as a food preservative in some foods).

11. References

11.1 Criteria for Occupational Exposure to Benzene, HEW Publication No. NIOSH 74-137 (1974).

11.2 Buchwald, H. The Colorimetric Determination of Phenol in Air and Urine with a Stabilized Diazonium Salt, Ann. Occup. Hyg., 9, 7-14 (1966).

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METHYL ETHYL KETONE PEROXIDE

Measurements Research Branch

Analytical Method

Analyte:	Methyl ethyl ketone peroxide (MEKO)	Method No:	P&CAM 331
Matrix:	Air	Range:	0.31 - 3.1 mg/m^3 for a 250-L air sample
Procedure:	Absorption in dimethyl phthalate in impinger, colorimetric analysis	Precision:	0.052
Date Issued:	8/29/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 Methyl ethyl ketone peroxide is collected in a midget impinger containing 15 mL of dimethyl phthalate.

1.2 A 5-mL aliquot of the resulting solution is transferred to a stoppered, silanized test tube and diphenylcarbohydrazide color reagent is added. Heating produces a violet color.

1.3 Spectrophotometric analysis is made at 565 nm and quantitation of the analyte is then accomplished by comparison to known standards.

2. Working Range, Sensitivity and Detection Limit

2.1 The probable range of the method is 0.31 to 3.1 mg/m^3.

2.2 The lowest analytically quantifiable level for this method was arbitrarily defined as the level corresponding to twice the absorbance of the blank or about 25 µg/10 mL in the analyzed solution. The upper limit is set by the fact that the absorbance vs. concentration curve is linear only to about 250 µg/10 mL in the analyzed solution. Performing a volumetric dilution can extend the range in 2.1 upward. However, the sample as analyzed must fall between twice the blank and 250 µg/10 mL to be usable.

3. Interferences

3.1 An interference with this analytical procedure could arise from other peroxides or any strong oxidant.

3.2 Most ketones will exhibit positive interference at high levels, except acetone which does not affect the analysis.

3.3 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 may catalyze this decomposition.

3.4 Since it is not possible to compensate for these interferences, care should be taken to preclude their presence where possible, for example, by carefully cleaning and silanizing all glassware. If the presence of ketones other than acetone is suspected, a separate sample should be taken and analyzed for ketones.

4. Precision and Accuracy

4.1 The overall precision of the method was 0.052 relative standard deviation. This figure was arrived at by including variances associated with pump error, and random error of analysis. Day-to-day changes in the slope of the standard curve were significant. If samples and standards are not run the same day, the relative standard deviation will be about twice as large.

4.2 Samples stored at freezer temperature showed a 10% loss over 21 days.

4.3 The accuracy of the analytical method was assessed by relating the MEKO content of the commercial material to primary standard $K_2Cr_2O_7$.

5. Advantages and Disadvantages

5.1 Collected samples are analyzed by a rapid instrumental method.

5.2 No sample elution or desorption is required because the sample is collected in a liquid medium.

5.3 A disadvantage of the method is the awkwardness of using midget impingers for collecting samples.

5.4 A disadvantage is relative non-specificity of the diphenylcarbohydrazide color reaction.

5.5 A disadvantage is the special care that must be taken in the conditioning of the glassware and in the storage of the samples.

6. Apparatus

6.1 Midget impingers, glass 25-mL, silanized.

6.2 Personal sampling pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative impinger and splash-over trap in the line to minimize errors associated with uncertainties in the volume sampled.

6.3 Test tubes, 18 mm X 150 mm, with glass stoppers, silanized.

6.4 Water bath, capable of holding a constant temperature of 85 ± 5 °C.

6.5 Cold water bath, 25 ± 5 °C.

6.6 Spectrophotometer, capable of reading at 565 nm.

6.7 Matched glass cells or cuvettes, 1-cm path length.

6.8 Stopwatch

6.9 Assorted laboratory glassware, all silanized. Pipets, Class A, volumetric transfer, various sizes; volumetric flasks, beakers, burette, graduated cylinders, Erlenmeyer flasks.

6.10 Shipping vials, silanized, 20 mL, Teflon-lined caps.

6.11 Cold chest, insulated, dry-ice cooled.

7. Reagents

7.1 Dimethyl phthalate, reagent grade.

7.2 Glacial acetic acid, reagent grade.

7.3 Diphenylcarbohydrazide, reagent grade.

7.3.1 Diphenylcarbohydrazide solution. Dissolve 0.25 g ± .01 g of diphenylcarbohydrazide in dimethyl phthalate and dilute to 100 mL. This solution is light sensitive and should be prepared in a darkened place fresh each day immediately before using. The rate of solution of diphenylcarbohydrazide is slow and may be speeded up by placing the flask in an ultrasonic bath. Solution should then rest long enough to cool and return to volume.

7.3.2 Color Reagent. Mix 30 mL of the 0.25% diphenylcarbohydrazide solution with 20 mL glacial acetic acid. Prepare fresh immediately before use.

7.4 Methyl ethyl ketone peroxide (MEKO), 60%, Technical Grade

MEKO Stock Solution. Pipet about 10 µL of the nominally 60% MEKO into a 50 mL pre-weighed flask. After accurately weighing the flask plus MEKO fill to volume with dimethyl phthalate. Wrap flask in foil. Working standards of MEKO containing 5 to 50 µg/mL of MEKO in dimethyl phthalate are made from the stock solution.

7.5 Reagents for Standardization of Commercial MEKO.

7.5.1 Starch indicator solution.

7.5.2 Potassium iodide, reagent grade.

7.5.3 Sodium thiosulfate solution, 0.1 N.

7.5.4 Isopropyl alcohol, reagent grade.

7.5.5 Sodium iodide, reagent grade. Sodium iodide solution. Dissolve 20 g sodium iodide in 100 mL isopropanol.

7.6 Sodium bisulfite.

7.7 Nochromix®.

7.8 5% dichlorodimethylsilane in toluene.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Initially all glassware should be washed in detergent, rinsed with tap water, then deionized water and then soaked overnight in a Nochromix® solution (made with concentrated sulfuric acid and a packet of Nochromix®). After the Nochromix® soak, glassware is rinsed with deionized water, dried in an oven and cooled to room temperature. Glassware is then silanized by filling with a 5% dichlorodimethylsilane in toluene solution (Sylon CT or equivalent) for 1 min. followed by a toluene, then a methanol rinse,then dried. After use, glassware should be rinsed with methanol, detergent washed, thoroughly rinsed with tap water followed by 4-5 rinsings with deionized water and then rinsed with methanol and

oven-dried at 120 °C overnight after each use. Allow glassware to cool down to room temperature before using.

8.1.2 Cleaning of Matched Spectrophotometric Cuvettes. The cuvettes, previously matched, should be kept scrupulously clean and free of scratches, fingerprints, smudges and evaporated film residues and should be cleaned by detergent, followed by deionized water rinses, and then acetone.

8.2 Collection and Shipping of Samples

8.2.1 Pipet 15 mL of dimethyl phthalate into each impinger. Wrap in aluminum foil.

8.2.2 Connect a foil-wrapped impinger to an empty impinger positioned between the exit arm of the first impinger and a personal sampling pump using a short piece of flexible tubing. Connect the empty impinger to the sampling pump using flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the first impinger.

8.2.3 Turn on the pump to begin sample collection. Care should be taken to measure the sampling time as accurately as possible. Record atmospheric pressure and temperature. If pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1.7 L/min. A sample size of at least 240 liters is recommended (approximately 2.5 hrs sampling time).

8.2.4 After sampling, the contents of each impinger should be quantitatively transferred to silanized, aluminum foil-wrapped vials and tightly sealed. They should be placed in the cold chest as quickly as feasible.

8.2.5 Whenever possible, hand delivery of the samples packed in dry ice is recommended. Otherwise, special cases containing dry ice should be used to ship the samples. Mark "Fragile" on the container.

8.2.6 A "blank" impinger should be handled in the same way as the other samples (fill, seal and transport) except that no air is sampled through the impinger.

8.2.7 Samples of the bulk liquid which contain the MEKO should be submitted to the laboratory in exactly the same manner as the samples (i.e. in silanized, aluminum foil-wrapped vials in the cold chest).

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8.2.8 Storage. After receipt in the laboratory, the vials are stored in the freezer. (Note: Analysis should be completed as soon as possible. Samples stored as long as three weeks have shown 10% loss of sample.)

8.3 Analysis of Samples

8.3.1 Transfer in duplicate exactly 5.0 mL of each sample into a silanized test tube.

8.3.2 Pipet 5.0 mL of the diphenylcarbohydrazide color reagent into each of the tubes, stopper and invert several times to mix.

8.3.3 Loosen the stopper and heat the test tubes in a water bath at 85 $\pm$ 5 °C for 15 minutes.

8.3.4 Cool in a room temperature water bath for exactly 5 minutes.

8.3.5 Zero the spectrophotometer with dimethyl phthalate vs. air.

8.3.6 Read the absorbance of the samples at 565 nm in a spectrophotometer vs. air, when a stable value is obtained.

8.4 Disposal of MEKO solutions: Prepare 250 mL of a saturated aqueous solution of sodium bisulfite in a 1-L beaker. Store in a hood. Add all waste solutions containing MEKO to this beaker. Allow to stand for a week before disposing of the two phase mixture.

9. Calibration and Standardization

9.1 Standardization of commercial MEKO. The 60% MEKO should be standardized initially and weekly thereafter to determine its true concentration.

9.1.1 First standardize the sodium thiosulfate solution, 0.1 N, by following NIOSH Manual of Analytical Methods, Vol. 1, P&CAM 209, paragraphs 7.6 to 7.9 or follow directions in any analytical chemistry text. Alternatively standardized thiosulfate may be purchased from any one of several suppliers.

9.1.2 Weigh out 1 g of the nominally 60% MEKO in a 100 mL volumetric flask. Record weight to nearest mg. Dilute to 100 mL with isopropanol, cover flask with foil.

9.1.3 In a 250-mL iodine flask, place approximately 25 mL isopropyl alcohol. Add 5 mL glacial acetic acid. Then add 10 mL of the 20% sodium iodide in isopropyl alcohol solution to the flask.

9.1.4 Pipet exactly 10 mL of the MEKO solution from 9.1.2 above, into the flask, cover and let stand in the dark for 15 min.

9.1.5 Add 10 mL distilled water immediately before titrating.

9.1.6 Titrate with 0.1 N sodium thiosulfate from a yellow to colorless end point. Record the volume in mL used.

9.1.7 A blank containing all reagents except MEKO also should be titrated in exactly the same way.

9.1.8 Calculation of Weight % MEKO.

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

where:
C_S = % MEKO 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 MEKO used(g)
4.405 = constant containing the milliequivalent weight of MEKO (as the cyclic dimer) and various dilution factors

9.2 Aliquots of the MEKO stock standard (Section 7.4.1) are diluted to prepare the various working standards. Dimethyl phthalate is used as the solvent in preparing all standards. Prepare stock and working standards fresh daily. Wrap the volumetric flasks in aluminum foil.

9.3 Prepare at least 3 standards over the range of expected concentrations.

9.4 Analyze as in Section 8.6.

9.5 The standards and unknowns are treated exactly alike and analyzed during the same time period using the same batch of reagents.

9.6 Construct a calibration curve by plotting absorbance against concentration of MEKO in μg/10 mL of solution. Extrapolate to zero concentration. This is the "blank" value. Any sample whose absorbance is less than twice the "blank" should be reported as less than that level.

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10. Calculations

10.1 From the standard curve, find the concentrations of the samples in µg MEKO/10 mL. Convert to air concentrations as follows:

$$C_A = \frac{3(C_f - C_B)}{V_A}$$

where: C_A = air concentration in mg/m^3
C_f = concentration of MEKO in µg/10 mL in the analyzed solution
V_A = volume of air sampled in liters
C_B = concentration of the sample blank (if greater than twice the reagent blank)

10.2 For personal sampling pumps with rotameters only, the following correction should be made:

$$V_A = f \times t \sqrt{\frac{P_1 T_2}{P_2 T_1}}$$

where: V_A = corrected volume
P_1 = atmospheric pressure during pump calibration (mm Hg)
P_2 = atmospheric pressure during sampling (mm Hg)
T_1 = ambient temperature during pump calibration (^oK)
T_2 = ambient temperature during sampling (^oK)
f = sample flow rate (L/min)
t = sampling time (min)

11. References

11.1 NIOSH Manual of Analytical Methods, Second Ed., Vol. 1, U. S. Dept. HEW, NIOSH, Cincinnati, Ohio 45226, 1977, Method No. P&CAM 209.

11.2 Mair, R. D. and Graupner, A. J., Determination of Organic Peroxides by Iodine Liberation Procedures, Analytical Chemistry, 36, 194 (1964).

11.3 Hamm, D. L., Hammond, E. G., Parvanah, V. and Snyder, H. E., J. Am. Oil Chem. Soc. 42, 920 (1965).

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MONOCHLOROACETIC ACID
Measurements Research Branch
Analytical Method

Analyte:	Monochloracetic Acid	Method No.:	P&CAM 332
Matrix:	Air	Range:	0.35 to 29 mg/m^3 in 3 L of air
Procedure:	Adsorption on silica gel, desorption with water, ion chromatography	Precision:	≤0.08
Date Issued:	7/31/80		
Date Revised:		Classification:	B (Accepted)

1. Synopsis

1.1 A known volume of air is drawn through a silica gel tube to adsorb the monochloroacetic acid vapor present.

1.2 The silica gel in the tube is transferred to a small vial where the monochloroacetic acid is desorbed with reagent-grade water.

1.3 An aliquot of the desorbed sample is injected into an ion chromatograph.

1.4 The height of the resulting peak is determined and compared with the peak heights obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

2.1 The overall method was tested by collecting samples from atmospheres containing monochloroacetic acid in the approximate range of 0.35 to 29 mg/m^3 at 25 to 27 °C and at a relative humidity of 80% or greater. The sampling and analytical method was validated with nominal sample loadings of 1 to 80 µg of monochloroacetic acid per 100-mg bed of silica gel.

2.2 The slope of the analytical calibration curve was 1.01 µmho/µg when peak heights were plotted as a function of the amount of monochloroacetic acid injected.

2.3 The lowest analytically quantifiable level for this method was determined to be about 1 µg of monochloroacetic acid per sorbent sample extracted with 2.00 mL of reagent-grade water. The instrumental detection limit was about 20 ng/mL of monochloroacetic acid in reagent-grade water; the relative standard deviation of replicate determinations of standards at this level was 10%.

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3. Interferences

3.1 The ion chromatographic operating conditions described below will separate fluoride, chloride, dichloroacetate, trichloroacetate, glycolate, and acetate ions from monochloroacetate ion. Acids or salts of all of these anions except fluoride are among those likely to be collected with monochloroacetic acid in air.

3.2 Chloroacetyl chloride is expected to be a positive interferent in the determination of monochloroacetic acid because it has been reported that chloroacetyl chloride is efficiently collected by silica gel and is hydrolyzed to monochloroacetic acid in an analysis procedure similar to that required for this method (see Reference No. 11.2).

3.3 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of monochloroacetic acid.

3.4 Any substance that has the same retention time as monochloroacetic acid with the ion chromatographic operating conditions described in this method is an interferent. Therefore, retention time data cannot be considered proof of chemical identity.

3.5 If the possibility of interference exists, changing the separation conditions (column length, eluent flow rate, eluent strength, etc.) may circumvent the problem.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the values of the relative standard deviation (RSD) for the replicate measurements were inhomogeneous and, therefore, were not pooled. The RSD over the range of the method was estimated to be ≤8.1% with data obtained from the concentration level where the poorest precision was obtained (i.e., 0.35 mg/m^3). The pooled RSD for the analytical method was 1.6% for 18 sorbent samples spiked with 1 to 80 µg of monochloroacetic acid and stored for 24 h.

4.2 The concentration of monochloroacetic acid in test atmospheres was determined in control experiments with an independently calibrated continuous monitor based on solution conductivity. The determinations with sorbent sampling gave values that averaged 90% of those determined with the continuous monitor over the range of the method.

4.3 The breakthrough volume of the sorbent tube was found to be greater than 100 L with a sampling rate of 0.2 L/min at a monochloroacetic acid concentration of 60 mg/m^3, a sampling temperature of 42 °C, and relative humidities of greater than 80% and less than 10%. The breakthrough volume was also found to be greater than 100 L at a

monochloroacetic acid concentration of 35 mg/m^3, a sampling temperature of 27 °C, and relative humidities of greater than 90% and less than 10%.

4.4 Samples of monochloroacetic acid on silica gel were found to be stable at 25 °C for 7 d and for 32 d if stored at 0 °C after the seventh day. These samples were stored in the dark.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the ion chromatographic procedure. The samples are analyzed by means of a quick instrumental method.

5.2 One disadvantage of the method is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of accurate performance (±5%) at the 0.05 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Silica gel, 20/40 mesh (Catalog No. 226-10-01, SKC, Inc., Eighty-Four, PA), is used to pack the tubes as described below.

6.3 Silica gel tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d. containing two sections of 20/40-mesh silica gel—a 100-mg sorbing section and a 50-mg backup section—held in place with three silanized glass wool plugs. During packing, care should be taken to avoid crushing the silica gel. The ends of the tubes are sealed with Teflon tape and then with plastic caps to prevent contamination during storage. The average pressure drop across nine typical sorbent tubes was found to be 2.6 in. H_2O (0.6 kPa) at 25 °C at a sampling rate of 0.2 L/min; the RSD was 10%. Note: Do not use commercially available silica gel tubes with urethane plugs. The monochloroacetic acid may be adsorbed on the plugs during sampling and cannot be quantitatively recovered by the procedure described below.

6.4 Ion chromatograph (Dionex Corporation, Sunnyvale, CA).

6.5 Anion precolumn, Dionex (3 mm i.d. by 150 mm long), Dionex anion separator columns (3 mm i.d. by 250 mm long and 3 mm i.d. by 500 mm long), and Dionex anion suppressor column (6 mm i.d. by 250 mm long).

6.6 Glass vials, 20-mL, with aluminum-lined plastic screw caps.

6.7 Microliter syringes, 10-μL and convenient sizes for making dilutions.

6.8 Pipets, 1.00-mL, 2.00-mL, and convenient sizes for making dilutions.

6.9 Ultrasonic bath.

6.10 Plastic syringes, sterile single-use 3-cc (available from Becton, Dickinson and Co., Rutherford, NJ).

6.11 Filter discs, Mitex (Teflon), 13 mm in diameter, 5-μm pore size (available from Millipore Corp., Bedford, MA, Catalog No. LSWP01300).

6.12 Filter holders, polypropylene, 13 mm with Luer-lok connections (available from Millipore Corp., Catalog No. SX0001300).

7. Reagents

7.1 Sodium bicarbonate, ACS reagent grade or better.

7.2 Reagent-grade water, distilled and deionized to meet ASTM Type 1 standard specifications for reagent water.

7.3 Monochloroacetic acid, 99% or purer.

8. Procedure

8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, distilled water, acetone, and reagent-grade water (in that order).

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, open the ends of the tube by removing the plastic caps and Teflon tape. The tubes are not flame sealed.

8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of silica gel is the backup layer and is positioned nearer the sampling pump.

8.2.3 Place the silica gel tube in a vertical position during sampling to prevent channeling through the tube.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.2.5 Sample the air at 0.05 to 0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 100 L at 0.2 L/min.

8.2.6 Report the temperature and pressure of the air being sampled and measured.

8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps and store the tubes in the dark.

8.2.8 To obtain a blank sample, process one unused silica gel tube in the same manner as the samples (break, seal, and transport) but do not sample air through this tube. Submit the one blank sample tube for every ten samples, but in no case submit less than three blank tubes.

8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

8.2.10 Ship nine to twelve unopened silica gel tubes so that desorption efficiency studies can be performed on the same type and lot of silica gel used for sampling.

8.2.11 Log samples as soon as they are received in the laboratory.

8.2.12 Refrigerate all samples stored longer than 7 d.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the silica gel tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer each section of silica gel in a tube to a separate vial. Add the glass wool plug near the tube inlet to the vial containing the sorbing section; add the other two glass wool plugs to the vial containing the backup section.

8.3.2 Desorption of Samples. After the two sections of a tube are transferred to small vials, pipet 2.00 mL of reagent-grade water into the vial containing the sorbing section and 2.00 mL into the vial containing the backup layer. Cap each vial immediately after the water has been added. Extract the sealed sorbent samples by ultrasonification for 30 min at room temperature.

8.3.3 Operating Conditions for the Ion Chromatograph

- Eluent: 1.5 mM $NaHCO_3$.
- Flow rate: 138 mL/h.
- Sample loop volume: 0.5 mL.
- Precolumn: 3 mm i.d. by 150 mm long.

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- Separator columns in tandem: 3 mm i.d. by 250 mm long,
  3 mm i.d. by 500 mm long.

- Suppressor column: 6 mm i.d. by 250 mm long.

8.3.4 Injection: First, draw about 1 mL of a sample extract or standard through a 13-mm Teflon filter into a 3-cc syringe. Flush the sample loop with about 0.5 mL of the sample extract or standard; then inject 0.5 mL of filtered extract or standard into the ion chromatograph. A duplicate determination can be made by injecting a second 0.5-mL aliquot. Rinse the sample loop with 1 to 2 mL of water between the determinations of separate samples; do not rinse the loop between duplicate injections.

8.3.5 Measurement of Peak Height. Multiply the peak height by the attenuator setting necessary to keep the peak on scale. Determine the apparent concentration from a standard curve prepared as discussed in Section 9. If the peak height indicates an apparent concentration above 40 µg/mL, dilute the sample solution to 10-40 µg/mL for reanalysis.

8.3.6 At the end of each workday, inject six to ten 0.5-mL aliquots of 0.1 M $NaHCO_3$ to remove heavier inorganic anions such as nitrate, phosphate, and especially sulfate from the separator columns.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of silica gel. Also, for a given batch of silica gel the desorption efficiency may vary with the weight of contaminant adsorbed. (The silica gel used for the study of this method gave a desorption efficiency of 0.996 with a relative standard deviation of 1.0% for a loading of 1 µg of monochloroacetic acid on a 100-mg bed of sorbent material.)

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve monochloroacetic acid in reagent-grade water to give stock solutions with concentrations such that 1.0 to 80 µg of monochloroacetic acid will be injected onto the sorbent in no more than 5 µL of a stock solution. Place silica gel in an amount equivalent to that found in the larger section of the tube (100 mg) in a small vial and cap the vial. Inject an aliquot of the appropriate stock solution into the vial. Allow each vial to stand overnight to ensure complete adsorption of

monochloroacetic acid onto the silica gel. Prepare standards by injecting an identical amount of monochloroacetic solution into 2.00 mL of reagent-grade water. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of monochloroacetic acid found in a sample versus the desorption efficiency.

9. Calibration and Standardization

To make a stock standard solution, add 10 g of monochloroacetic acid to 100 mL of reagent-grade water. By serial dilution with reagent-grade water, prepare a series of working standards varying in concentration over the range of 0.5 to 40 µg/mL. Follow the dilution scheme presented below.

Initial concn	Aliquot volume, mL	Final diluted volume, mL	Final concn
100 mg/mL	1	100	1 mg/mL
1 mg/mL	1	10	100 µg/mL
100 µg/mL	1	100	1 µg/mL
100 µg/mL	1	10	10 µg/mL
100 µg/mL	2	10	20 µg/mL
100 µg/mL	4	10	40 µg/mL
100 µg/mL	5	10	50 µg/mL
50 µg/mL	1	10	5 µg/mL
50 µg/mL	1	100	0.5 µg/mL

Analyze the standard solutions under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve plot the concentration of the standards in µg/2 mL (or µg/sample) versus peak height. To ensure accurate analyses, determine standards at concentrations about 25% above and below the apparent sample concentrations.

10. Calculations

10.1 Read the sample weight in µg from the standard curve.

10.2 Blank corrections are not expected to be necessary but, if the analysis shows a blank correction is needed, make the correction as follows:

$$W_F = W_s - W_b$$

where: W_F = corrected amount (µg) on the front section of the silica gel tube
W_S = amount (µg) found on the front section of the silica gel tube
W_b = amount (µg) found on the front section of the blank silica gel tube

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (µg) in the front section
W_F = amount (µg) after blank correction
D = desorption efficiency corresponding to the weight, W_F.

Calculate the corrected amount on the backup section, M_B, similarly.

10.4 Express the concentration, C, of monochloroacetic acid in the air sampled in mg/m^3, which is numerically equal to µg/L.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = corrected amount (µg) of monochloroacetic acid found on front section
M_B = corrected amount (µg) of monochloroacetic acid found on backup section
V = volume (L) of air sampled.

10.5 If desired, the results may be expressed in ppm by volume at 25°C (298 K) and 760 torr.

$$C(ppm) = C(\mu g/L) \times \frac{24.45}{94.50} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled
T = temperature (°C) of air sampled
24.45 = molecular volume (L/mol) at 25°C and 760 torr
94.50 = molecular weight of monochloroacetic acid.

11. References

11.1 Dillon, H. K.; Mason, D. W.; Boyd, K. W. "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, Alabama.

11.2 McCullough, P. R.; Worley, J. W. "Sampling of Chloroacetyl Chloride in Air on Solid Support and Determination by Ion Chromatography". Anal. Chem. 1979, 51(8), 1120-2.

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NIOSH Contract No. 210-78-0012

BISPHENOL A* AND DIGLYCIDYL ETHER OF BISPHENOL A**

Measurement Support Branch

Analytical Method

Analyte:	Bisphenol A (BPA), Diglycidyl Ether of Bisphenol A (DGEBA)	Method No.:	P&CAM 333
		Range:	0.441-1.77 mg/m^3 (BPA) 0.441-1.78 mg/m^3 (DGEBA)
Matrix:	Air		
		Precision:	0.018 (BPA) 0.027 (DGEBA) (analytical)
Procedure:	Filter collection, acetonitrile extraction, HPLC		
Date Issued:	8/29/80		
Date Revised:		Classification:	D (Operational)

1. Synopsis

A known volume of air is drawn through a glass fiber filter to collect BPA and DGEBA (as particulate) from the air. The exposed filter is then transferred to a screw cap vial and extracted with acetonitrile. An aliquot of this solution is injected into a high performance liquid chromatograph (HPLC). Peak areas are determined and compared with calibration curves derived from peak areas obtained from injections of standard solutions.

2. Working Range, Sensitivity and Detection Limit

2.1 The probable useful analytical range of this method is 0.4-511 µg BPA and 0.6-513 µg DGEBA per sample. However, the method has been evaluated for the 127-511 µg per sample or 0.551-1.77 mg/m^3. The air concentration range is based on a 288-L air sample. Samples with levels greater than 511 µg can be analyzed by increasing the volume of the extraction solvent or by decreasing the sensitivity setting of the HPLC detector or the quantity of the aliquot injected into the HPLC.

2.2 The detection limits for BPA and DGEBA by this method are 0.2 and 0.3 µg per filter respectively when the filter is extracted with 2-mL of acetonitrile and a 50-µL aliquot is injected into the HPLC.

3. Interferences

3.1 Any compound collected on the filter which has the same retention time as either BPA or DGEBA, under the operating conditions of this method, may interfere with the analysis and may be mistaken for the

*4,4'-Isopropylidenediphenol

**2,2-Bis[4-(2',3'-epoxypropoxy) phenyl]propane

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analyte. By altering the composition of the mobile phase, a separation of BPA and DGEBA from the interfering material might be obtained.

3.2 If compounds other than BPA or DGEBA are known or suspected to be present in the atmosphere sampled, information regarding their identities should be transmitted with the samples to the laboratory.

3.3 If filter media other than the glass fiber filter are used for sample collection, materials may be extracted from the filter which will interfere with the analysis.

4. Precision and Accuracy

4.1 The relative standard deviation for the analytical method in the range of 127-511 µg /filter is 0.018 for BPA and 0.027 for DGEBA.

4.2 Bisphenol A recovery is 99.5% based on eighteen fortified glass fiber filters, six replicates at each of three loading levels: 127, 247, and 511 µg bisphenol A per sample.

4.3 DGEBA recovery is 99.3% based on eighteen fortified glass fiber filters, six replicates at each of three loading levels: 127, 250, and 513 µg DGEBA per sample.

4.4 The collection efficiencies for BPA and DGEBA as particulate by glass fiber filters have not been determined.

5. Advantages and Disadvantages

5.1 An advantage of the method is the specificity of the HPLC procedure in the absence of recalcitrant interferences.

5.2 A disadvantage related to the analysis of a large number of samples by this method is the relatively high cost of UV-grade acetonitrile.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 The sampler system consists of:

A filter holder for a 37-mm filter, Millipore or equivalent.

Glass fiber filter, 37-mm diameter, Gelman type A, or equivalent.

Cellulose backup pad, 37-mm diameter, Millipore or equivalent.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate is needed. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 HPLC and Accessories

6.2.1 High performance liquid chromatograph (HPLC) equipped with a variable wavelength ultraviolet detector.

6.2.2 A prepacked octadecyl silane reverse phase column, 0.63-cm i.d. by 30-cm long, Waters Associates μBondapack C_{18}, or equivalent.

6.2.3 Potentiometric strip chart recorder, 10-mV.

6.2.4 An electronic integrator if desired.

6.3 Glassware

6.3.1 A 100-μL glass syringe for injection of the samples.

6.3.2 Screw capped vials, 5-mL, with teflon-lined caps.

6.3.3 Pipettes and volumetric flasks of appropriate sizes for the preparation of standards.

6.3.4 Millipore all-glass filter apparatus, 47-mm, or equivalent.

6.4 Miscellaneous Apparatus

6.4.1 Analytical balance, Mettler H2OT or equivalent.

6.4.2 Ultrasonic cleaner, Mettler Electronics Corp., or equivalent.

6.4.3 Swinney Filter, Millipore xx3001200 or equivalent.

7. Reagents

7.1 Acetonitrile, distilled in glass, UV-grade (Burdick and Jackson Laboratories, Muskegon, Mich., or equivalent).

7.2 4,4'-Isopropylidenediphenol (bisphenol A) for the preparation of standards.

7.3 2,2-Bis[4-(2',3'-epoxypropoxy)phenyl]propane, the diglycidyl ether of bisphenol A for preparation of standards.

7.4 Water, deionized, filtered (Milli-Q or equivalent).

8. Procedure

8.1 Cleaning of Equipment. Wash all glassware used for the analysis with detergent; rinse with distilled water and dry completely.

8.2 Collection of Air Samples

8.2.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge

of the filter. The glass fiber filter is held in place by a cellulose backup pad, and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.2.2 Clip the cassette to the worker's lapel. Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.2.3 A sample size of approximately 288 liters is recommended. Sample at a flow rate of 1.6 liters per minute. The flow rate should be known with an accuracy within ± 5%.

8.2.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy particulate loading, by the presence of oil mists, or by other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.2.5 Terminate sampling after the predetermined time and note sample flow rate, collection time, and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.2.6 Following collection, the sample cassette should be firmly sealed with the plugs in both the inlet and outlet ends.

8.2.7 Carefully record sample identity and all relevant sample data.

8.2.8 Blank. With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same procedures as the samples, except that no air is drawn through it. Label this as a blank.

8.2.9 Shipping. The filter cassettes should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the glass fiber filter from the sampler and place in a 5-mL screw cap vial. Add 2-mL of acetonitrile and cap the vial. Place the sample in an ultrasonic cleaner for 20 minutes (or shake for 5 minutes in a vortex mixer). Filter each sample through a 0.5-μm Millipore Fluoropore filter or equivalent, before injection. Blanks and spiked standards (See Section 9.2) are treated in the same manner.

8.3.2 Solvent Preparation. Acetonitrile should be filtered through a Millipore FHUP filter in the 47-mm all-glass filter apparatus. Water should be filtered using an HAWP filter (or equivalent).

8.3.3 Liquid Chromatography Conditions. The typical operating conditions for the liquid chromatograph are as follows:

Solvent A is 60% acetonitrile, 40% water (v/v).

Solvent B is 100% acetonitrile

Total solvent flow rate through the column is constant at 1.0 mL/min.

The UV-detector wavelength is set at 230-nm. The sensitivity setting is adjusted to give a full scale deflection for the highest standard.

A linear solvent gradient from 0% solvent B to 100% solvent B over a 30 minute period is run.

8.3.4 Injection of the Sample. Inject 50-µL of the sample using the 100-µL glass syringe. It may be necessary to decrease the volume of sample injected to keep the analyte peak on scale.

8.3.5 Measurement of Peak Area. Measure the area of the sample peak manually or with an electronic integrator.

9. Calibration and Standardization

9.1 Stock solutions of BPA and DGEBA are prepared by accurately weighing (approximately) 100-mg of each analyte in a 10-mL volumetric flask. The flask is diluted to the mark with acetonitrile. The stock solution is diluted 1:10 and 1:100 for use in preparing standards.

9.2 This method was evaluated, and the calibration curve found to be linear by spiking glass fiber filters over the following concentration range:

Low concentration	5-µL of 1:100 stock solution
High concentration	22-µL of 1:10 stock solution

The analyst should prepare standards by spiking six filters with the stock solutions as follows:

Amount	Dilution
5 - µL	1:100
10 - µL	1:100
20 - µL	1:100
5 - µL	1:10
10 - µL	1:10
20 - µL	1:10

9.3 Each spiked filter is extracted in 2-mL of acetonitrile along with the samples. The standards must be analyzed during the same time period as the field samples and under the same chromatographic conditions. This procedure will minimize the effect of day-to-day variations of the detector response or of the composition of the mobile phase.

9.4 A standard curve is generated by plotting the quantity of BPA and DGEBA in each standard versus the peak area obtained from the chromatogram or electronic integrator. Using the chromatographic conditions specified in 8.3.3, BPA elutes in about 4.5 minutes and DGEBA in about 9.0 minutes.

10. Calculations

10.1 The amount of BPA or DGEBA corresponding to the peak area in each particular sample is obtained from the standard curve. The quantity in ng is adjusted by a correction factor (to one mL) to account for the volume of each sample injected, thus giving the concentration of each sample in ng/mL. The total sample weight can be obtained by multiplying by the extraction volume which is 2 mL.

10.2 If a peak with the same retention time as BPA or DGEBA is present in the blank, it may not be necessary to subtract it from the samples. The standards are prepared in the same manner as the samples and will also contain the blank amount.

10.3 If desired, the concentration of BPA or DGEBA in the air sampled, C, may be expressed in $\mu g/m^3$

$$C = \frac{W}{V_s} \div 1000$$

where: V_s = volume (liter) of air sampled

W = weight (μg) of BPA or DGEBA in the sample

11. References

11.1 Szap, P., I. Kesse, and J. Klapp, The Analysis of Bisphenol A by High Pressure Liquid Chromatography. J. Liq. Chromatogr., 1, 89 (1978)

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PENTACHLOROETHANE

Measurements Research Branch

Analytical Method

Analyte:	Pentachloroethane	Method No.:	P&CAM 335
Matrix:	Air	Range:	14 to 5,370 μg/m^3 in 3 L of air
Procedure:	Adsorption on Porapak R,® desorption with hexane, GC/ECD	Precision:	0.075
Date Issued:	8/29/80		
Date Revised:		Classification:	B (Accepted)

1. Synopsis

   1.1 A known volume of air is drawn through a tube containing Porapak R to trap the pentachloroethane vapor present.

   1.2 The Porapak R in the tube is transferred to a small vial where the pentachloroethane is desorbed with hexane.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph equipped with an electron capture detector (ECD).

   1.4 The height of the resulting peak is determined and compared with the peak heights obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The sampling and analytical method was tested with nominal sample loadings of about 40 to 16,900 ng of pentachloroethane per sorbent tube. The samples were collected from atmospheres containing pentachloroethane in the range of 14 to 5,370 μg/m^3 at 25 to 26 °C and at a relative humidity of 80% or greater.

   2.2 The slope of the analytical calibration curve was typically 0.2 pA/pg when peak heights were plotted as a function of the quantities of pentachloroethane injected.

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2.3 The lowest analytically quantifiable level (LAQL) for this method was found to be about 40 ng of pentachloroethane per sorbent sample. (Sorbent samples were extracted with 2 mL of the solvent.) The instrumental detection limit was estimated to be about 4 ng of pentachloroethane in 2 mL of the extraction solvent; the relative standard deviation of replicate determinations at this level was 5%.

3. Interferences

3.1 The gas chromatographic operating conditions described below in Section 8.3.3 were found to separate the following conpounds from pentachloroethane: trichloroethylene; tetrachloroethylene; 1,1,2,2-tetrachloroethane; hexachloroethane; and four of the isomers of tetrachloropropane (1,1,1,2-; 1,1,1,3-; 1,1,2,2-; and 1,1,2,3-tetrachloropropane). One isomer, 1,2,2,3-tetrachloropropane, could not be separated from the analyte; another, 1,1,3,3-tetrachloropropane, was not tested. Large concentrations of 1,1,2,2-tetrachloroethane may obscure the analyte peak.

3.2 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of pentachloroethane.

3.3 Any substance that has the same retention time as pentachloroethane with the gas chromatographic operating conditions described in this method is an interferent. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, carrier flow, detector, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for replicate measurements was 7.5% for seventeen sorbent samples challenged with 14 to 5,370 $\mu g/m^3$ of pentachloroethane in air. The pooled relative standard deviation for the analytical method was 1.9% for seventeen sorbent samples spiked with 40.3 to 40,300 ng of pentachloroethane.

4.2 A gas sampling loop coupled to a gas chromatograph with an ECD was used to independently monitor the concentration of pentachloroethane in test atmospheres sampled for evaluation of the method. The determinations with sorbent sampling gave values averaging 100% of those found with the monitor over the range of the method.

4.3 The 5% breakthrough volume of the sorbent tube was found to be about 15 L with sampling rates of 0.14 to 0.20 L/min at concentrations near 100 mg/m^3, at a relative humidity greater than 80%, and at a sampling temperature of 40 °C.

4.4 Samples of pentachloroethane (about 40-ng quantities) sorbed from the test atmospheres with the sorbent tubes were found to be stable at 25 °C for 7 d and an additional 21 d if stored at 0 °C. These samples were stored in the dark.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential interferences are avoided by the gas chromatographic procedure. The samples are analyzed by means of a quick instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the sorbent tube. When the sample value obtained for the backup section of the tube exceeds 20% of that found on the front section, the possibility of sample loss exists.

5.3 Another disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of accurate performance (±5%) at 0.05 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Sorbent tubes: Pyrex tubes, 7 cm long with a 6 mm o.d. and a 4 mm i.d., flame sealed at both ends. Each tube contains two sections of 50/80 mesh Porapak R—a 70-mg sorbing section and a 35-mg backup section. The Porapak R is precleaned by Soxhlet extraction (4 h with a 4:1 acetone/methanol mixture and 4 h with hexane) and then dried under vacuum at 75 °C overnight.

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The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated with a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 5 in. H_2O (1.2 kPa) at a sampling rate of 0.2 L/min. This type of tube is available from SKC, Inc. (Eighty-Four, PA); its catalog number is 226-59-04.

6.3 Gas chromatograph equipped with a ^{63}Ni electron capture detector.

6.4 Nickel GC column, 2 mm i.d. by 2 m long, packed with 3% OV-17 on 100/120-mesh Chromsorb W HP.

6.5 Vials, 2 mL, with serum caps containing Teflon-lined silicone rubber septa.

6.6 Microliter syringes, 10-μL and convenient sizes for making dilutions.

6.7 Pipets, convenient sizes for making dilutions.

6.8 Ultrasonic bath.

7. Reagents

7.1 Hexane, "distilled in glass".

7.2 Pentachloroethane, 96% pure (Aldrich Chemical Co.).

7.3 A mixture of 5% methane, 95% argon (or other appropriate carrier and purge gas) for the electron capture detector.

8. Procedure

8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, distilled water, acetone, and hexane (in that order).

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break the ends of the tubes to provide an opening that is at least 2 mm (one-half the internal diameter of the tube).

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8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of sorbent is the backup layer and is positioned nearer the sampling pump.

8.2.3 Place the sorbent tube in a vertical position during sampling to prevent channeling through the tube.

8.2.4 Air being sampling should not be passed through any hose or tubing before entering the tube.

8.2.5 Sample at 0.05 to 0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 10 L.

8.2.6 Record the temperature and pressure of the air being sampled.

8.2.7 Immediately after sampling, seal the two ends of the tube with Teflon tape and plastic caps. Store the tube in the dark.

8.2.8 For every ten samples taken, process one sorbent tube not exposed to pentachloroethane in the same manner as the samples (break, seal, and transport). Do not sample air through this tube. The tube should be labeled as a blank.

8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

8.2.10 Ship nine to twelve unopened sorbent tubes so that desorption efficiency studies can be performed on the same lot of Porapak R used for sampling.

8.2.11 Log and immediately refrigerate samples when they are received at the laboratory. Store the tubes during refrigeration in an airtight container to prevent contamination by the diffusion of chemicals through the plastic caps.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the sorbent tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer the sorbing section to a 2-mL vial and the backup section to a 1-mL vial. Discard the metal spring. Place the glass wool plug into the vial containing the sorbing section and the foam plugs into the vial with the backup section.

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8.3.2 Desorption of samples: After the two sections of a tube are transferred to small vials, pipet 2.00 mL of the solvent into the 2-mL vial and 1.00 mL of solvent into the 1-mL vial. Crimp a serum cap into place on each vial immediately after the solvent has been added. Extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature.

8.3.3 GC Conditions

- Carrier gas, 30 mL/min.
- Detector purge gas, 80 mL/min.
- Injection port temperature, 240 °C.
- Column temperature 70 °C.
- Detector temperature, 250 °C.
- Under these conditions, the analyte elutes in 3.5 min.

8.3.4 Injection. Inject a 5-µL aliquot of a sample extract or standard into the gas chromatograph by the solvent flush technique. Use 1 µL of hexane as the solvent flush. Maintain a 1-µL air gas between the solvent flush and the 5-µL aliquot.

8.3.5 Measurement of Peak Height. The product of peak height and attenuator setting is linear over the concentration range of about 2 to 270 ng/mL. The peak height is multiplied by the attenuator setting necessary to keep the peak on scale. Results are read from a standard curve prepared as discussed in Section 9. If peak heights indicate an apparent concentration above 270 ng/mL, dilute the sample solution appropriately for reanalysis.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of Porapak R. Also for a given batch of sorbent, the desorption efficiency may vary with the weight of contaminant adsorbed. In laboratory tests, Porapak R (Lot No. 828) gave an average desorption efficiency of 0.980 with a pooled RSD of 1.9% for loadings of pentachloroethane in the range of 40.3 to 40,300 ng.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third should be an intermediate level. Dissolve the analyte in hexane to prepare stock solutions. The concentrations should be such that no more than 5 μL of a stock solution will be injected onto the sorbent. Inject an aliquot of the appropriate stock solution into the sorbing section of a sorbent tube while sampling 3 L of analyte-free air through the tube at 0.2 L/min. Cap the tube and store it overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 2.00 mL of the solvent. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of pentachloroethane found in a sample versus the desorption efficiency.

9. **Calibration** and Standardization

9.1 **Prepare** a stock standard solution by diluting 5 μL (8.4 mg) of **pentachloroethane** to 100 mL with hexane. By serial dilutions **with** the solvent, prepare a series of working standards varying **in** concentration over the range of 2 to 270 ng/mL. Follow the **dilution** shceme presented below:

Initial concn, ng/mL	Aliquot volume, mL	Final diluted volume, mL	Final concn, ng/mL
84,000	8	100	6,720
6,720	4	100	269
6,720	2	100	134
134	5	10	67.0
67	5	10	33.5
33.5	5	10	16.8
16.8	1	10	1.68

The standard solutions are stable indefinitely at room temperature if kept in airtight containers.

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9.2 Determine the working standards under the same GC conditions and during the same time period as the samples. Alternate the determination of standards and samples. Establish a standard curve by plotting the concentrations of the standards in ng/mL versus peak heights.

10. Calculations

10.1 Determine the sample weight in ng from the standard curve.

10.2 Blank corrections are not expected to be necessary, but if the analysis shows a blank correction is needed, the correction is:

$$W_F = W_s - W_b$$

where: W_F = corrected amount (ng) on the front section of the sorbent tube.

W_s = amount (ng) found on the front section of the sorbent tube.

W_b = amount (ng) found on the front section of the blank sorbent tube.

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (ng) in the front section.

W_F = amount (ng) after blank correction.

D = desorption efficiency corresponding to the weight W_F.

Calculate the corrected amount on the backup section, M_B, similarly.

10.4 Express the concentration, C, of pentachloroethane in the air sampled in $\mu g/m^3$, which is numerically equal to ng/L.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = corrected amount (ng) of pentachloroethane found on front section.

M_B = corrected amount (ng) of pentachloroethane found on backup section.

V = volume (L) of air sampled.

10.5 If desired, the results may be expressed in ppb at 25 °C (298 K) and 760 torr.

$$C(ppb) = C(ng/L) \times \frac{24.45}{202.3} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.

T = temperature (°C) of air sampled.

24.45 = molar volume (L/mol) at 25 °C and 760 torr.

202.3 = molecular weight (g/mol) of pentachloroethane.

11. References

11.1 "Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for Pentachloroethane"; NIOSH Contract No. 210-78-0012; Southern Research Institute, Birmingham, Alabama, 1980.

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NIOSH Contract No. 210-78-0012

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TEPP

Measurement Research Branch

Analytical Method

Analyte:	TEPP (Tetraethyl Pyrophosphate)	Method No.:	P&CAM 336
Matrix:	Air	Range:	0.025-0.102 mg/cu m
Procedure:	Adsorption on Chromosorb 102, desorption with toluene, GC-FPD.	Precision ($\overline{CV}_T$):	0.086
		Classification:	E (Proposed)
Date Issued:	8/31/79		
Date Revised:			

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1. Synopsis

   1.1 A known volume of air is drawn through a Chromosorb 102 tube to trap the organic vapors present. The sampling tube consists of two Chromosorb 102 tubes connected in series. This arrangement is necessary to prevent migration during storage.

   1.2 The Chromosorb 102 in each tube is transferred to a vial and the TEPP (tetraethyl pyrophosphate) is desorbed with a solution of toluene and analyzed by gas chromatography.

   1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

   2.1 This method was evaluated over the range of 0.0258-0.102 mg/cu m at an atmospheric temperature of 21.5°C and atmospheric pressure of 735.3 mm Hg using a 48-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at 90% relative humidity when sampling a test atmosphere at 2 times the OSHA standard (OSHA standard 0.05 mg/cu m - skin). This method is capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the absorptive capacity of the sorbent tube. This capacity varies with the concentration of TEPP and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (100-mg sorbent) reaches 5% of the concentration in the test gas mixture. When an atmosphere at

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90% relative humidity containing 0.40 mg/cu m of TEPP was sampled at 0.18 liter per minute, no breakthrough was observed after 300 minutes, at which time this test was concluded. The capacity of the Chromosorb 102 tube is at least 25 ug under the conditions of this breakthough experiment.

2.3 The detection limit of this method was not rigorously determined but is estimated to be at least 0.1 µg/mL.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, solvent composition, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling metnod in the range of 0.02578 to 0.1019 mg/cu m was 0.0863. This value corresponds to a 0.00452 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 The accuracy of this method has not been determined. The desorption efficiency was determined to be 1.068 for a collector loading of 1.18 µg. In storage stability studies the mean of generated samples analyzed after seven days was 103.5% of the mean of samples analyzed immediately after collection. Experiments performed in these studies are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 When the sample value obtained for the backup sorbent tube exceeds 25% of that found on the front tube, the possibility of sample loss exists.

5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

5.4 The accuracy of the method has not yet been determined.

6. Apparatus

6.1 Sampling Equipment

6.1.1 Sampling Pump. A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate.

6.1.2 Sampling Tubes. Two separate sampling tubes are recommended. The sampling tube consists of a glass tube, 7-cm long with a 6-mm O.D. and 4-mm I.D., packed with 20/40 mesh Chromosorb 102. Before use the Chromosorb must be extracted with 50/50 methanol/acetone solution in a Soxhlet extractor for two hours and then dried at 115°C for one hour in a vacuum oven. The front adsorbing tube contains 100 mg of Chromosorb 102 and the backup tube contains 50 mg. A plug of silylated glass wool is placed in front of and behind the adsorbing section. The sampling tubes are connected with a small piece of tygon tubing. The pressure drop across the two tubes in series must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.2 Gas chromatograph equipped with a flame photometric detector and phosphorus filter.

6.3 Column, 6-ft x 1/4-in O.D. glass, Superpak 20M (Analabs, Inc.).

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Sample vials, 2-mL with Teflon-lined caps.

6.6 Microliter syringes, 10- and 500-microliter and other convenient sizes for preparing standards.

6.7 Pipettes, 1- and 5-mL, both delivery type.

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7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Toluene.

7.2 TEPP (Tetraethyl pyrophosphate), purified.

7.3 Tripropyl phosphate, reagent grade, or other suitable internal standard. The appropriate concentration of the internal standard is prepared in toluene.

7.4 TEPP stock solution, 1.18 mg/mL. Prepare by adding 10 µL of TEPP to 100 mL of toluene. If the internal standard method is to be used, use internal standard solution instead of toluene.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sampling tube in the line; the tube is described in Section 6.1.2. This will minimize the errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, remove the caps from the two ends of the front and backup sorbent tubes.

8.3.2 The tube containing 50 mg of Chromosorb 102 is used as a backup and should be positioned nearest the sampling pump.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the sorbent tube.

8.3.5 A sample size of 48 liters is recommended. Sample at an approximate flow rate of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 Record the ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 The sorbent tubes should be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples, submit a sorbent tube which has been handled in the same manner as the sample tubes (uncover, seal and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Unused, capped sorbent tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency may vary from one batch of Chromosorb 102 to another. Record the batch number of the Chromosorb 102 used.

8.3.10 Capped sorbent tubes should be packed tightly and padded before they are shipped to prevent tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each sorbent tube is scored with a file in front of the section of Chromosorb 102 and broken open. The glass wool is removed and discarded. The Chromosorb 102, 100 mg or 50 mg, is transferred to a 2-mL vial. The two tubes are analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 1.0 mL of toluene is pipetted into each 2-mL vial. The vial is capped immediately after solvent addition and then agitated. Desorption should be done for 60 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 mL/min (50 psig) nitrogen carrier gas flow
2. 20 mL/min (50 psig) hydrogen gas flow to detector
3. 40 mL/min (50 psig) air flow to detector
4. 200°C injector temperature
5. 200°C manifold temperature (detector)
6. 115°C column temperature

The solvent front appears after approximately 20 seconds. A retention time of approximately 120 seconds is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The retention time

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for the internal standard, tripropyl phosphate is approximately 300 seconds.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Chromosorb 102 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of cleaned Chromosorb 102 used for sample collection.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of TEPP found in the samples. The desorption efficiency must be determined for each concentration level of TEPP found in the samples analyzed.

The analytical samples are prepared as follows: 100 mg Chromosorb 102 is measured into a 2-mL vial. This Chromosorb 102 must be from the same batch as that used in obtaining the samples. A known amount of TEPP is injected directly into the Chromosorb 102 by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µL aliquot is used to prepare the analytical samples.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5, 1 and 2X the OSHA standard) were prepared by adding an amount of TEPP equivalent to that present in a 48-liter sample at

the selected level. This reqired the addition of 1, 2, and 4 µL of TEPP solution (1.18 mg/mL) to the Chromosorb 102 for 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand at least overnight to assure complete adsorption of the analyte onto the Chromosorb 102. A parallel blank tube was treated in the same manner except that no sample was added to it.

The procedure described can be used to prepare the analytical samples which are analyzed to determine desorption efficiency over the concentration range of interest.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 1.0 mL of toluene.

The desorption efficiency (D.E.) equals the weight in µg recovered from the Chromosorb 102 divided by the weight in µg added to the Chromosorb 102, or

$$D.E. = \frac{\text{Weight (µg) recovered - Blank (µg)}}{\text{Weight (µg) added}}$$

The desorption efficiency may be dependent on the amount of TEPP collected on the Chromosorb 102. Plot the desorption efficiency versus weight of TEPP found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

9.1 A series of standards varying in concentration over the range corresponding to 48-liter collections at 0.1-3 times the OSHA standard is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. This is done in order to minimize variations in FPD response. It is convenient to express concentration of standards in terms of µg per 1.0 mL since the samples are desorbed in 1.0 mL of toluene. A calibration curve is established by plotting peak area versus concentration in µg per 1.0 mL.

9.2 From the stock standard solution (Section 7.4) prepare at least five working standards to cover the concentration range of 0.24-7.2 µg/mL. Transfer two 60-µL aliquots of the stock solution to 10 mL volumetric flasks and dilute to 10 mL with toluene.

9.3 For the internal standard method use toluene containing a predetermined concentration of the internal standard. The internal standard concentration should fall within the linear range

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instrumental response. The area ratio of analyte to internal is plotted against the analyte concentration expressed in µg/mL.

10. Calculations

10.1 Read the weight, in µg, of TEPP corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 1.0 mL and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in front (100-mg) sample tube

µg blank = µg found in front (100-mg) blank tube

10.3 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front tube.

Divide the weight found in the front tube by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Weight (Front Tube)}}{\text{D.E.}}$$

This procedure is followed for the backup (50-mg) tube.

10.4 Add the corrected amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sample flow rate

t = sampling time

P_1 = atmospheric pressure during calibration of sampling pump (mm Hg)

P_2 = atmospheric pressure of air during sampling (mm Hg)

T_1 = ambient temperature during calibration of sampling pump (°K)

T_2 = ambient temperature of air sampled (°K).

10.6 The concentration of TEPP in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.4)}}{\text{Air Volume Sampled (liters)}}$$

10.7 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg)

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{290.2} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

290.2 = molecular weight of TEPP

760 = standard pressure (mm Hg)

298 = standard temperature (°K).

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for TEPP, No. P&CAM 336, prepared under NIOSH Contract No. 210-76-0123.

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NIOSH Contract No. 210-76-0123

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SCP METHODS

S43-i

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Methyl Methacrylate

Analyte:	Methyl Methacrylate	Method No.:	S43
Matrix:	Air	Range:	193 - 725 mg/cu m
OSHA Standard:	100 ppm (410 mg/cu m)	Precision ($\overline{CV}_T$):	0.063
Procedure:	Adsorption on XAD-2, desorption with carbon disulfide, GC/FID	Validation Date:	7/6/79

1. Synopsis

1.1 A known volume of air is drawn through a tube containing XAD-2 resin to trap the organic vapors present.

1.2 The XAD-2 is transferred to a vial and the methyl methacrylate is desorbed with carbon disulfide. An aliquot of this sample solution is injected into a gas chromatograph equipped with a flame ionization detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 193-725 mg/cu m at an atmospheric temperature of 20°C-24°C and an atmospheric pressure of 762 mm Hg using a 3-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the method depends on the adsorptive capacity of the XAD-2. This capacity may vary with the concentration of methyl methacrylate in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 400 mg XAD-2) reaches 5% of the concentration in the test gas mixture. Five percent breakthrough occurred after 116 minutes at a sampling rate of 0.0551 liter per minute at a relative humidity of 90% and at a concentration of 786 mg/cu m of methyl methacrylate.

2.3 The detection limit of the method was not determined.

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3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 193-725 mg/cu m was 0.0628, This value corresponds to a 25.75 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 In validation experiments this method was found to be capable of coming within ±25% of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1 and 2 times the OSHA standard were 2.7% higher than the dynamically generated test concentrations (n = 17). The desorption efficiency was determined to be 96.3% for a collector loading of 0.564 mg. In the storage stability studies, the mean of samples analyzed after seven days was within 3.6% of the mean of samples analyzed after one day. Experiments performed in the study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling for 60 minutes whose flow is accurate to within ±5% at the recommended flow rate.

6.1.2 Sampling Tubes. The sampling train consists of an XAD-2 tube (20/50 mesh). The tubes are glass tubes with both ends flame-sealed, 7-cm long with an 8-mm O.D. and a 6-mm I.D. The XAD-2 used must be prewashed as in section 7.5. The front section contains 400 mg XAD-2; the backup section, 200 mg. A plug of silylated glass wool is placed at each end of the sorbent tube and is used to separate the two sections. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.2 Gas chromatograph with a flame ionization detector.

6.3 Column, 20-ft x 1/8-in stainless steel, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Microliter syringes 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots.

6.6 Pipettes, 2-mL, delivery type.

6.7 Volumetric flasks, 25 mL or other convenient sizes for making standard solutions.

7. Reagents

Wherever possible, reagents used should be ACS reagent grade or better.

7.1 Methyl methacrylate, chromatographic quality.

7.2 Carbon disulfide, reagent grade.

7.3 Undecane, 99% or other suitable internal standard. The appropriate solution of the internal standard is prepared in carbon disulfide.

7.4 Stock standard solution, 0.282 mg/mL methyl methacrylate. Prepare by adding 3 mL methyl methacrylate to 10 mL volumetric flask and diluting with carbon disulfide to 10 mL. If the internal standard method is used, use internal standard solution instead.

7.5. Pre-cleaned Resin. XAD-2 resin (20/50 mesh) can be obtained from Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Twenty-four hour extractions are then performed successively with water, methanol and

methylene chloride. Resin has been prepared in this manner using charges of about 700 grams of resin and 1.5 liters of each solution. The resin is dried in a fluidized bed using nitrogen gas at room temperature. The drying process is terminated when essentially no solvent is detected in the effluent. A final quality control check is performed by desorbing a portion of the resin and analyzing the resulting solution by gas chromatography. Residual solvent should be less than 1000 ppm in concentration. Finally, several washings with carbon disulfide are recommended to reduce possible interferences to a minimum when the sorbent is desorbed with this solvent. This can be done in a beaker of the appropriate volume. The resin is then air-dried.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3.1 Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes (3-mm).

8.3.2 The section containing 200 mg of XAD-2 is used as a backup and should be positioned nearest the sampling pump. The XAD-2 tube should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the XAD-2 tube.

8.3.4 A sample size of 3 liters is recommended. Sample at a known flow rate between 0.03 to 0.05 per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 Immediately after sampling the XAD-2 tube must be capped with the supplied plastic caps.

8.3.6 One of the XAD-2 tubes should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every ten samples.

8.3.7 Unused XAD-2 tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency may vary from one batch of XAD-2 to another. Record the batch number of the XAD-2 used.

8.3.8 Capped XAD-2 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each tube is scored with a file and broken open. The glass wool is removed and discarded. The front XAD-2 section tube is transferred to a 5-mL screw-cap sample vial. The separating section of glass wool is removed and discarded. The second, 200-mg section is transferred to another container and is analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 mL of carbon disulfide is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 mL of carbon disulfide containing a known amount of internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 mL/min (60 psig) nitrogen carrier gas flow
2. 30 mL/min (25 psig) hydrogen gas flow to detector
3. 300 mL/min (60 psig) air flow to detector
4. 220°C injector temperature
5. 230°C manifold temperature (detector)
6. 100°C column temperature

A retention time of approximately five minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately eight minutes.

8.4.4 Injection of Sample. A 2-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of XAD-2 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% for a loading equivalent to a collection at the OSHA standard level. If the desorption efficiency is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of methyl methacrylate found in the samples.

The analytical samples are prepared as follows: XAD-2 resin, equivalent to the amount in the front section (400-mg), is measured into a 5-mL screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of methyl methacrylate in carbon disulfide (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µL aliquot is used to prepare the analytical samples.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5, 1 and 2X the OSHA standard) were prepared by adding an amount of methyl methacrylate equivalent to a 3-liter sample at the selected level. A stock solution containing 282 milligrams of methyl methacrylate per milliliter of carbon disulfide was prepared. Two, four and eight microliter aliquots of the solution were added to the XAD-2 resin vials to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand overnight to assure complete adsorption of the analyte onto the resin. A parallel blank vial was treated in the same manner except that no sample was added to it.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 mL of carbon disulfide with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare calibration standards by using 2.0 mL of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the vial divided by the weight in mg added to the vial, or

$$D.E. = \frac{\text{Average Weight (mg) recovered - Blank (mg)}}{\text{Weight (mg) added}}$$

The desorption efficiency may be dependent on the amount of methyl methacrylate collected on the resin. Plot the desorption efficiency versus weight of methyl methacrylate found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standardization

9.1 A series of standards varying in concentration over the range corresponding to a 3-liter collection at 0.1 - 3 times the OSHA standard is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. This is done in order to minimize the effects of variations in FID response. It is convenient to express concentration of standards in terms of ng per 2 mL since the samples are desorbed in 2 mL of carbon disulfide. A calibration curve is established by plotting peak area versus concentration in mg/2 mL.

9.2 From the stock standard solution (Section 7.4) prepare at least five working standards to cover the range of 0.113-3.39 mg/2 mL. These are prepared by diluting 2-60 µL aliquots of the stock solution to 10 mL with carbon disulfide.

9.3 For the internal standard method, use carbon disulfide containing a predetermined amount of internal standard. The internal standard concentration used should be approximately 70% of the analyte concentration for a standard solution representing a 3-liter collection at twice the OSHA standard. The area ratio of the analyte to the internal standard is plotted against the analyte concentration in mg per 2.0 mL.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg per 2.0 mL and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample:

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in the sample vial
mg blank = mg found in blank vial

10.3 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the weight of the analyte found in the front section of the tube by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

A similar procedure is followed for the backup (200 mg) section.

10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump

using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{100.12} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
100.12 = molecular weight of methyl methacrylate
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Methyl Methacrylate, No. S43, prepared under NIOSH Contract No. 210-76-0123.

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Methyl Acetylene-Propadiene Mixture*

Analyte:	Methyl Acetylene-Propadiene Mixture	Method No.:	S85
Matrix:	Air	Range:	480-1990 ppm
OSHA Standard:	1000 ppm (1800 mg/cu m)	Precision ($\overline{CV}_T$):	0.048
Procedure:	Collection in gas sampling bag, flame ionization detection	Validation Date:	4/13/79

1. Synopsis

1.1 An air sample is pumped into a gas sampling bag with a personal sampling pump.

1.2 The MAPP content of the sample is determined as total hydrocarbon by flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 480-1990 ppm at an atmospheric temperature of 20°C and atmospheric pressure of 760 mm Hg using a 3-liter sample volume.

2.2 Under the instrumental conditions used in the validation study, a 0.5-mL injection of a 500 ppm MAPP standard resulted in a peak whose height was 70% of full scale on a 1-millivolt recorder. The amplifier of the gas chromatograph was set on range 10 and attenuation 4, and the recorder at attenuation 8.

2.3 The limit of detection is estimated at less than 10 ng MAPP. Using a 0.5-mL gas sampling loop, this corresponds to a level of approximately 11 ppm.

3. Interferences

3.1 When compounds other than MAPP are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

* MAPP

3.2 The sample is analyzed for total hydrocarbon content, and any substance which produces a response using the flame ionization detector will be an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 480-1990 ppm was 0.048. This value corresponds to a 48 ppm standard deviation at the OSHA standard. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit averaged 8.2% lower than the dynamically generated test concentrations (n = 18). Storage stability studies on samples collected from a test atmosphere at a concentration of 998 ppm indicated that collected samples are stable for at least 7 days. The mean of samples analyzed after 7 days were within 3.3% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is portable and involves no liquids. The samples in bags are analyzed by means of a quick instrumental method.

5.2 One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling or shipping. It is difficult to ship the samples by air.

5.3 The analytical method is specific only for total hydrocarbon content, and it is subject to interferences.

6. Apparatus

6.1 Personal Sampling Pump. A personal sampling pump capable of filling a gas sampling bag at approximately 0.05 liter/minute is required. Each personal pump should be calibrated to within ±5%. Although sample volume is not used to determine sample concentration, the pump should be calibrated to make certain that the collected sample represents a time-weighted average concentration and to avoid over filling the bags; i.e., a maximum sampling time can be determined based on the flow rate and sample volume which is less than 80% of the volume of the bag.

The personal sampling pump must be fitted with an outlet port so it is capable of filling a bag. To ensure a leak-free apparatus, adjust the pump so that it delivers at the proper flow rate, and attach the pump outlet to a water manometer with a short piece of flexible

tubing. Turn the pump on and observe the water level difference; it should be capable of pumping against a pressure of at least 30 cm of water. If it does not, the pump is incapable of filling the sampling bag and cannot be used.

6.2 Gas Sampling Bag. Five-liter capacity, five-layer sampling bags manufactured by Calibrated Instruments, Inc. (731 Saw Mill River Road, Ardsley, New York 10502) were found to be satisfactory for sample collection and storage for at least 7 days. This bag is fitted with a metal valve and hose bib. The valves used in validation studies were found to leak when in the open position. It is necessary to wrap the valve stem connection with Teflon tape or Parafilm to ensure a leak-free connection. For the preparation of calibration standards in the laboratory, Saran or Tedlar bags could be used.

Before sampling each bag should be analyzed as a "blank" just prior to use to ensure that no contamination is present.

6.3 Gas chromatograph, equipped with a flame ionization detector and 0.5-mL gas sampling loop.

6.4 Tubing (20 ft long x 1/8-in I.D. stainless steel) equipped with proper column fittings. No column packing is used in the method.

6.5 Area Integrator. An electronic integrator or some other suitable method for measuring peak areas.

6.6 Gas-tight Syringes. Convenient sizes for preparing standards.

6.7 Regulator for compressed air which is capable of metering gas at approximately 1 liter/minute. The gas line from the regulator should be equipped with a septum-tee for standards preparation.

6.8 Water Manometer.

6.9 Thermometer.

7. Reagents

7.1 MAPP, technical product.

7.3 Helium, purified.

7.3 Hydrogen, prepurified.

7.4 Air, filtered, compressed.

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8. Procedure

8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the valve and bleeding out the air sample. The use of a vacuum pump is recommended although this procedure can be carried out by manually flattening the bags. The bags are then flushed with air and evacuated. This procedure is repeated at least twice. Prior to use, background hydrocarbon content should be determined by the analytical method. If it is unacceptably high, the bags should be flushed again.

Bags should be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Check for any discernable leaks and any volume changes or slackening of the bag, especially along seams and in the valve stem, for at least a one-hour period.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, attach a small piece of Teflon tubing to the hose bib of the five-layer gas sampling bag. Rubber tubing should not be used.

8.2.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump. Make sure that all connections are tight and leak-free. The bag valve must be fully opened during sampling.

8.2.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required. No tubing is attached to the inlet of the pump.

8.2.4 A sample size of 3-4 liters is recommended. Sample at a flow rate of 0.05 liter/minute or less, but not less than 0.01 liter/minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.2.5 Set the flow rate as accurately as possible using the manufacturer's directions. Although the volume of sample collected is not used in determining the concentration, it is necessary to keep the volume to 80% or less of the bag's capacity. Observe the bag frequently to ensure that it is filling properly.

8.2.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation. Also record sampling time, flow rate, and type of sampling pump used.

8.2.7 The gas sampling bag should be labeled appropriately and sealed tightly.

8.2.8 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of their being punctured during shipping. Do not ship the bags by air, unless they are stored in a pressurized cabin.

8.3 Analysis of Samples

8.3.1 GC Conditions. The typical operating conditions for the gas chromatograph are:

25 mL/min hydrogen to detector
25 mL/min helium carrier gas flow
100 mL/min air to detector
125°C detector temperature
injector port and column at ambient conditions.

Note: The gas chromatograph is being used as a total hydrocarbon analyzer since the column is not packed.

8.3.2 Analysis. Attach the gas sampling bag to the sample loop of the gas chromatograph with a short piece of flexible tubing. Open the valve of the bag and fill the loop by using a vacuum pump or manually applying pressure to the sample bag. Allow the loop to attain atmospheric pressure, and inject the sample. One peak will elute in approximately one minute. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.3.3 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and the results are read from a standard curve as discussed in Section 9. Peak heights may also be used for quantitation.

9. Calibration and Standardization

9.1 It is recommended that the MAPP used as a standard be taken from a cylinder that is no more than 50% depleted. This is to assure the relative composition of the components in the mixture, since studies (Reference 3) have shown that the fraction of less volatile components may be abnormally high when 80% or more of the cylinder is depleted.

9.2 A series of standards, varying in concentration over the range of 0-3000 ppm is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in ppm versus peak area.

9.3 Completely evacuate and flush several times with air a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Using a calibrated source of air equipped with a septum-tee, meter a known

amount of air into the bag. Inject appropriate aliquots of MAPP via a gas-tight syringe through the septum. Knead the bag to ensure adequate mixing. Prepare at least 5 working standards to cover the range of 0-3000 ppm.

9.4 The concentration of the bag in ppm equals the volume of MAPP in milliliters divided by the amount of air in liters x 10^3

$$\text{ppm} = \frac{\text{volume of MAPP (mL)}}{\text{volume of air (L)}} \times 10^3$$

9.5 Prepare a standard curve by plotting concentration in ppm vs peak area, after correction for the blank.

10. Calculations

10.1 Read the concentration in ppm, corresponding to each peak area from the standard curve.

10.2 It is not recommended that the concentration of MAPP be expressed in mg/cu m, because MAPP is a mixture and has no specific molecular weight.

11. References

11.1 Documentation of the NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U. S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Methyl Acetylene-Propadiene Mixture, prepared under NIOSH Contract No. 210-76-0123.

11.3 Huston, Robert F., Cyril A. Barrios, and Robert A. Holleman, "Weathering and Stability of Methyl Acetylene-Propadiene-Hydrocarbon Mixtures," Journal of Chemical and Engineering Data, 15(1), (1970), 168.

Methylamine

Analyte:	Methylammonium ion	Method No.:	S148
Matrix:	Air	Range:	6.24-28.1 mg/cu m
OSHA Standard:	10 ppm (12.7 mg/cu m)	Precision ($\overline{CV}_T$):	0.058
Procedure:	Adsorption on silica gel, desorption with deionized, distilled water, ion chromatography/electrolytic conductivity detection	Validation Date:	7/6/79

1. Synopsis

1.1 A known volume of air is drawn through a glass tube containing silica gel to collect methylamine. The sample is spiked with concentrated hydrochloric acid to stabilize the amine.

1.2 Methylamine is extracted from the silica gel with 10 mL of deionized, distilled water, and the resulting sample is analyzed by ion chromatography using electrolytic conductivity detection.

2. Working Range, Senstitivity, and Detection Limit

2.1 This method was validated over the range of 6.24-28.1 mg/cu m at an atmospheric temperature of 25°C and pressure of 762 mm Hg, using 24-liter samples. For this sample size, the working range is estimated to be 1.5-45 mg/cu m. The upper limit of the range of the method is dependent on the capacity of the silica gel.

2.2. The sensitivity of the method for the instrumental conditions used during the validation study was 3 μmho/cm/microgram methylammonium ion. In other words, a 100-microliter injection of a 14 microgram/mL solution of methylamine gave a peak whose height was 40% of full scale on a 1-volt recorder. The ion chromatograph was set on range 10 μmho/cm.

2.3 The detection limit of the analytical method is estimated to be 100 ng of methylamine per injection, corresponding to a 100-microliter aliquot of a microgram/mL standard. This corresponds to 10 micrograms per sample.

2.4 The upper limit of the range of the method depends on the adsorptive capacity of the silica gel. This capacity may vary with the concentrations of methylamine and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the adsorbing section of the collection tube (containing 300 mg of silica gel) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 275 minutes at an average sampling rate of 0.188 liter/minute and relative humidity of 83% and temperature of 20°C. The breakthrough test was conducted at a concentration of 25.4 mg/cu m.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any cation that has the same retention time as methylammonium ion at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.3 Organic amines and ammonia, if present in large amounts, may be collected on the silica gel and reduce the capacity of the sorbent. Ammonia, at levels greater than 20 mg/cu m for a 24-liter collection volume, will interfere in the analytical method.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 6.24-28.1 mg/cu m was 0.058. This value corresponds to a standard deviation of 0.737 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit were an average of 6.7% lower than the taken concentrations (n=18). The desorption efficiency was determined to be 0.986 for a collector loading of 0.150 mg. In storage stability studies, the mean of samples analyzed after 7 days were within 0.8% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 The collection device is small, portable and involves no liquids.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the silica gel tube. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

5.4 The method requires a field spike of concentrated hydrochloric acid.

5.5 In the sample analysis the retention time of the methylamine varies with varying concentrations of methylamine. Therefore, identification of the methylamine peak in samples must be done with standards whose peak heights are within 25% of the sample peak height.

5.6 The retention time of the methylamine gradually decreases with successive injections throughout the day, which causes a gradual increase in the peak height. Because of this, samples must be quantified based on an adjacent standard.

6. Apparatus

6.1 Silica Gel Sampling Tubes. The sampling tube consists of a glass tube with both ends unsealed (7-cm long with an 8-mm O.D. and a 6-mm I.D.) packed with 45/60 mesh chromatographic grade silica gel*. Each tube contains two sections of silica gel, separated by a plug of silylated glass wool. The front adsorbing section contains 300 mg of silica gel and the backup section contains 150 mg. A plug of silylated glass wool is placed at each end of the tube. The sampling tube should contain no metal retaining clips or polyurethane foam because they would later be dissolved by the HCl.

The pressure drop across the tube must be no greater than 13 inches of water at a flow rate of 0.20 liter/minute.

6.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative silica gel tube in the line to minimize associated with uncertainties in the volume sampled.

6.3 Manometer.

6.4 Thermometer.

6.5 Dionex ion chromatograph Model 10 or 14** equipped with a 100-microliter sample loop and an electrolytic conductivity detector.

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*The silica gel is manufactured by Coast Engineering Laboratory and is commercially available through Applied Science Laboratories, Inc., State College, PA. Other sources were found to have large amounts of impurities.

**Dionex Corporation, Sunnyvale, CA.

6.6 Columns: 3-mm I.D. x 150-mm long Dionex cation precolumn; two 6-mm I.D. x 250-mm long Dionex cation analytical columns connected in series; 9-mm I.D. x 250-mm long Dionex cation suppressor column.

6.7 Filtration unit for protection of the cation analytical column from particulate contamination: Swinnex (13-mm) or equivalent fitted with 13-mm diameter/0.8-micrometer pore size cellulose ester membrane filters. The filter unit can be obtained from Millipore.

6.8 Filtration unit for cleaning eluent solutions: 47-mm filter holder fitted with a 47-mm diameter/0.8-micrometer pore size cellulose ester membrane filter.

6.9 Tweezers.

6.10 Syringes: 10-mL with luer-lock or luer-slip connection.

6.11 Scintillation Vials: 20-mL, with Polyseal caps.

6.12 Volumetric Flasks: 10-, 100-, 250-mL.

6.13 Volumetric Pipets: 1-, 2-, 4-, 5-, and 10-mL units.

6.14 Ruler with millimeter graduations.

6.15 Syringe for dispensing HCl. 50-microliter, with glass barrel, Teflon tipped plunger, and inert (platinum or Teflon) needle.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Methylamine, 40% in H_2O.

Standardization of Methylamine Solution. Aqueous solutions of methylamine of nominal 40% (0.4 g/mL concentration can be obtained from commercial sources. Such solution will decrease in methylamine concentration when opened. Therefore, it is necessary to periodically standardize such solutions by titration with standard hydrochloric acid. Add 1 mL of the 40% solution to a 100-mL volumetric flask and add distilled water to the mark. Prepare 0.1 N hydrochloric acid and fill a 10-mL burette with it.

Titrate 5 mL of the diluted methylamine solution with the standard HCl, using three drops of methyl red or other suitable acid-base indicator. Calculate the concentration of the original nominally 40% methylamine solution in g/mL.

7.2 Concentrated hydrochloric acid.

7.3 Ion Chromatograph eluent, 0.005 N HNO_3, add 1.25 mL concentrated nitric acid to 4 liters of deionized, distilled water. Filter to remove any particles greater than 1 micrometer.

7.4 0.1 N HNO_3. Add 25 mL concentrated nitric acid to 4 liters of of deionized, distilled water. The solution is filtered to remove any particles greater than 1 micrometer. This solution is used to clean the analytical column.

7.5 0.5 N NaOH. Dissolve 80 grams NaOH in 4 liters deionized distilled water. Filter to remove any particles greater than 1 micrometer. This solution is used to regenerate the suppressor.

7.6 Desorption efficiency stock standard: Prepare a one to ten dilution in water of the "40% methylamine" reagent.

7.7 Desorption efficiency standards: Spike 10 mL deionized, distilled water with 40 microliters of concentrated HCl. Spike this solution with the desorption efficiency stock standard (Section 7.6).

7.8 Working stock standards: Prepare by diluting the "40% methylamine reagent" 1 to 250 in deionized, distilled water. Working standards are then prepared by adding appropriate aliquots of the stock standard to 100 mL flasks containing about 50 mL deionized, distilled water and 400 microliters of concentrated hydrochloric acid. The level of the water is then brought up to the 100 mL mark. Neutral solutions of amines are subject to oxidation and should be prepared fresh when needed. Working standards containing spiked acid have been shown to be stable for at least a week.

8. Procedure

8.1 Cleaning of Equipment. All glassware used should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the caps from the ends of the silica gel tube. All tubes must be packed with silica gel from the same manufacturer's lot.

8.2.2 Attach the tubing from the sampling pump to the backup end (small section of silica gel) of the tube. Air being sampled should not pass through any hose or tubing before entering the sorbent tube.

8.2.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

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8.2.4 Set the flow rate as accurately as possible using the manufacturer's directions. A sample size of 24 liters is recommended. Sample at a flow rate between 0.02 and 0.2 liter/minute. Do not sample at a flow rate less than 0.02 liter/minute. Record the sampling time, flow rate, and type of sampling pump used.

8.2.5 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.6 Immediately after sampling, add 40 microliters of concentrated HCl to the front section of silica gel in the tube. Use a 50-microliter glass syringe with Teflon-tipped plunger and inert needle, so that the acid does not contact and react with the stainless steel. The silica gel may turn yellow when the acid is added because of iron impurities in the silica gel. Some of the acid will migrate to the backup section in a short period of time, thus, it is not necessary to add acid directly to the backup section.

8.2.7 The sampling tube should be capped with plastic caps immediately after adding HCl. Under no circumstances should rubber caps be used.

8.2.8 With each batch or partial batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank. A minimum of 18 extra silica gel tubes should be provided for desorption efficiency determinations.

8.2.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Transfer the front section of silica gel to a 20 mL scintillation vial. Transfer the last glass wool plug and the backup section to another clean vial. Label each appropriately for separate analysis

8.3.2 Desorption. Add 10 mL of dionized distilled water to each sorbent section and cap the vials. Shake the mixtures occassionally over a period of 45 minutes.

8.3.3 Ion Chromatograph Conditions. The typical operating conditions for the ion chromatograph are:

Columns: Two 6-mm I.D. X 250-mm long cation separator columns connected in series
Column Temperature: Ambient
Pump: 40% of total capacity
Column Pressure: 480 psig
Flow Rate: 184 mL/hr
Mobile Phase: 0.005 N HNO_3
Average Retention Time: 22 min
Average Retention Volumne: 66 mL

8.3.4 Filtration and Injection. The sample is drawn into a 10-mL syringe. The filtration unit with filter is attached to the syringe and about 2 mL of the sample is flushed through the sample loop of the ion chromatograph. The sample is then injected onto the ion exchange columns. The syringe and filter unit should be rinsed with deionized water between injections. The filter should be changed when the pressure required to expel the sample through the filter unit increases.

8.3.5 The peak height of the sample peak is measured in mm with a ruler and the results are calculated using an adjacent standard as discussed in Section 9. It is not recommended to quantitate sample peaks using an electronic area integrator. The output of the ion chromatograph is not compatible with most electronic integrators and reproducible results cannot be obtained.

8.3.6 Sample blanks must be analyzed following the same procedure as that used for the samples.

8.3.7 To maintain optimum resolution capabilities, particularly between methyl ammonium ion and any ammonium ion, the separater columns should be cleaned at the end of the day with 0.1 N HNO_3 for about ten minutes. This cleaning procedure will also increase the retention times.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound can vary from one laboratory to another and from one batch of silica gel to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of silica gel.

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8.4.2 Silica gel tubes, prepared as described in Section 6, are used to determine desorption efficiency. Samples are prepared by injecting an appropriate amount of the desorption efficiency stock standard (Section 7.6) directly into the front section of silica gel to represent 24-liter air samples at 0.5X, 1X, and 2X the OSHA standard. Forty microliters of concentrated hydrochloric acid are added to each sample, and the samples are capped. A parallel blank tube should be treated in the same manner except that no methylamine is added to it. Six tubes at each of three levels are prepared in this manner and allowed to stand at least overnight to ensure complete adsorption of the amine onto the silica gel. Standards are prepared by spiking identical amounts of analyte and 40 microliters of concentrated HCl into 10 ml deionized, distilled water. Samples, blanks, and standards are treated and analyzed in Section 8.3.

8.4.3 The desorption efficiency (D.E.) equals the average weight in micrograms recovered from the tube divided by the weight in micrograms added to the tube, or

$$D.E. = \frac{\text{Average weight recovered } (\mu g) - \text{Blank } (\mu g)}{\text{Weight added } (\mu g)}$$

The desorption efficiency may be dependent on the amount of methylamine collected on the silica gel. Plot the desorption efficiency versus weight of methylamine found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for methylamine, is prepared and analyzed under the same IC conditions and during the same time period as the unknown samples. The methylamine peak height is directly proportional to the methylamine concentration over the range. This peak height measurement is used in the calculations. However, the retention time decreases and peak height increases throughout the day. Therefore the calculation for each sample must be based on an adjacent standard. Also the retention time of the methylamine varies slightly with varying concentration of methylamine (20% decrease in retention time for a 30 fold increase in concentration). Therefore the adjacent standard peak height should be within 25% of the peak height of the sample.

9.2 From the working stock standard solution (Section 7.8) appropriate aliquots are withdrawn and dilutions are made. Prepare at least 5 working standards to cover the range of 3.0-90 micrograms/mL. This range is based on a 24-liter sample.

9.3 Analyze the samples as described in Section 8.3.

10. Calculations

10.1 Using peak height measurements calculate the weight in micrograms collected in each sample on the basis of an adjacent standard.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in front sample tube

μg blank = μg found in front blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.4) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected micrograms/sample.

$$\text{Corrected micrograms/sample} = \frac{\text{Total weight (Section 10.3)}}{\text{D.E.}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = flow rate sampled (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of methylamine in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liters/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of methylamine
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report No. 148 for Methylamine, prepared under NIOSH Contract No. 210-76-0123.

Nitroethane

Analyte:	Nitroethane	Method No.:	S219
Matrix:	Air	Range:	147-600 mg/cu m
OSHA Standard:	100 ppm (310 mg/cu m)	Precision ($\overline{CV}_T$):	0.060
Procedure:	Adsorption on XAD-2, desorption with ethyl acetate, GC/FID	Validation Date:	1/20/78
		Revised:	11/1/79

1. Principle of the Method

1.1 A known volume of air is drawn through a series of tubes containing XAD-2 resin to trap the organic vapors present. The sampling train consists of two separate tubes--a front adsorbing tube and a backup tube; this sampling arrangement is necessary to prevent sample migration during storage.

1.2 The XAD-2 in each tube is transferred to respective vials and the nitroethane is desorbed with ethyl acetate. An aliquot of this sample solution is injected into a gas chromatograph equipped with a flame ionization detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 147.4-604 mg/cu m at an atmospheric temperature of 22°C and an atmospheric pressure of 777 mm Hg using a 3-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the XAD-2 resin. This capacity varies with the concentrations of nitroethane and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 600 mg XAD-2) reaches 5% of the concentration in the test gas mixture. When an atmosphere at 90% relative humidity containing 585 mg/cu m of nitroethane was sampled at 0.049 liter per minute, 5% breakthrough was observed after 98 minutes (capacity = 4.8 liters or 2.8 mg). The sample size recommended is less than two-thirds the 5% breakthrough capacity to minimize the probability of overloading the sampling tube.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 147.4-604 mg/cu m was 0.0602. This value corresponds to an 18.66 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analytical method was 2.2% lower than the "true" concentration for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 314 mg/cu m indicate that collected samples are stable for at least seven days.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of nitroethane found on the backup XAD-2 tube exceeds 25% of that found on the front tube, the probability of sample loss exists.

5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect

the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling between 0.03 and 0.05 liter per minute for 60 minutes. The pump must be accurate to within ±5% at the recommended flow rate.

6.1.2 Sampling Tubes. The sampling train consists of two separate XAD-2 tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with a 10-mm O.D. and a 8-mm I.D. The XAD-2 used must be prewashed with ethyl acetate and dried. The front tube contains 600 mg XAD-2; the backup tube, 300 mg. A plug of silylated glass wool is placed at each end of the sorbent tubes. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

Note that this sampling tube scheme is necessary to prevent sample migration upon storage.

6.2 Gas chromatograph with a flame ionization detector.

6.3 Column, 20-ft x 1/8-in stainless steel, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Microliter syringes, 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots.

6.6 Pipettes, 2-ml, delivery type.

6.7 Volumetric flasks, 25-ml or other convenient sizes for making standard solutions.

7. Reagents

Wherever possible, reagents used should be ACS reagent grade or better.

7.1 Nitroethane, chromatographic quality.

7.2 Ethyl acetate, reagent grade.

7.3 1-Hexanol, 99% or other suitable internal standard. The appropriate solution of the internal standard is prepared in ethyl acetate.

7.4 Pre-cleaned Resin. XAD-2 resin (20/50 mesh) can be obtained from Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Twenty-four hour extractions are then performed successively with water, methanol, and methylene chloride. Resin has been prepared in this manner using charges of about 700 grams of resin and 1.5 liters of each solvent. The resin is dried in a fluidized bed using nitrogen gas at room temperature from a liquid nitrogen cylinder. The drying process is terminated when essentially no solvent is detected in the effluent. A final quality control check is performed by desorbing a portion of the resin and analyzing the resulting solution by gas chromatography. Residual solvent should be less than 1000 ppm in concentration. Finally, several washings with ethyl acetate are recommended to reduce possible interferences to a minimum when the sorbent is desorbed with this solvent. This can be done in a beaker of the appropriate volume. The resin is then air-dried.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative resin tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes (4-mm). Connect the front 600-mg tube to the 300-mg backup tube with a short piece of tubing.

8.3.2 The tube containing 300 mg of XAD-2 is used as a backup and should be positioned nearest the sampling pump. The XAD-2 tube series should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the front XAD-2 tube.

8.3.4 A sample size of 3 liters is recommended. Sample at a known flow rate between 0.03 and 0.05 liters per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 Immediately after sampling the two XAD-2 tubes must be separated and each tube capped with the supplied plastic caps. The tubes should be identified to distinguish each corresponding pair of front and backup tubes.

8.3.6 One set of XAD-2 tubes (a 600-mg tube and a 300-mg backup tube) should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This set of tubes should be labeled as a blank. Submit one blank for every ten samples.

8.3.7 Unused XAD-2 tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency may vary from one batch of XAD-2 to another. Record the batch number of the XAD-2 used.

8.3.8 Capped XAD-2 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each tube is scored with a file and broken open. The glass wool is removed and discarded. The XAD-2 in each tube is transferred to a 5-ml screw-cap sample vial. Each tube is analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 ml of ethyl acetate is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 ml of ethyl acetate containing a known amount of internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) nitrogen carrier gas flow
2. 30 ml/min (25 psig) hydrogen gas flow to detector
3. 300 ml/min (60 psig) air flow to detector
4. 160°C injector temperature
5. 200°C manifold temperature (detector)
6. 120°C column temperature

A retention time of approximately nine minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately seventeen minutes.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of XAD-2 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of nitroethane found in the samples.

The analytical samples are prepared as follows: XAD-2 resin, equivalent to the amount in the front section (600-mg), is measured into a 5-ml screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of nitroethane in ethyl acetate (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µl aliquot is used to prepare the analytical samples.

Six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) are prepared by adding an amount of nitroethane equivalent to a 3-liter sample at the selected level. A stock solution containing 235.1 milligrams of nitroethane per milliliter of ethyl acetate is prepared. Two, four and eight microliter aliquots of the solution are added to the XAD-2 resin vials to produce 0.5, 1, and 2X the OSHA standard level. The analytical samples are allowed to stand overnight to assure complete adsorption of the analyte onto the resin. A parallel blank vial is treated in the same manner except that no sample is added to it.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 ml of ethyl acetate with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of ethyl acetate containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in µg recovered from the vial divided by the weight in µg added to the vial, or

$$D.E. = \frac{\text{Average Weight (µg) recovered - Resin Blank (µg)}}{\text{Weight (µg) added}}$$

The desorption efficiency may be dependent on the amount of nitroethane collected on the resin. Plot the desorption efficiency versus weight of nitroethane found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

A series of standards varying in concentration over the range of interest is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples in order to minimize variations in FID response. It is convenient to express concentration of standards in terms of µg per 2.0 ml since the samples are desorbed in 2.0 ml of ethyl acetate. A calibration curve is established by plotting peak area versus concentration in µg per 2.0 ml.

9.1 Prepare a stock standard solution containing 235.1 mg/ml of nitroethane in ethyl acetate.

9.2 From the above stock solution, appropriate aliquots are added to 2.0 ml of ethyl acetate. Prepare at least 5 standards to cover the range of 0.46-1.86 milligrams/sample. The range is based on a 3-liter air sample.

9.3 For the internal standard method, use ethyl acetate containing a predetermined amount of the internal standard. The internal standard concentration used for these studies was approximately 70% of the analyte concentration for a standard solution representing a 3-liter collection at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in µg per 2.0 ml.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg per 2.0 ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the sample blank (Section 8.3) must be made for each sample:

µg = µg sample - µg blank

where:

µg sample = µg found in sample vial

µg blank = µg found in blank vial

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{75.07} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
75.07 = molecular weight of nitroethane
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Nitroethane, No. S219, prepared under NIOSH Contract No. 210-76-0123.

Analyte:	Nitromethane	Method No.:	S220
Matrix:	Air	Range:	123-501 mg/cu m
OSHA Standard:	100 ppm (250 mg/cu m)	Precision ($\overline{CV}_T$):	0.078
Procedure:	Adsorption on Chromosorb 106, desorption with ethyl acetate, GC/AFID	Validation Date:	1/19/79

1. Synopsis

1.1 A known volume of air is drawn through a tube containing Chromosorb 106 to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

1.2 The Chromosorb 106 in each tube is transferred to screw-capped vials immediately after collection. Prior to analysis, the nitromethane is desorbed with ethyl acetate. An aliquot of this sample solution is injected into a gas chromatograph equipped with an alkali flame ionization detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 123-501 mg/cu m at atmospheric temperatures of 20 and 24°C and atmospheric pressures of 767, 769 and 774 mm Hg using a 3-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the absorptive capacity of the Chromosorb 106. This capacity varies with the concentration of nitromethane and other substances in the air. When an atmosphere at 90% relative humidity containing 517.6 mg/cu m of nitromethane was sampled at 0.0478 liter per minute, 5% breakthrough was observed after 105 minutes (capacity = 5.019 liters or 2.598 mg). The sample size recommended is less than two thirds the 5% breakthrough capacity to minimize the probability of overloading the sampling tube.

2.3 The detection limit was not determined.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 123-501 mg/cu m was 0.0775. This value corresponds to a 19.38 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1, and 2 times the OSHA standard were 0.3% lower than the dynamically generated test concentrations (n = 17). The desorption efficiency was determined to be 0.942 for a collector loading of 0.335 mg. In storage stability studies, the mean of samples analyzed after seven days was within 3.1% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of nitromethane found on the backup Chromosorb 106 section exceeds 25% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling at 0.05 liter per minute for 60 minutes. The pump must be accurate to within ±5% at the recommended flow rate.

6.1.2 Sampling Tubes. The sampling tube consists of a glass tube, 10-cm long with a 10-mm O.D. and 8-mm I.D., packed with two sections of 60/80 mesh Chromosorb 106. The front adsorbing section contains 600 mg and the backup section contains 300 mg. The two sections are separated by a portion of silylated glass wool. A plug of silylated glass wool is placed at each end of the sorbent tube. The pressure drop across the tube was found to be less than one inch of mercury at a flow rate of 50 mL per minute.

6.1.3 Sample vials, 12-mL with Teflon-lined screw caps. Immediate transfer of collected samples is recommended.

6.2 Gas chromatograph with a nitrogen-phosphorous or alkali flame ionization detector.

6.3 Column, 6-ft x 1/4-in O.D. (4 mm I.D.) packed with 10% SP1000 on 80/100 mesh Supelcoport.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Microliter syringes, 10- and 100-microliter, and other convenient sizes for making standards and for taking sample aliquots.

6.6 Pipettes, 2-mL, delivery type.

6.7 Volumetric flasks, 10-mL or other convenient sizes for making standard solutions.

7. Reagents

Wherever possible, reagents used should be ACS reagent grade or better.

7.1 Nitromethane, 99%.

7.2 Ethyl acetate.

7.3 Pre-cleaned resin. Chromosorb 106 resin (60/80 mesh) is washed according to NIOSH procedure recommended for nitropropane

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by Soxhlet extraction in acetone for approximately two hours. The resin is then air-dried in a hood. It should be emphasized that alternate methods of cleaning may lead to inadequate storage stability.

7.4 Nitrogen, purified.

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sorbent tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the seals at the ends of the tubes should be removed.

8.3.2 The section containing 300 mg of Chromosorb 106 is used as a backup and should be positioned nearest the sampling pump. The Chromosorb 106 tube should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the front section of the Chromosorb 106 tube.

8.3.4 A sample size of 3 liters is recommended. Sample at a known flow rate between 0.03 and 0.05 liter per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 The Chromosorb 106 should be transferred to properly labeled screw-capped vials immediately after sampling.

8.3.6 One Chromosorb 106 tube should be handled in the same manner as the sample tube, except for the taking of an air sample. This sample should be labeled as a blank.

Submit one blank for every batch or partial batch of ten samples.

8.3.7 A sufficient number of unused Chromosorb 106 tubes should be available for use in desorption efficiency studies in conjunction with these samples, because desorption efficiency may vary from one batch of Chromosorb 106 to another. Record the batch number of the Chromosorb 106 used.

8.3.8 Capped sample vials should be packed tightly and padded before they are shipped to minimize vial breakage during shipping.

8.4 Analysis of Samples

8.4.1 Desorption of Sample. Prior to analysis, 5.0 mL of ethyl acetate is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 5.0 mL of ethyl acetate containing a known amount of internal standard. No internal standard was used in these validation experiments.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 20 mL/min (40 psig) helium carrier gas flow
2. 30 mL/min (2.5 psig) hydrogen gas flow to detector
3. 50 mL/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 300°C manifold temperature (detector)
6. 100°C column temperature

A retention time of approximately two minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3.

8.4.3 Injection of Sample. A 2-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

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8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 106 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of nitromethane found in the samples.

The analytical samples are prepared as follows: Chromosorb 106, equivalent to the amount in the front section (600 mg), is measured into a 12-mL screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of nitromethane in ethyl acetate (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µL aliquot is used to prepare the analytical samples.

Six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) are prepared by adding an amount of nitromethane equivalent to a 3-liter sample at the selected level. A stock solution containing 147.8 milligrams of nitromethane per milliliter of ethyl acetate is prepared. Aliquots (2.5, 5.0 and 10.0 µL) of the solution are added to the Chromosorb 106 vials to produce samples at 0.5, 1 and 2X the OSHA standard level. The analytical samples are allowed to stand overnight to assure complete adsorption of the analyte onto the sorbent. A parallel blank vial is treated in the same manner except that no sample is added to it.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 5.0 mL of ethyl acetate with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare calibration standards by using 5.0 mL of ethyl acetate containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the vial divided by the weight in mg added to the vial, or

$$D.E. = \frac{\text{Average Weight (mg) recovered - Resin Blank (mg)}}{\text{Weight (mg) added}}$$

The desorption efficiency may be dependent on the amount of nitromethane collected on the sorbent. Plot the desorption efficiency versus weight of nitromethane found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards varying in concentration over the range corresponding to 3-liter collections at 0.1-3 times the OSHA standard is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. This is done in order to minimize variations in AFID response. It is convenient to express concentration of standards in terms of mg per 5.0 mL since the samples are desorbed in 5.0 mL of ethyl acetate. A calibration curve is established by plotting peak area versus concentration in mg per 2.0 mL.

9.1 Prepare a stock standard solution containing about 14.78 mg/mL of nitromethane in ethyl acetate.

9.2 From the above stock solution, appropriate aliquots are added to 5.0 mL of ethyl acetate. Prepare at least five standards to cover the range of 0.07-2.2 milligrams/sample. The range is based on a 3-liter air sample.

9.3 For the internal standard method, use ethyl acetate containing a predetermined amount of the internal standard. The internal standard concentration used should be approximately 70% of the analyte concentration for a standard solution representing a 3-liter collection at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg per 5.0 mL.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg per 5.0 mL and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the sample blank (Section 8.3) must be made for each sample:

mg = mg sample - mg blank

where:

mg sample = mg found in sample vial

mg blank = mg found in blank vial

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{61.04} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
61.04 = molecular weight of nitromethane
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Nitromethane, No. S220, prepared under NIOSH Contract No. 210-76-0123.

Analyte:	Sulfuryl Fluoride	Method No.:	S245
Matrix:	Air	Range:	2.54 - 10.29 ppm
OSHA Standard:	5 ppm (21 mg/cu m)	Precision ($\overline{CV}_T$):	0.025
Procedure:	Collection in gas sampling bag, GC with flame photometric detection	Validation Date:	6/8/79

1. Synopsis

1.1 An air sample is pumped into a gas sampling bag with a personal sampling pump.

1.2 The sulfuryl fluoride content of the sample is determined by gas chromatography using flame photometric detection in the sulfur mode.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 2.54-10.29 ppm at an atmospheric temperature of 20°C and atmospheric pressure of 760 mm Hg using a 3-liter sample volume.

2.2 Under the instrumental conditions used in the validation study, a 2-mL injection of a 3 ppm sulfuryl fluoride standard resulted in a peak whose height was 64% of full scale on a 1-millivolt recorder. The amplifier of the gas chromatograph was set on range 10^4 and attenuation 1.

2.3 The limit of detection is estimated at less than 0.8 ng sulfuryl fluoride. Using a 2.5 mL gas sampling loop, this corresponds to a level of approximately 0.1 ppm.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any sulfur compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

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4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.54-10.29 ppm was 0.025. This value corresponds to a standard deviation of 0.1 ppm at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedure can be found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The average of the concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit were 2.0% lower than the dynamically generated test concentrations (n=18). In storage stability studies, the mean of samples analyzed after 7 days was within 0.6% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples in bags are analyzed by means of a quick instrumental method.

5.2 One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling and shipping.

5.3 It is difficult to ship the samples by air.

6. Apparatus

6.1 Personal Sampling Pump. A personal sampling pump capable of filling a gas sampling bag at approximately 0.05 liter/minute is required. Each personal pump should be calibrated to within ±5%. Although sample volume is not used to determine sample concentration, the pump should be calibrated to make certain that the collected sample represents a time-weighted average concentration and to avoid over filling of the bags; i.e., a maximum sampling time can be determined based on the flow rate and sample volume which is less than 80% of the volume of the bag.

The personal sampling pump must be fitted with an outlet port so it is capable of filling a bag. To ensure a leak-free apparatus, adjust the pump so that it delivers at the proper flow rate, and attach the pump outlet to a water manometer with a short piece of flexible tubing. Turn the pump on and observe the water level difference; it should push at least 30 cm of water. If it does not, the pump is incapable of filling the sampling bag and cannot be used.

6.2 Gas Sampling Bag. Five-liter capacity, five-layer sampling bags (Calibrated Instruments, Inc., 731 Saw Mill River Road, Ardsley, New York 10502) were found to be satisfactory for sample collection and

storage for at least 7 days. This bag is fitted with a metal valve and hose bib. The valves used in validation studies were found to leak when in the open position. It is necessary to wrap the valve stem connection with Teflon tape or Parafilm to ensure a leak-free connection. For the preparation of calibration standards in the laboratory, Saran or Tedlar bags can be used.

6.3 Gas chromatograph, equipped with a flame photometric detector in the sulfur mode and 2-mL gas sampling loop.

6.4 Column (0.5-m X 2-mm I.D. glass) packed with 60/80 mesh Carbosieve S (Supelco, Inc.).

6.5 Area Integrator. An electronic integrator or some other suitable method for measuring peak areas.

6.6 Gas-tight Syringes. Convenient sizes for preparing standards.

6.7 Regulator for compressed air which is capable of metering gas at approximately 1 liter/minute. The gas line from the regulator should be equipped with a septum-tee for standards preparation.

6.8 Water manometer.

6.9 Thermometer.

6.10 Stopwatch

7. Regents

All reagents used must be ACS reagent grade or better.

7.1 Sulfuryl fluoride, 100%.

7.2 Helium, purified.

7.3 Air, filtered, compressed.

7.4 Hydrogen, prepurified, compressed.

7.5 Oxygen, purified, compressed.

8. Procedure

8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the valve and bleeding out the air sample. The use of a vacuum pump is recommended although this procedure can be carried out by manually flattening the bags. The bags are then flushed with air and evacuated. This procedure is repeated at least twice.

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Bags should be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Check for any discernable leaks and any volume changes or slackening of the bag, especially along seams and in the valve stem, for at least a one-hour period.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, attach a small piece of Teflon tubing to the valve fitting of the five-layer gas sampling bag. Rubber tubing should not be used.

8.2.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump. Make sure that all connections are tight and leak-free. The bag valve must be fully opened during sampling.

8.2.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required. No tubing is attached to the inlet of the pump.

8.2.4 Sample at a flow rate of 0.05 liter/minute or less. Set the flow rate as accurately as possible using the manufacturer's directions. Although the volume of sample collected is not used in determining the concentration, it is necessary to keep the volume to 80% or less of the bag's capacity. Observe the bag frequently to ensure that it is filling properly.

8.2.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation. Also record sampling time, flow rate, and type of sampling pump used.

8.2.7 The gas sampling bag should be labeled appropriately and sealed tightly.

8.2.8 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of being punctured during shipping. Do not ship the bags by air, unless they are stored in a pressurized cabin.

8.3 Analysis of Samples

8.3.1 GC Conditions. The typical operating conditions for the gas chromatograph are:

45 mL/min helium carrier gas flow
150 mL/min hydrogen flow to detector
40 mL/min air flow to detector
20 mL/min oxygen flow to detector
110°C column temperature
225°C detector temperature

8.3.2 GC Analysis. Attach the gas sampling bag to the sample loop of the gas chromatograph with a short piece of flexible tubing. Open the valve of the bag and fill the loop by using a vacuum pump or manually applying pressure to the sample bag. Allow the loop to attain atmospheric pressure, and inject the sample. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. A retention time of approximately 4 minutes is to be expected using the above conditions.

8.3.3 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and the results are read from a standard curve as discussed in Section 9.

9. Calibration and Standardization

A series of standards, varying in concentration over the range of 0.5-15 ppm is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in ppm versus peak area. A logarithmic plot may be used to obtain a linear curve for this detector.

9.1 Completely evacuate and flush several times with air a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Using a calibrated source of air equipped with a septum-tee, meter 3-4 liters of air into the bag. Inject appropriate aliquots of sulfuryl fluroide via a gas tight syringe through the septum. Knead the bag to ensure adequate mixing. Prepare at least 5 working standards to cover the range of 0.5-15 ppm. Analyze these standards as in 8.3.

9.2 The concentration of the bag in ppm equals the volume of sulfuryl fluoride in mL divided by the amount of air in L x 10^3.

$$\text{ppm} = \frac{\text{Volume of sulfuryl fluoride (mL)}}{\text{volume of air (L)}} \times 10^3$$

10. Calculations

10.1 Read the concentration in ppm, corresponding to each peak area from the standard curve.

10.2 Another method of expressing concentration is mg/cu m.

$$\text{mg/cu m} = \text{ppm} \times \frac{\text{M.W.}}{24.45} \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight, 102.07 g/mole
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

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11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Sulfuryl Fluoride, prepared under NIOSH Contract No. 210-76-0123.

Chlordane

Analyte:	Chlordane (octachloro-3a, 4,7,7a-tetrahydro-4,7-methanoindane and isomers)	Method No.:	S278
		Range:	0.156-1.17 mg/cu m
Matrix:	Air	Precision ($\overline{CV}_T$):	0.070
OSHA Standard:	0.5 mg/cu m	Validation Date:	6/8/79
Procedure:	Filter/sorbent collection, extraction with toluene, GC-ECD		

1. Synopsis

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the particulate chlordane present. A Chromosorb 102 sorbent tube is placed behind the filter to trap the vapors present.

1.2 The filter and sorbent are transferred to a jar or other suitable container and extracted with toluene. The plastic filter holder and stainless steel support screen are rinsed with hexane and treated as a separate sample.

1.3 An aliquot of the sample is analyzed by injection into a gas chromatograph equipped with an electron capture detector. For quantitation the areas of the resulting chlordane peaks are compared with those obtained from the injection of standards.

1.4 The method measures exposure to chlordane (octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane and isomers), not technical chlordane. (Technical chlordane contains other chlorinated hydrocarbons.)

2. Working Range, Sensitivity and Detection Limit

2.1 The method was validated over the range of 0.1563-1.171 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 760 mm Hg using a 120-liter sample. The method is capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the method is dependent both on the filter loading since this will affect flow measurement and on the absorptive capacity of the Chromosorb 102. After 240 minutes of sampling at a rate of 1 liter per minute and a temperature of 21°C, the effluent from the sorbent tube was below the detection level. The primary sorbent tube contained 11.5% of the

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chlordane collected by the sampling train. The test was conducted at an average concentration of 1.1 mg/m^3.

2.3 The detection limit of the analytical method was not rigorously determined but is estimated to be 0.4 µg/sample.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their supsected identities should be transmitted with the sample.

3.2 Any compound that can be detected by the electron capture detector and has the same retention time as chlordane at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total sampling and analytical method in the range of 0.1563-1.171 mg/m^3 was 0.0704. This value corresponds to a standard deviation of 0.035 mg/m^3 at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ± 25% of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1 and 2 times the OSHA standard were 3% higher than dynamically generated concentrations (n = 17). The analytical recovery was determined to be 1.023% for a collector loading of 29.98 µg. In storage stability studies, the mean of samples analyzed after seven days was within 7.3% of the mean of six samples analyzed after one day after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids. Interferences are minimal.

5.2 The samples are analyzed by means of a quick, instrumental method.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and sorbent tube. This drop will affect the flow rate and cause the volume to be imprecise because the pump is calibrated for one filter and sorbent tube only.

5.4 The amount of sample that can be taken is limited by the number of micrograms that the chromosorb tube will hold before overloading. When the amount of chlordane found on the backup section of the chromosorb exceeds 25% of that found on the front section, the probability of sample loss exists.

6. Apparatus

6.1 Sampling Equipment

6.1.1 Filter. The filter unit consists of a 37-mm diameter, 0.8 micrometer pore size, mixed cellulose ester membrane filter (Millipore AA or equivalent).

6.1.2 Filter Holder. The filter is placed in a two-piece 37-mm filter holder held together by tape or a shrinkable band. The filter is supported in the holder by a stainless steel screen (Mine Safety Appliances Co., catalog number 456224).

6.1.3 Chromosorb 102 Tubes. The tubes are constructed of glass tubing with both ends unsealed. The tubes are 10-cm long with an 8-mm O.D. and 6-mm I.D. The front section contains 100 mg of 20/40 mesh Chromosorb 102, and the backup section contains 50 mg. The Chromosorb 102 is held in place with 3-mm plugs of silanized glass wool. A 3-mm plug also separates the two sections. The chromosorb should be washed with toluene and air-dried before being packed in the tubes. To minimize the problem of the resin adhering to the walls of the glass tube, the tubes should be rinsed with acetone and dried prior to packing.

6.1.4 Thermometer.

6.1.5 Barometer.

6.1.6 Stopwatch.

6.2 Gas chromatograph equipped with an electron capture detector.

6.3 Column, 6 ft x 4 mm I.D. glass packed with 1.5% SP 2250/1.95% 2401 on 100/120 Supelcoport. This packing of mixed silicones on an acid-washed, DMCS-treated diatomite support is obtained from Supelco Inc., Bellefonte, PA.

6.4 A syringe or fixed volume automatic sample injector. A 2-µL sample volume was used for these studies.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes, convenient sizes for making standard solutions.

6.7 Volumetric flasks, convenient sizes for making standard solutions and sample dilutions.

6.8 Pipets, 1 and 10 mL and other convenient sizes for preparing sample dilutions.

6.9 Ointment jars, two ounce, squat form with Teflon-lined screw caps.

6.10 Teflon-capped sample vials.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Chlordane, 95%, contains approximately 60% chlordane and its octachlorinated isomers and 40% hexa-, hepta-, and nonachlors.

7.2 Chlordane, stock solution 6 mg/mL. Dissolve 10 mg of chlordane in 1 mL toluene. (Determine actual concentration by appropriate dilution and analysis by gas chromatography).

7.3 Toluene, distilled in glass.

7.4 Hexane, distilled in glass.

7.5 p,p'-DDT, 98%, Supelco Inc., internal standard. Final concentration for analysis to be 0.4 µg/mL in toluene or hexane as required.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water followed by distilled water, and dried.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling train in line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter holder and close firmly to insure that the edge of the filter is sealed. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder,

sample leakage may occur around the filter. The filter is supported by a stainless steel screen. The filter holder is held together by plastic tape or a shrinkable band.

8.3.2 Remove the filter holder plugs and sorbent tube caps and assemble the sampling train by connecting the sorbent tube to the filter holder. Attach the outlet of the sorbent tube to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.

8.3.4 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 120 minutes. The flow rate should be known within an accuracy of $\pm$5%.

8.3.5 Turn the pump on and begin sample collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available. record the elevation.

8.3.7 After sampling remove the sorbent tube and Luer-lock adapter from the outlet of the filter holder and connect to the inlet side. Cap the open end of the sorbent tube and plug the outlet of the filter holder with the plug supplied. Do not use rubber caps.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Obtain a blank sample by handling one sampling train in the same manner as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples or partial batch of ten samples.

8.3.10 The sampling train should be shipped in a suitable container designed to prevent damage in transit.

8.3.11 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a Teflon cap. Never transport, mail or ship the bulk sample in the same container as sample or blank filters.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully transfer the filter with tweezers to a two-ounce wide-mouthed Teflon-capped ointment jar.

2. Remove the glass wool plug from the sorbent tube and add it and the front section of the Chromosorb 102 to the same container as the filter.

3. Add 10 mL toluene to each sample and swirl intermittently during a half-hour period. Then dilute a 1-mL aliquot to 10 mL for analysis. If an internal standard is desired, p,p'-DDT may be used at a final concentration of 0.4 mg/mL in the sample to be analyzed. For convenience, a working solution at this concentration may be used for all extractions and dilutions.

4. Place the back-up Chromosorb 102 section in a different container and add 10 mL toluene. Analyze this solution separately without further dilution.

5. Place the stainless steel support screen in a separate two-ounce wide-mouthed ointment jar. Using 10-mL volumetric pipette, rinse the insides of the top and bottom sections of the filter holder into the jar containing the screen using hexane as the solvent. Swirl the jar to mix the contents and facilitate the washing of the screen. These samples should not require further dilution. If an internal standard is desired, the p,p'-DDT may be dissolved in hexane to yield a final concentration of 0.4 µg/mL in the solution to be analyzed.

8.4.2 GC-ECD Conditions

Column Temperature:	205°C
Injector Temperature:	250°C
ECD Temperature:	300°C
Carrier gas (95% argon/ 5% methane) flow:	75 mL/minute
Injection volume:	2 µL

8.4.3 Filtration of Samples. If an automatic injector is used the sample should be filtered through a Teflon filter (1.0 µm pore size) using a 5-mL syringe fitted with a Swinney filter holder or equivalent. The filtrate should be placed in Teflon-capped vials.

8.4.4 Injection. A 2-µL sample injection is recommended for this analysis. The sample may be injected either by using an appropriate syringe or filling a fixed volume automatic injector. Duplicate injections of the same solution should show no more than a 3% difference in area.

8.4.5 Measurement of Area. The area of the sample peaks is measured by an electronic integrator or some other suitable means of area measurement and results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Recovery

8.5.1 Special Consideration. Since chlordane is sold only as a mixture of hexa-, hepta-, octa-, and nonachlorinated compounds it is necessary to determine the percentage of chlordane and its isomers in the standard used. Peaks due to chlordane and its related compounds have been identified by various authors (see Refs. 11.3 and 11.4) and based on these sources, five peaks have been selected to use for quantitation (see Figure S278-1).

By obtaining a gas chromatogram of the sample and dividing the area of the five selected peaks by the total area of all the peaks, the percentage of chlordane is determined. Using these findings the milligrams of chlordane standard weighed out was multiplied by 0.57 x 0.95 (stated purity) to give the amount present in the calibration solutions and for spiking purposes. Hence it is necessary to weigh out approximately 10 mg per mL of solution to obtain the desired 6 mg/mL of chlordanes.

8.5.2 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery determinations should cover the range of interest.

8.5.3 Procedure for Determining Recovery. A known amount of chlordane equivalent to that present in a 120-liter sample at the selected level is added to the mixed cellulose ester membrane filter and Chromosorb 102 placed in a suitable container. A stock solution containing 6 mg of chlordane per milliliter toluene is prepared by weighing out approximately 10 mg per milliliter solvent of the pesticide mix. Add 5, 10 and 20 microliter

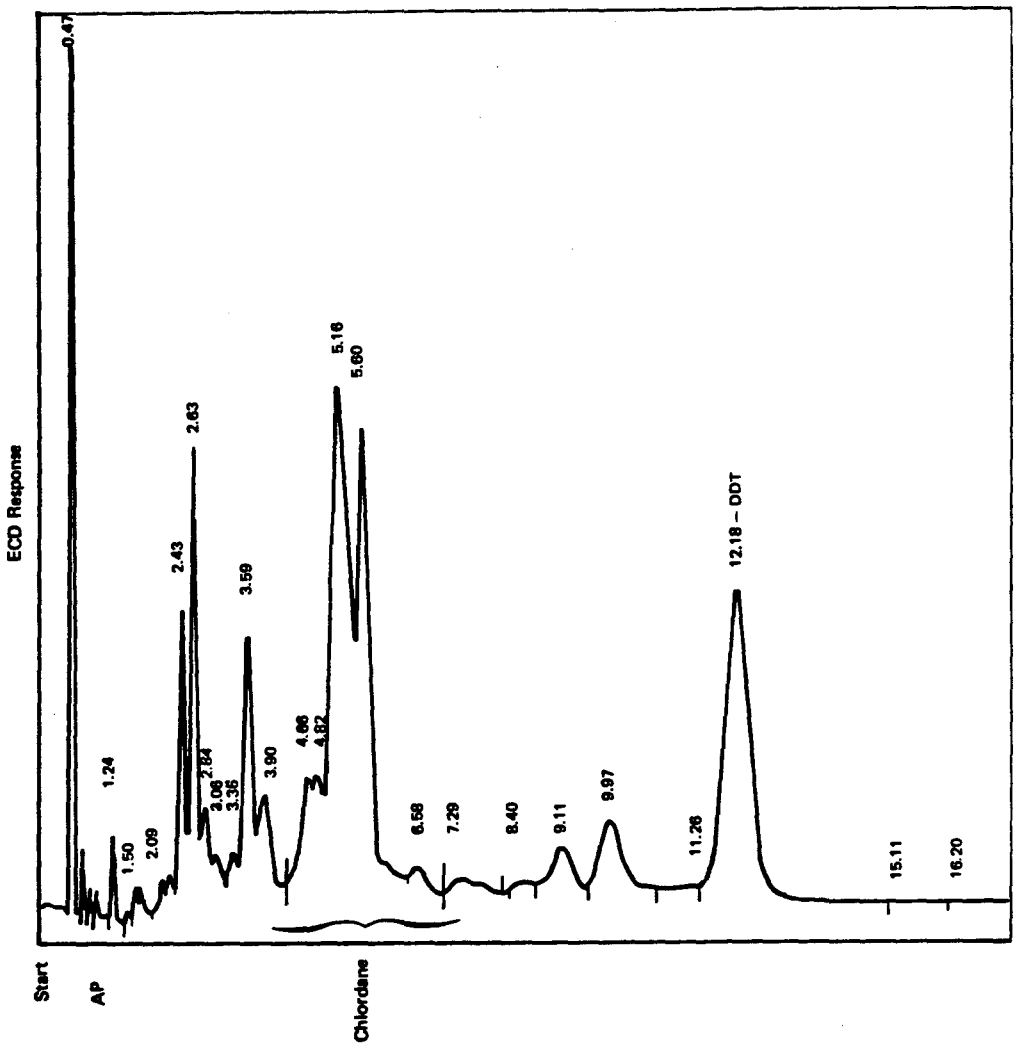

FIGURE S278-1 CHROMATOGRAM OF CHLORDANE ANALYTICAL STANDARD

aliquots of the solution to the combined filter and Chromosorb 102 and air-dry to produce samples equivalent to 0.5, 1.0 and 2.0 times the OSHA standard for a 120-liter collection. Six samples at each of the three levels are prepared. A parallel blank sample is also prepared except that no chlordane is added to it. All samples are then extracted and analyzed as described in Section 8.4.

The sample recovery equals the average weight in µg recovered from the sample divided by the weight in µg added to the sample, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered - Blank (µg)}}{\text{Weight (µg) Added}}$$

9. Calibration and Standardization

9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/mL versus peak area of the five selected peaks. The use of an internal standard such as DDT (final concentration 0.4 µg/mL) is recommended.

9.2 From the stock standard solution (Section 7.4) appropriate aliquots are withdrawn and dilutions are made in toluene. Prepare at least six working standards to cover the range of 0.05 to 1.8 µg/mL. This range is based on a 120-liter sample.

9.3 Analyze samples as described in Section 8.4. These samples need not be filtered.

9.4 Prepare a standard calibration curve by plotting concentration of chlordane in µg/mL versus peak area of the five selected peaks.

10. Calculations

10.1 Read the weight, in µg, corresponding to the peak area from the standard curve. Multiply the µg found per mL by the dilution factor for the sample in question.

10.2 A correction for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where

µg sample = µg found in sample filter and sorbent

µg blank = µg found in blank filter and sorbent

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled (liter/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of chlordane in the air sample can be expressed in mg/cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.2)}}{\text{Volume of Air Sampled (liters)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report No. S278 for Chlordane prepared under NIOSH Contract No. 210-76-0123.

11.3 Brooks, G.T., Chlorinated Insecticides, Vol. 1, Chapter 3, CRC Press, Inc., Cleveland, Ohio, 1974.

11.4 Thompson, D.W., J.A.O.A.C., Vol. 53, No. 5, 1015-1017 (1970).

Analyte:	Demeton-O[a] and Demeton-S[b]	Method No.:	S280
Matrix:	Air	Range:	0.06-0.33 mg/cu m
OSHA Standard:	0.1 mg/cu m - skin	Precision ($\overline{CV}_T$):	0.08
Procedure:	Collection on mixed cellulose ester filter followed by XAD-2, desorption with toluene, GC/FPD	Validation Date:	8/3/79

1. Synopsis

1.1 A known volume of air is drawn through a filter cassette containing a 37-mm mixed cellulose ester filter (MCEF) followed by a glass tube containing XAD-2 sorbent to trap the two isomers of demeton.

1.2 The filter and sorbent are combined and the demeton-O and S isomers are desorbed with toluene as one sample. This sample is analyzed by gas chromatography utilizing a phosphorous sensitive flame photometric detector. Each isomer elutes separately and is quantitated individually.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 0.03-0.14 mg/cu m for demeton-O and 0.03-0.19 mg/cu m for demeton-S at an atmospheric temperature of 25°C and pressure of 757 mm Hg, using a 480 liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method depends on the absorptive capacity of the XAD-2 and the collection efficiency of the MCEF used. This capacity may vary with the concentration of each demeton isomer and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection device (the MCEF and the tube containing 150 mg of XAD-2) reaches 5% of the concentration in the test mixture. Breakthrough did not occur with the demeton isomers at a concentration of 74.5 mg/cu m for demeton-O and at a concentration of 91.8 mg/cu m for demeton-S after sampling for 730 minutes at a sampling rate of approximately 1.0 liter/minute and a relative humidity of 81% and temperature of 23°C.

[a] 0,0-diethyl O-2 (ethylthio) ethyl phosphorothioate (I)
[b] 0,0-diethyl S-2 (ethylthio) ethyl phosphorothioate (II)

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2.3 Under the instrumental conditions used in the study, a sensitivity of approximately 1000 mV-sec/ng was obtained for either isomer.

2.4 The detection limit of the method is estimated to be 0.1 microgram for either isomer per sample.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as either demeton-O or demeton-S at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.06-0.33 mg/cu m (for both isomers combined) was 0.080. The value corresponds to a 0.080 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 1. Details of the test procedures are found in Reference 2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at three levels in the range of the OSHA environmental limit for demeton-O averaged 102.2% higher than the dynamically generated test concentrations (n = 17). The concentrations obtained for demeton-S averaged 99.2% higher than the dynamically generated test concentrations (n = 17). The recovery of demeton-O was determined to be 0.977 and 1.007 for a sorbent and filter loading of 19.04 micrograms, respectively. The recovery of demeton-S was determined to be 0.980 and 0.967 for a sorbent and filter loading of 33.4 micrograms, respectively. Desorption efficiency tests were performed using samples containing both isomers. In storage stability studies, the mean of demeton-O samples analyzed after 7 days was within 5% of the mean of samples analyzed immediately after collection. The means of demeton-S samples analyzed after 7 days was within 4% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 The precision of the method is limited by the reproducibility of the pressure drop across the sampling device. This drop will affect the

flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one sampler only.

6. Apparatus

6.1 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined with 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative sampling device in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Filter unit. The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer, supported by a stainless steel screen on a 37-mm two-piece cassette filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.

6.3 XAD-2 Tubes. The sampling tube consists of a glass tube with both ends unsealed, 7-cm long with a 8-mm O.D. and a 6-mm I.D. packed with two sections of 20/50 mesh XAD-2.* The two sections in the sampling tube include a front absorbing section containing 150 mg of XAD-2 and a backup section containing 75 mg. A plug of silylated glass wool is placed at the ends of the tube and between the two sections of XAD-2. The pressure drop across the total sampling device must be less than 1 inch of mercury at a flow rate of 1.0 liter/minute. Before use the XAD-2 must be extracted in a Soxhlet extractor first with water, then methanol, and finally methylene chloride for 20-24 hours per extraction. The XAD-2 is then dried at 50°C for 2 hours in a vacuum oven.

Immediately prior to packing, the empty glass tubes should be rinsed with acetone and dried to eliminate the problem of XAD-2 adhering to the walls of the glass tubes. The tubes are capped with plastic caps at each end.

6.4 The filter cassette and sorbent tube are connected with a short piece of plastic tubing. The open cassette is plugged and the sorbent tube end capped.

6.5 Manometer.

6.6 Thermometer.

6.7 Gas chromatograph equipped with a phosphorous sensitive flame photometric detector.

6.8 Column (6-ft long x 1/4-in O.D. glass) packed with 1.5% OV-17/1.95% OV-210 on 80/100 mesh Gas-Chrom Q.

6.9 An electronic integrator or some other suitable method of determining peak areas.

*XAD-2 is a porous polymer manufactured by Rohm and Haas Company.

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6.10 Microliter Syringes: 10-microliter, 50-microliter.

6.11 Pipets: 5-mL and other convenient sizes for preparing standards.

6.12 Volumetric Flasks: Convenient sizes for preparing standard solutions.

6.13 Scintillation Vials: 20-mL with Teflon-lined screw caps or equivalent.

6.14 Stopwatch.

6.15 Manometer.

6.16 Tweezers.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Demeton-O/Demeton-S mixture of known composition. The mixture is commercially available containing approximately 20% demeton-O and 75% demeton-S. An analysis of the mixture should be provided by the supplier. The mixture of isomers is reported to be more stable than the separated isomers.

7.2 Stock standard. Approximately 2.4 mg/mL Demeton-O and 8.3 mg/mL Demeton-S. Prepare a solution by taking 50 microliters of concentrate (7.1 above) and diluting to 5mL with toluene.

7.3 Toluene

7.4 Methanol

7.5 Methylene Chloride

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples.

8.2.1 Immediately before sampling, remove the cap and plug from the ends of the cassette and sampling tube. All tubes must be packed with XAD-2 from the same manufacturer's lot and the same cleanup batch.

8.2.2 Connect the sampling train to the pump with the XAD-2 backup section nearest the sampling pump.

8.2.3 The sampling device should be placed in a vertical direction during sampling to minimize channeling through the XAD-2.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.2.5 Set the flow rate as accurately as possible using the pump manufacturer's directions. A sample size of 480 liters is recommended. Sample at a flow rate of 1.0 liter/minute. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and the sampling should be terminated at any evidence of a problem.

8.2.6 Record sampling time, flow rate, and type of sampling pump used. The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.7 After sampling, carefully remove the filter from the cassette with tweezers and place in a 20-mL scintillation vial with the front section of the XAD-2 sorbent and front glass wool plug. Cap the sorbent tube containing the back section. Under no circumstances should the sampling devices be left open to the the air. The filter and sorbent are combined in order to prevent losses from the filter upon storage.

8.2.8 With each batch or partial batch of ten samples, submit one sampling device from the same lot of devices used for sample collections. This tube and filter must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this tube and filter as blanks. A minimum of 24 extra XAD-2 tubes should be provided for desorption efficiency determinations, if these tests have not been performed prior to sampling.

8.2.9 Capped vials and sorbent tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the sample vials and sorbent tubes.

8.3 Analysis of Samples

8.3.1 Remove the plastic caps from both ends of the XAD-2 sorbent tube and transfer the back XAD-2 section to a scintillation vial separate from the vial containing the filter and front XAD-2 section. Pipet 5 mL of toluene into each vial and cap. The two samples are analyzed separately.

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8.3.2 Swirl the sample vigorously. Desorption is complete within 15 minutes. Analysis should be completed within one day after the sample is desorbed.

8.3.3 GC conditions. The typical operating conditions for the gas chromatograph are:

55 mL/min	carrier gas	N_2
35 mL/min		air
150 mL/min		H_2
20 mL/min		O_2

165°C column temperature
200°C inlet manifold temperature
210°C detector manifold temperature

8.3.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eleiminate difficulties arising from blow back or evaporation of solvent within the syring needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2-microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2-microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0-microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.3.5 Using the column recommended in Section 6.8, demeton-O would have a retention time of 4.0 minutes; and demeton-S, a retention time of 7.5 minutes under the conditions described above.

The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

8.4.1 In the validation study, samples collected of demeton test atmospheres showed that the majority of demeton-S was collected on the filter and the majority of demeton-o was collected on the sorbent. Since the desorption efficiency of a particular

compound may vary from one laboratory to another and also from one batch of XAD-2 to another, it is recommended that the desorption efficiency be determined for demeton-0 from XAD-2.

8.4.2 It is recommended that desorption efficiency be determined before samples are collected. A desorption efficiency of greater than 95% should be obtained. If not, a new clean-up batch or manufacturer's lot of XAD-2 sorbent should be tested prior to collection of samples. XAD-2 sample tubes, prepared as described in Section 6.3, are used to determine desorption efficiency. The XAD-2 must be from the same batch as that used in obtaining the samples. A known amount of a toluene solution (Section 7.2) is injected directly into the XAD-2 with a microliter syringe, and the tube is capped with plastic caps. The amount injected is equivalent to that present in a 480-liter air sample at the selected level.

Six tubes at each of four levels (0.25X, 0.5X, 1X, and 2X the OSHA standard) for the 0 isomer are prepared in this manner and allowed to stand overnight to assure complete adsorption of the demeton-0 onto the XAD-2 sorbent. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed as described in Section 8.3.

8.4.3 The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg) - Blank (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency may be dependent on the amount of the demeton-0 adsorbed on the XAD-2. Plot the desorption efficiency versus the weight of the isomer found. This curve is used in Section 10.4 to correct for adsorption losses.

A desorption efficiency of greater than 95% is expected in which case no correction would be necessary. Desorption efficiency of less than 95% may cause inaccuracies that cannot be corrected by use of a DE factor.

9. Calibration and Standardization

9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for each demeton isomer is prepared and analyzed under the same GC conditions and during the same period as the unknown samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.

A curve is established for each isomer by plotting concentration in mg/5 mL versus peak area.

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9.2 From the stock standard solution (Section 7.2) appropriate aliquots are withdrawn and dilutions are made in toluene. Prepare at least 5 working standards to cover the range of 2-8 mg/mL for each isomer. This range is based on a 480-liter sample.

9.3 Analyze the samples as described in Section 8.3.

9.4 Prepare a standard calibration curve for each isomer by plotting the concentration of each isomer in mg/5 mL versus peak area.

10. Calculations

10.1 Read the weight of each isomer in mg corresponding to each peak area from the corresponding standard curve. No volume correction is needed, because the standard curve is based on mg/5 mL toluene and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each isomer in the sample

mg = mg sample - mg blank

where:

mg sample = mg found in combined filter and front section of sample tube

mg blank = mg found in combined blank filter and front section of blank tube.

A similar procedure is followed for the backup section.

10.3 Add the weights of each isomer found in the front and backup sections to determine the total weight of each isomer in the samples.

10.4 Read the desorption efficiencies of demeton-O from the curve (Section 8.4.3) for the amount found in the sample. Divide the total weight of demeton-O by the appropriate desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Weight demeton-O (Section 10.3)}}{\text{D.E.}}$$

10.5 Add the corrected mg/sample of demeton-O to the mg/sample of demeton-S to obtain the total weight of both isomers in the sample.

Total mg = Corr mg demeton-O + mg demeton-S

10.6 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Corrected Volume} = f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

f = flow rate sampled (liters/min)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.7 The concentration of demeton in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Total mg (Section 10.5) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.6)}}$$

11. References

1. Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

2. Backup Data Report No. S280 for Demeton (Systox) prepared under NIOSH Contract No. 210-76-0123.

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Endrin

Analyte:	Endrin	Method No.:	S 284
Matrix:	Air	Range:	0.06 - 0.31 mg/cu m
OSHA Standard:	0.1 mg/cu m - skin	Precision (CV_T):	0.071
Procedure:	Collection on MCEF/ Chromosorb 102, desorption with toluene, GC/EC	Validation Date:	7/6/79

1. Synopsis

1.1 A known volume of air is drawn through a 37-mm mixed cellulose ester filter (MCEF), contained in a two-piece cassette filter holder followed by a glass tube containing Chromosorb 102 to trap endrin particulate and vapor.

1.2 Endrin is desorbed from the filter, filter cassette, and Chromosorb 102 with toluene, and the samples are analyzed by gas chromatography using an electron capture detector.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 0.06-0.31 mg/cu m at an atmospheric temperature of 26°C and atmospheric pressure of 762 mm Hg, using a 120-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method depends on the adsorptive capacity of the filter and the Chromosorb 102. This capacity may vary with the concentrations of endrin and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 200 mg of Chromosorb 102) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 240 minutes at an average sampling rate of 0.943 liter/minute and relative humidity of 81% and temperature of 26°C. The breakthrough test was conducted at a concentration of 0.257 mg/cu m.

2.3 Under the instrumental conditions used in the validation study, a sensitivity of approximately 1,100 mV sec/ng was obtained.

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2.4 The detection limit of the method is estimated to be at least 20 nanograms endrin per sample or 20 picograms per injection.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as endrin at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.06-0.31 mg/cu m was 0.71. This value corresponds to a 0.007 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit averaged 0.6% lower than the dynamically generated test concentrations (n=18). The desorption efficiency was determined to be 0.981 for a sorbent loading of 1.228 micrograms. A recovery of 0.980 was determined for a filter loading of 6.14 micrograms. In storage stability studies, the mean of samples analyzed after 7 days was within 0.6% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The sample is analyzed by means of a quick, instrumental method.

5.2 The precision of the method is limited by the reproducibility of the pressure drop across the filter and sorbent tube. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one sampling device only.

6. Apparatus

6.1 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. Each personal sampling pump must be calibrated with a representative sampling device in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Filter unit. The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.8 micrometer, supported by a stainless steel screen on a 37-mm two-piece cassette filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.

6.3 Chromosorb 102 Tubes. The sampling tube consists of a glass tube with both ends unsealed (7 cm long X 6 mm I.D.) packed with two sections of 20/40 mesh Chromosorb 102.* Before packing the tubes, the Chromosorb 102 must be cleaned to remove residual organic materials which may alter its sorptive characteristics. A Soxhlet extraction is used to extract the Chromosorb 102 for two hours with a 1:1 solution of methanol:acetone, followed by one hour drying in a vacuum oven at 115°C. Desorption efficiency tests should be performed prior to use, as described in Section 8.4.

To prepare the sampling tubes, the glass tubes are rinsed with acetone and dried, and packed with the cleaned sorbent. The front section contains 200 mg Chromosorb 102, and the backup section contains 100 mg Chromosorb 102. A plug of silylated glass wool is placed between the two sections and at each end. The pressure drop across the tube must not exceed 1 inch of mercury at a flow rate of 1.0 L/min.

6.4 Sampling Device. The filter cassette and sorbent tube are connected with a short piece of plastic tubing, placing the front sorbent section nearest the cassette. The open cassette is plugged and the sorbent tube end capped.

6.5 Gas chromatograph equipped with a Ni 63 electron capture detector and linearizer.

6.6 Column (6-ft long x 4-mm I.D. glass) packed with 3% OV-1 on 100/120 mesh Chromosorb Q.

6.7 An electronic integrator or some other suitable method of determining peak areas.

6.8 Microliter Syringes: 10-microliter.

6.9 Pipets. 10-mL and other convenient sizes for preparing standards.

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*Chromosorb 102 is a porous polymer manufactured by Johns-Manville Company.

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6.10 Volumetric Flasks. Convenient sizes for preparing standard solutions.

6.11 Scintillation Vials. 20-mL with Teflon-lined screw caps or equivalent.

6.12 Stopwatch.

6.13 Manometer.

6.14 Tweezers.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Toluene.

7.2 Hexane.

7.3 Acetone.

7.4 Methanol.

7.5 Xylene.

7.6 Endrin.

7.7 Endrin Stock Standard Solution. Weigh out approximately 30 mg of endrin, dissolve in 1 mL xylene and dilute to 10 mL with hexane.

7.8 95% Argon/5% methane mixture, purified.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the cap and plug from the ends of the cassette and sorbent tube. All tubes must be packed with Chromosorb 102 from the same manufacturer's lot and the same cleanup batch.

8.3 8.2.2 The tube is connected to the pump with backup section nearest the sampling pump.

8.2.3 The sampling device should be placed in a vertical direction during sampling to minimize channeling through the Chromosorb 102.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter/minute. The flow rate should be known with an accuracy of 5%.

8.2.6 Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.2.7 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.2.8 After sampling, carefully remove the filter from the filter cassette with tweezers and place in a clean glass 20-mL scintillation vial. Transfer the front glass wool plug and front Chromosorb 102 section to the same vial, and cap. Cap the tube containing the backup Chromosorb 102 section with plastic caps. Reassemble the filter cassette and cap the inlet and outlet with plastic plugs. Under no circumstances should rubber caps or plugs be used. The sampling devices should not be left open to the air. The filter and sorbent are combined in order to prevent losses from the filter upon storage.

8.2.9 With each batch or partial batch of ten samples, submit one sampling device from the same lot of sampling devices used for sample collection. This filter, cassette, and sorbent tube must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this cassette, filter, and sorbent tube as blanks. A minimum of 18 extra Chromosorb 102 tubes should be provided for desorption efficiency determinations, if these tests have not been performed prior to sampling.

8.2.10 Capped sampling devices and vials should be packed tightly and padded before they are shipped to minimize breakage during shipping. Postal regulations and DOT procedures should be followed when mailing samples.

8.2.11 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined

cap or equivalent. This sample should not be transported in the same container as the samples.

8.3 Analysis of Samples

8.3.1 Pipet 5.0 mL of toluene into the vial containing the filter and front Chromosorb 102 section, and cap. Mix the solution by swirling.

8.3.2 Remove the plastic caps from the sorbent tube containing the backup Chromosorb 102 section and transfer the entire contents to a separate glass vial. Pipet 5.0 mL toluene into the vial, cap, and mix.

8.3.3 Desorption is complete within 15 minutes. Analysis should be completed within one day after the sample is desorbed.

8.3.4 Wash the filter cassette parts by the following procedure: Pipet 10.0 mL of hexane into a glass scintillation vial and mark the level. Remove the contents and allow to dry. Place the bottom-part cassette on the open marked vial. Invert the top-part cassette and place it on the bottom-part cassette. Hold the metal screen over the set-up with clean tweezers. Rinse the screen with 10.0 mL hexane, allowing the rinse to drain from top cassette through bottom cassette to the marked vial. Remove any remaining rinse from the cassette parts with clean disposable pipet and deposit in the marked vial. Dilute with hexane to the marked levels. Cap immediately.

8.3.5 GC Conditions. The typical operating conditions for the gas chromatograph are:

60 mL/min carrier gas
23 mL/min purge
} (40 psig) argon/methane

175°C injector manifold temperature
280°C detector manifold temperature
160°C column temperature

8.3.6 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow-back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to

separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0-microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

A retention time of approximately 5 minutes is to be expected for endrin under the above conditions and using the column recommended in Section 6.

8.3.7 The area of the analyte peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 102 to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Chromosorb 102. It is recommended that the desorption efficiency of Chromosorb 102 be determined prior to collection of samples. A desorption efficiency of 95% or greater should be obtained. If lower results are obtained a different clean-up batch or manufacturer's lot of Chromosorb 102 should be tested. Since the filter and sorbent are combined for analysis, a correction due to desorption (or recovery) would not be appropriate unless it was exactly the same for the filter as well as for the sorbent. In the validation study quantitative recoveries were obtained for both filters and sorbents.

8.4.2 Chromosorb 102 sample tubes, prepared as described in Section 6.3 are used to determine desorption efficiency. The Chromosorb 102 must be from the same batch as that used in obtaining the samples. A known amount of a toluene solution of endrin containing 3.05 mg/mL (Section 7.7) is injected directly into the front section of Chromosorb 102 with a microliter syringe, and the tube is capped with plastic caps. The amount injected is equivalent to that present in a 120-liter air sample at the selected level.

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Six tubes at each of three levels (0.1X, 0.25X, and 0.5X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the endrin onto the Chromosorb 102. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

8.4.3 Standards are prepared by adding the appropriate volume of spiking solution to 5.0 mL of toluene with the same syringe used in preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

8.4.4 The desorption efficiency (D.E.) equals the average weight in µg recovered from the tube divided by the weight in µg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (µg) - Blank (µg)}}{\text{Weight added (µg)}}$$

The desorption efficiency may be dependent on the amount of endrin collected on the Chromosorb 102. A desorption efficiency of greater than 95% is expected, in which case no correction would be necessary. Desorption efficiency of less than 95% may cause inaccuracies that cannot be corrected by use of a DE factor.

9. Calibration and Standardization

9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the analyte, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/5.0 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the electron capture detector response.

9.2 From the stock standard solution of endrin in toluene (Section 7.7), appropriate aliquots are withdrawn and dilutions are made in toluene. Prepare at least 5 working standards to cover the range 1.2-36 micrograms/5 mL. This range is based on a 120-liter sample.

9.3 Analyze the standards as described in Section 8.3.

9.4 Prepare a standard calibration curve by plotting concentration of endrin in micrograms/5 mL versus peak area.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak area from the standard curve. No volume corrections are needed for the filter and sorbent samples because the standard curve is based on micrograms/5.0 mL and the volume of sample injected is identical to the volume of the standard standards injected. The amount collected on the cassette is multiplied by 2 to correct for the 10.0 mL cassette wash volume.

10.2 Corrections for the blank must be made for each sample

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg = sample = μg found in front section of sample tube and filter
μg = blank = μg found in blank tube and filter

A similar procedure is followed for the backup section and the cassette.

10.3 Add the weights found in the front and backup sections and the cassette wash to determine the total weight of the sample.

10.4 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

f = flow rate sampled (liters/min)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

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10.5 The concentration of endrin in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Total } \mu\text{g (Section 10.3)}}{\text{Corrected air volume sampled (liters) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D. C., Order No. 017-033-00231-2.

11.2 Backup Data Report No. S284 for Endrin, prepared under NIOSH Contract No. 210-76-0123.

Phosdrin (Mevinphos®)

Analyte:	Phosdrin	Method No.:	S296
Matrix:	Air	Range:	0.0270-0.145 mg/cu m
OSHA Standard:	0.1 mg/m^3	Precision ($\overline{CV}_T$):	0.069
Procedure:	Adsorption on Chromosorb 102, desorption with toluene, GC/FPD	Validation Date:	7/6/79

1. Synopsis

1.1 A known volume of air is drawn through a tube containing Chromosorb 102 to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

1.2 The Chromosorb 102 in each tube is transferred to respective vials and the phosdrin is desorbed with toluene. An aliquot of this sample solution is injected into a gas chromatograph equipped with a flame photometric detector.

1.3 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 0.027-0.145 mg/cu m at atmospheric temperatures of 24.0 and 23.7, and atmospheric pressures of 772.3 and 760.0 mm Hg using a 240-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the absorptive capacity of the Chromosorb 102. This capacity varies with the concentrations of phosdrin and other substances in the air. When an atmosphere at greater than 80% relative humidity containing 0.197 mg/cu m of phosdrin was sampled at 1.0 liter per minute, 0.6% breakthrough was observed after 360 minutes. With the sample volume used, the upper limit is estimated to be in excess of 260 µg phosdrin per sample or 1.11 mg/cu m.

2.3 The detection limit was not rigorously determined but is estimated to be at least 0.2 µg under the conditions used.

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3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.027-0.145 mg/cu m was 0.0694. This value corresponds to a 0.007 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1, and 2 times the OSHA standard were 3.9% greater than the dynamically generated test concentrations (n = 18). The desorption efficiency was determined to be 0.951 for a collector loading of 13.30 µg. In storage stability studies, the mean of samples analyzed after seven days was within 1.6% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of phosdrin found on the backup Chromosorb 102 section exceeds 25% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling at 1.0 liter per minute for 240 minutes. The pump must be accurate to within ±5% at the recommended flow rate.

6.1.2 Sampling Tubes. The sampling tube consists of a glass tube, 10-cm long with an 8-mm O.D. and a 6-mm I.D., packed with two sections of 20/40 mesh cleaned Chromosorb 102. The front adsorbing section contains 100 mg and the backup section contains 50 mg. The two sections are separated by a portion of silylated glass wool. A plug of silylated glass wool is placed at each end of the sorbent tube. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1.0 liter per minute.

6.2 Gas chromatograph with a flame photometric detector.

6.3 Column, 6-ft x 1/4 in O.D. (2-mm I.D.) glass, packed with Super-Pak 20M.

6.4 An electronic integrator or some other suitable method for measuring peak areas.

6.5 Microliter syringes, 10- and 100-microliter, and other convenient sizes for making standards and for taking sample aliquots.

6.6 Pipettes, 1-mL, delivery type.

6.7 Volumetric flasks, 10-mL or other convenient sizes for making standard solutions.

6.8 Sample vials, 2-mL with Teflon-lined screw caps.

7. Reagents

Wherever possible, reagents used should be ACS reagent grade or better.

7.1 Phosdrin, analytical grade (available from Chem Service, Inc., Westchester, PA).

7.2 Toluene, reagent grade.

7.3 Phosdrin stock solution, 6 mg/mL. Weigh 60 mg of analytical grade phosdrin into a tared 10-mL volumetric flask. Dissolve the phosdrin using 10 mL of toluene.

7.4 Helium, purified.

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

7.7 Pre-cleaned Resin. Chromosorb 102, 20/40 mesh (Johns Manville Corp., or Analabs, Inc.) is purified by Soxhlet extraction using a 1:1 methanol acetone solution for two hours. The resin is then dried at 115°C in a vacuum oven for one hour.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sorbent tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the caps at the ends of the sampling tubes should be removed.

8.3.2 The section containing 50 mg of Chromosorb 102 is used as a backup and should be positioned nearest the sampling pump. The Chromosorb 102 tube should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the front section of the Chromosorb 102 tube.

8.3.4 A sample size of 240 liters is recommended. Sample at a known flow rate between 0.2 and 1.0 liter per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 The Chromosorb 102 tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling.

8.3.6 One Chromosorb 102 tube should be handled in the same manner as the sample tubes, except for the taking of an

air sample. This tube should be labeled as a blank. Submit one blank for every batch or partial batch of ten samples.

8.3.7 A sufficient number of unused Chromosorb 102 tubes should be available for use in desorption efficiency studies in conjunction with these samples, because desorption efficiency may vary from one batch of Chromosorb 102 to another. Record the batch number of the Chromosorb 102 used. A minimum of eighteen tubes should be submitted.

8.3.8 Capped Chromosorb 102 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.9 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes. This sample should not be transported in the same container as the samples.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis each tube is scored with a file and broken open. The glass wool is removed and, with the Chromosorb 102 in each tube, is transferred to a 2-mL screw-cap sample vial. Each tube is analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 1.0 mL of toluene is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 28 mL/min (53 psig) helium carrier gas flow
2. 50 mL/min (50 psig) hydrogen gas flow to detector
3. 200 mL/min (50 psig) air flow to detector
4. 190°C injector temperature
5. 215°C manifold temperature (detector)
6. 170°C column temperature

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A retention time of approximately two minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 102 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of phosdrin found in the samples.

The analytical samples are prepared as follows: Chromosorb 102, equivalent to the amount in the front section (100-mg), is measured into a 2-mL screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of phosdrin in toluene (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µL aliquot is used to prepare the analytical samples.

Six analytical samples at each of the three concentration levels (0.5, 1 and 2X the OSHA standard) are prepared by adding an amount of phosdrin equivalent to a 240-liter sample at the selected level. A stock solution containing

6 milligrams of phosdrin per milliliter of toluene is prepared. Aliquots (2.0, 4.0 and 8.0 µL) of the solution are added to the Chromosorb 102 vials to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples are allowed to stand overnight to assure complete adsorption of the analyte onto the sorbent. A parallel blank vial is treated in the same manner except that no sample is added to it.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 1.0 mL of toluene with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

The desorption efficiency (D.E.) equals the average weight in µg recovered from the vial divided by the weight in µg added to the vial, or

$$DE = \frac{\text{Average Weight (µg) Recovered - Blank (µg)}}{\text{Weight (µg) Added}}$$

The desorption efficiency may be dependent on the amount of phosdrin collected on the sorbent. Plot the desorption efficiency versus weight of phosdrin found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards varying in concentration over the range corresponding to 240-liter collections at 0.1-3 times the OSHA standard is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. This is done in order to minimize the effect of variations in FPD response.

9.1 From the stock solution listed in Section 7.3 prepare at least five standards to cover the concentration range of 2.4-72.0 µg/mL. This is done by adding 4-120 µL aliquots of the stock solution to 10 mL of toluene in volumetric flasks or other suitable containers.

9.2 The series of standards is analyzed under the same conditions and during the same time period as the unknown samples. It is convenient to express concentration of standards in µg/1.0 mL because the samples are desorbed in this amount of solvent. Curves are established by plotting concentrations in µg/1.0 mL versus peak area.

10. Calculations

10.1 Read the weight, in µg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on µg per 1.0 mL and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the sample blank (Section 8.3.6) must be made for each sample:

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample vial

µg blank = µg found in blank vial

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{123.54} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature (°C) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

123.54 = molecular weight of phosdrin

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Phosdrin (Mevinphos®), No. S296, prepared under NIOSH Contract No. 210-76-0123.

Pyrethrum

Analyte:	Pyrethrum	Method No.:	S298
Matrix:	Air	Range:	1.413-8.47 mg/cu m
OSHA Standard:	5.0 mg/cu m	Precision ($\overline{CV_T}$):	0.0702
Procedure:	Filter collection, extraction with acetonitrile, HPLC	Validation Date:	8/3/79

1. Synopsis

A known volume of air is drawn through a glass fiber filter to trap the pyrethrum aerosol present. The filter is transferred to a sample jar and extracted in 10 mL of acetonitrile. An aliquot of the sample is injected into a high performance liquid chromatograph equipped with a UV detector set at 225 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 1.413-8.47 mg/cu m using a 120-liter sample. This method may be extended to higher values by further dilution of the sample solution.

2.2 The detection limit of the analytical method is estimated to be 1 µg per mL for a 25-µL injection at a range of 0.1 absorbance units with a recorder range of 10 mV full scale.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any other compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data based on a single set of conditions cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 1.413-8.47 mg/cu m was 0.0702. This value corresponds to a 0.351 mg/cu m standard deviation at the OSHA standard level. Statistical information may be found in Reference 11.1.

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4.2 In validation experiments, this method was found to be capable of coming within 25% of the "true value" on the average of 95% of the time over the validation range. The concentrations obtained at 0.5, 1 and 2 times the OSHA standard were 0.8% lower than the dynamically generated test concentrations. The analytical method recovery was determined to be 106.1% for a collector loading of 0.300 mg. In storage stability studies the mean of samples analyzed after seven days was within 5% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of organic particulate has the following components:

6.1.1 Filter. The filter unit consists of a 37-mm diameter, glass fiber filter (minimum of 99.9% retention for particles of 0.3 μm) and a 37-mm diameter cellulose backup pad.

6.1.2 Filter Holder. The filter is placed in a two-piece filter holder held together by tape or a shrinkable band.

6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate is needed. The pump must be calibrated with a representative filter unit in the line.

6.1.4 Thermometer.

6.1.5 Barometer.

6.1.6 Stopwatch.

6.2 High pressure liquid chromatograph equipped with a detector capable of UV detection at 225 nm.

6.3 HPLC column (30-cm x 3.9-mm I.D. stainless steel) packed with μ-Bondapak C_{18}, Waters Associates, Milford, Mass., or equivalent.

6.4 A syringe or fixed volume sample loop for HPLC injection. A 25-µL sample volume was used for the validation studies.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes in convenient sizes for making standard solutions.

6.7 Volumetric flasks in convenient sizes for making standard solutions.

6.8 Squat form 2-oz. ointment jars with Teflon film gaskets and screw caps.

6.9 A 10-mL pipette.

6.10 Tweezers.

7. Reagents

Whenever possible reagents used should be ACS reagent grade or better.

7.1 Pyrethrum (20.00%) analytical standard solution from McLaughlin Gormley King Co.

Note: Analytical grade pyrethrum comes as a solution varying in concentration from 20% to 60% depending on the supplier. The actual analysis is supplied with the standard.

7.2 Acetonitrile, distilled in glass.

7.3 Isopropanol, distilled in glass.

7.4 Pyrethrum stock solution, 60 mg/mL. Prepare by diluting 3 mL of the above standard solution to 10 mL in isopropanol.

7.5 HPLC mobile phase, 85% acetonitrile - 15% water.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the two-piece filter holder and close firmly to insure that the edge of the filter is

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sealed. The filter is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.2.2 Remove the filter holder plugs and attach to the personal sampling pump tubing. Clip the filter holder to the worker's lapel.

8.2.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.

8.2.4 A sample size of at least 120 liters is recommended. Sample at a flow rate of one liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.2.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and readjusted as necessary. If the rotameter cannot be readjusted, terminate sampling.

8.2.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.2.7 After sampling, holders should be firmly sealed with filter holder plugs in both the inlet and outlet.

8.2.8 Carefully record sample identity and all relevant sample data.

8.2.9 Obtain a blank sample by handling one filter in the same manner as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples or partial batch of ten samples.

8.2.10 A bulk sample of the suspected material should be submitted to the laboratory in a glass container lined with a Teflon cap.

8.2.11 The filter holders should be shipped in a suitable container designed to prevent damage in transit. Never transport the bulk sample in the same container as the sample or blank filters.

8.3 Analysis of Samples

8.3.1 Preparation of Samples

1. Open the filter holder. Carefully remove the filter from the holder with the aid of tweezers and transfer to the 2-oz ointment jar.

2. Add 10 mL of acetonitrile to the jar and cap the unit. Gently swirl the jar to ensure that the filter is thoroughly wetted. Allow to stand for thirty minutes with intermittent swirling of the jar.

8.3.2 Analysis by High Pressure Liquid Chromatograph. The mobile phase is 85% acetonitrile and 15% water. The typical operating conditions for the liquid chromatograph are:

1. 1.0 mL/min solvent flow rate

2. Ambient column temperature

3. 400 psi system pressure

4. 225 nm UV detection wavelength

8.3.3 Injection. A 25-µL sample aliquot is recommended for this analysis. The sample may be injected either by using an appropriate syringe or by filling a fixed volume sample loop, provided that reproducibility requirements are satisfied. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.3.4 Measurement of Area. The area of the two major sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed in Section 9.

8.3.5 The retention times of the two sample peaks are approximately 315 and 415 seconds under these conditions (see Figure S298-1).

8.4 Determination of Analytical Method Recovery

8.4.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery determinations should cover the concentration range of interest.

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8.4.2 Procedure for Determining Recovery. A known amount of pyrethrum, equivalent to that present in a 120-liter sample at the selected level, is added to a glass fiber filter and air-dried. A stock solution containing 60.0 milligrams of pyrethrum per milliliter of isopropanol is prepared. Add 5, 10 and 20-microliter aliquots of the solution to the filter and air-dry to produce samples equivalent to 120-liter collections at 0.5, 1 and 2 times the OSHA standard. Six filters at each of the three levels are prepared and allowed to stand overnight. A parallel blank filter is also prepared except no sample is added to it. All filters are then extracted and analyzed as described in Section 8.3.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Recovered - Filter Blank (mg)}}{\text{Weight (mg) Added}}$$

9. Calibration and Standardization

9.1 From the stock solution listed in Section 7.4, prepare at least six standards to cover the concentration range of 0.006 - 0.180 mg/mL. This may be done by adding from 1 to 30 microliter aliquots of the stock solution to 10 mL acetonitrile in ointment jars. Analysis is done as described in Section 8.3.

9.2 The series of standards is analyzed under the same HPLC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/mL versus peak area of the two major peaks.

Note: Pyrethrum is a mixture of at least six components. Because of their similarities, the mixture chromatographs as two major peaks. The minor peaks have been shown by mass spectrometry not to be pyrethrums.

10. Calculations

10.1 Read the concentration in mg/mL corresponding to the sample peak area from the standard curve. Multiply the mg found per mL by the dilution factor of ten.

10.2 Corrections for the sample blank (Section 8.2.9) must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter

mg blank = mg found in sample blank filter

10.3 Divide the weight of analyte found on each filter by the recovery (Section 8.4) to obtain the corrected mg/sample.

$$\text{Corrected mg sample} = \frac{\text{Weight found}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min). If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = sampling flow rate (Lpm)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m, which is numerically equal to µg/L, by

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ L/cu m}}{\text{Air Volume Sampled (L)}}$$

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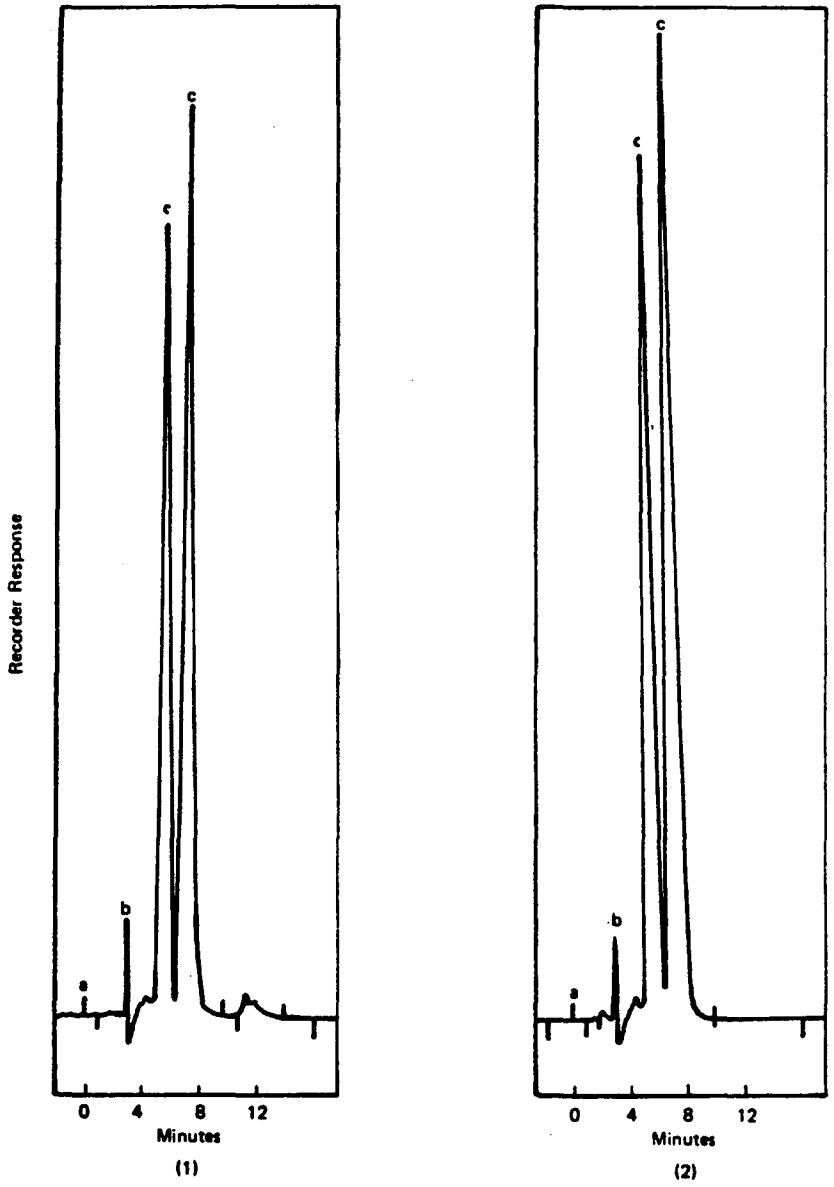
11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.

11.2 Backup Data Report for Pyrethrum, S298, prepared under NIOSH Contract No. 210-76-0123, 8/3/79.



(1) Standard solution: a = point of injection; b = solvent peak; c = pyrethrum peaks

(2) Generated sample extracted from filter: a = point of injection; b = solvent peak; c = pyrethrum peaks

FIGURE S298–1 LIQUID CHROMATOGRAM OF PYRETHRUM

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Analyte:	Ronnel	Method No.:	S299
Matrix:	Air	Range:	2.82-17.1 mg/cu m
OSHA Standard:	10 mg/cu m	Precision ($\overline{CV}_T$):	0.080
Procedure:	Filter/sorbent collection, extraction with toluene, GC/FPD	Validation Date:	8/3/79

1. Synopsis

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter followed by a Chromosorb 102 sorbent tube to trap the particulate and vapors present.

1.2 The filter and sorbent are transferred to a jar or other suitable container and ronnel is extracted with toluene.

1.3 An aliquot of the sample is injected into a gas chromatograph equipped with a phosphorus flame photometric detector.

1.4 The area of resulting sample peak is used as a measure of analyte concentration by comparison with corresponding areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

2.1 The method was tested over the range of 2.815-17.11 mg/cu m at an atmospheric temperature and pressure of 27°C and 761.7 mm Hg, using a 120-liter sample. The method may be capable of measuring smaller amounts if the analytical recovery is adequate. Analytical recovery must be determined over the range used.

2.2 The upper limit of the method depends upon the adsorptive capacity of the Chromosorb 102. This capacity may vary with the concentration of ronnel in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. Five percent breakthrough was not observed for up to 210 minutes at a sampling rate of 1.0 liter per minute and relative humidity of 85% and temperature of 24°C. The breakthrough test was conducted at an average concentration of 26.99 mg/cu m.

2.3 The detection limit of the analytical method was not rigorously determined but is estimated to be at least 0.2 µg/sample.

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3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Volatile phosphorus-containing compounds are the only major possible interferences due to the selectivity of the detector. Any such compound having the same retention time as the analyte will interfere. Retention time data based on a single set of conditions cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.815-17.11 mg/cu m was 0.080. This value corresponds to a 0.80 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedure are found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average of 95% of the time over the validation range. The concentrations measured at 0.5, 1 and 2 times the OSHA standard were identical to the dynamically generated concentrations (n = 18). The analytical recovery was determined to be 99.7% for a collector loading of 0.588 mg. In storage stability studies, the mean of samples analyzed after seven days was within 6.4% of the mean of samples analyzed the day after collection. Experiments performed in these studies are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable and involves no liquids. Interferences are minimal and most of those which do occur may be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

5.2 The amount of sample that can be taken is limited by the number of micrograms that the tube will hold before overloading. When the amount of ronnel found on the backup section exceeds 25% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the sampling train. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one device only.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of mixed vapor/particulate samples has the following components:

6.1.1 Filter. The filter unit consists of a mixed cellulose ester membrane filter, 0.80 micrometer pore size and 37-mm diameter, supported by a stainless-steel screen (Mine Safety Appliances Co., catalog number 456224), and a 37-mm, two-piece filter holder held together by tape or a shrinkable band.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump is needed whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a representative sampling train in the line.

6.1.3 Chromosorb 102 Tubes. The tubes are constructed of glass tubing with both ends unsealed. The tubes are approximately 10-cm long with a 10-mm O.D. and an 8-mm I.D. The front section contains 100 mg of 20/40 mesh Chromosorb 102 and the backup section contains 50 mg. Chromosorb 102 is held in place in the tube with 3-mm plugs of silanized glass wool. A 3-mm plug also separates the two sections. To facilitate handling of the Chromosorb 102 resin, the tubes should be acetone rinsed and dried. This reduces the problem of the resin adhering to the walls of the tube.

6.1.4 Thermometer.

6.1.5 Barometer.

6.1.6 Stopwatch.

6.2 Connection of Filter Holder and Sorbent Tube. The Chromosorb 102 tube is connected to the outlet of the two-piece filter holder using a modified Luer-lock to 1/4-in I.D., tubing adapter (Millipore Corp., catalog number XX30025 64) and 1/4-in I.D., Tygon tubing.

6.3 Gas chromatograph equipped with a phosphorus specific flame photometric detector.

6.4 Column (6-ft x 2-mm I.D., glass) Superpak 20M (Analabs, Inc.).

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes in convenient sizes for making standard solutions.

6.7 Volumetric flasks in convenient sizes for making standard solutions.

6.8 Squat form ointment jars with Teflon film gaskets and screw caps for desorption of samples.

6.9 A 15-mL pipette.

6.10 Tweezers.

7. Reagents

Whenever possible reagents used should be ACS reagent grade or better.

7.1 Ronnel.

7.2 Toluene.

7.3 Hydrogen, prepurified.

7.4 Air, filtered, compressed.

7.5 Nitrogen, dried.

7.6 Helium, dried.

7.7 Ronnel, 24 mg/mL stock solution. Prepare by adding 24 milligrams of ronnel to a tared 2-mL septum capped vial. Add 1 mL of toluene to dissolve the ronnel.

7.8 Pre-cleaned Resin. Chromosorb 102, 20/40 mesh (Johns Manville Corp. or Analabs, Inc.) is purified by extraction in a Soxhlet extractor using 1:1 methanol acetone solution for two hours. The resin is then dried at 115°C in a vacuum oven for one hour.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative sampling train in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the two-piece filter holder and close firmly to insure that the center ring seals the edge of the filter. The mixed cellulose ester membrane

filter is held in place by a stainless steel screen and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the top piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter.

8.3.2 Remove the filter holder plugs and sorbent tube caps and assemble the sampling train. Attach the outlet of the sorbent tube to the personal sampling pump tubing. Clip the sampler to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter holder.

8.3.4 A sample size of 120 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 120 minutes.

8.3.5 Turn the pump on and begin collection. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be checked frequently and readjusted as needed. If the rotameter cannot be readjusted, terminate sampling.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 After sampling, remove the sorbent tube and Luer-lock adapter from the outlet of the filter holder and connect to the inlet side. Cap the open end of the sorbent tube and plug the outlet of the filter holder with the plugs supplied. Under no circumstances should rubber caps be used.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 With each batch of samples, submit one sampling train which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples.

8.3.10 The sampling train should be shipped in a suitable container designed to prevent damage in transit.

8.3.11 A bulk sample of the suspected material should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match

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air samples for identification purposes. This sample should not be transported in the same container as the sample.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the filter from the holder with the aid of appropriate tweezers and transfer to a 2-oz ointment jar.

2. Add the front glass wool plug from the sorbent tube and the front section of Chromosorb 102 to the same container as the filter.

3. Add 15 mL of toluene to the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

4. The backup Chromosorb 102 section is added to a different container and analyzed separately.

5. If the internal standard method is used, add the internal standard solution in place of toluene.

8.4.3 Analysis by Gas Chromatography. The typical operating conditions for the gas chromatograph are:

1. 20 mL/min (45 psig) helium carrier gas flow.
2. 35 mL/min (60 psig) hydrogen flow to detector.
3. 200 mL/min (60 psig) air flow to detector
4. 230°C injector temperature.
5. 250°C detector temperature.
6. 185°C column temperature.

A retention time of 4 minutes is expected for ronnel.

8.4.4 Injection of Sample. A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative can be used provided that duplicate injections of a solution agree well. No more that a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery determination should cover the concentration range of interest.

8.5.2 Procedure for Determining Recovery. A known amount of ronnel, equivalent to that present in a 120-liter sample at the selected level, is added to a mixed cellulose ester membrane filter and Chromosorb 102 in a 2-oz. ointment jar. A stock solution containing 240 milligrams of ronnel per milliliter of toluene is prepared. Add 2.5, 5.0 and 10.0 microliter aliquots of the solution to the filter and sorbent to produce samples equivalent to 120-liter collections at 0.5, 1 and 2 times the OSHA standard. Six samples at each of the three levels are prepared and allowed to stand overnight. A parallel blank sample is also prepared except that no sample is added to it. All samples are then extracted and analyzed as described in Section 8.4.

The sample recovery equals the average weight in mg recovered divided by the weight in mg added, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Recovered - Blank (mg)}}{\text{Weight (mg) Added}}$$

9. Calibration and Standardization

A series of standards, varying in the concentration range corresponding to approximately 0.1 to 3 times the OSHA standard for the samples under study, is prepared and analyzed under the same GC conditions. The standards should be interspersed throughout the set of samples.

9.1 From the stock solution listed in Section 7.7, prepare at least six standards to cover the concentration range of 0.12-3.6 mg/15 mL. This is done by adding from 5-150 microliter aliquots of the stock solution to 15 mL of toluene in ointment jars or other suitable containers. Analysis is done as described in Section 8.4.

9.2 The series of standards is analyzed under the same GC conditions and during the same time period as the unknown samples. It is convenient to express concentration of standards in mg/15 mL, because samples are extracted in this amount of solvent. Curves are established by plotting concentrations in mg/15 mL versus peak area.

9.3 For the internal standard use toluene containing a predetermined concentration of internal standard to desorb the samples. The concentration of internal standard used should be such that it falls within the linear range of detector response.

10. Calculations

10.1 Read the concentration in mg/15 mL corresponding to the sample peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/15 mL and the volume of the sample injected is identical to the volume of standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample
mg blank = mg found in blank

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected mg sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 For personal sampling pumps with rotameters only, the following corrections should be made:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) x 1000 liters per cu m}}{\text{Volume of Air Sampled in Liters}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, Washington, D.C., Order No. 017-33-00231-2.

11.2 Backup Data Report for Ronnel, NIOSH Method No. S299, prepared under NIOSH Contract No. 210-76-0123, August 3, 1979.

Organo (Alkyl) Mercury

Analyte:	Mercury	Method No.:	S342
Matrix:	Air	Range:	0.02-0.08 mg/cu m (Ceiling)
OSHA Standard:	0.04 mg/cu m - Ceiling 0.01 mg/cu m - 8-hr T.W.A.		0.004-0.017 mg/cu m (T.W.A.)
Procedure:	Adsorption on Carbosieve B, thermal desorption, flameless AA	Precision (CV_T):	0.100 (Ceiling) 0.070 (T.W.A.)
		Validation Date:	6/10/77

1. Synopsis

1.1 A known volume of air is drawn through a glass tube containing Carbosieve B (CB) to trap alkyl mercury vapors.

1.2 The sample is analyzed by thermally desorbing the alkyl mercury, decomposing it to mercury, and passing it through the absorption cell of a flameless atomic absorption spectrophotometer.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 0.02-0.08 mg/cu m (ceiling) at an atmospheric temperature of 23°C and atmospheric pressure of 760 mm Hg, using a 3-liter sample. The method was also validated over the range of 0.004-0.017 mg/cu m (T.W.A.) at an atmospheric temperature of 23°C and atmospheric pressure of 760 mm Hg using a 12-liter sample. The method is capable of measuring smaller amounts. A longer AA absorption cell path length may be needed for levels below 0.004 mg/cu m.

2.2 The upper limit of the range of the method depends in most part upon the capacity of the AA detector with the particular absorption cell used. This is due to non-Beer's Law behavior at the higher concentrations. To extend the range, a shorter absorption cell path length may be needed. Scale expansion can extend the measurable range to a limited degree. It is unlikely that the absorptive capacity of the CB will affect the upper limit of the range of the method in view of the analytical limitations.

Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 12 mg of CB) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.3 hours at an average sampling rate of 0.184 liter/minute and relative humidity of 86% and temperature of 20°C. The breakthrough test was conducted at a concentration of 0.385 mg/cu m.

2.3 The sensitivity of the method using a 0 to 1.0 absorbance scale is estimated to be at least 0.005 microgram Hg/0.01 absorbance for the 4-cm cell in this study. Greater sensitivity can be achieved with an optical cell of longer path length.

2.4 The lower limit of detection in the validation study was 0.001 microgram mercury.

3. Interferences

3.1 In atmospheres where elemental mercury is expected to be present, the sampling device should consist of a 0.8-micrometer/37-mm mixed cellulose ester filter followed by a silvered Chromosorb P (AgCP) sorbent tube and then the Carbosieve B sorbent tube. The mixed cellulose ester filter collects particulate mercury and AgCP collects elemental mercury. It has been reported that AgCP absorbs methyl mercury chloride while most other organo mercury compounds are not retained. In the validation study it was demonstrated with dimethyl mercury that collection efficiency is not decreased when using the MCEF/AgCP pre-collection media. Analysis of AgCP samples for mercury should be performed according to NIOSH Method No. S199.

3.2 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.02-0.08 mg/cu m (ceiling) was 0.100. This value corresponds to a 0.004 mg/cu m standard deviation at the OSHA standard ceiling level. The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.004-0.017 mg/cu m (T.W.A.) was 0.070. This value corresponds to a 0.0007 mg/cu m standard deviation at the T.W.A. standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

4.2 In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the ceiling OSHA environmental limit average 6.8% lower than the dynamically generated test concentration (n = 17).

The concentration obtained at 0.5, 1, and 2 times the T.W.A. OSHA environmental limit averaged 5.9% lower than the dynamically generated test concentrations (n = 18). Storage stability studies on samples collected from a test atmosphere at a concentration of 0.0107 mg/cu m (T.W.A.) indicated that collected samples are stable for at least 7 days. The mean of samples analyzed after 7 days were within 6.3% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal and the tubes are analyzed by means of a quick, instrumental method.

5.2 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

5.3. A disadvantage of the method is the care needed to avoid contamination of the outer surfaces of the sampling tubes.

5.4 Another disadvantage is that the complete sample is used in the analysis. However, the sample may be recollected on a AgCP tube after passage through the absorption cell and reanalyzed.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate. Each sampling pump must be calibrated with a representative CB tube and MCEF/AgCP (if used) in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Carbosieve B (CB) Sorbent Tubes: The sorbent tube consists of a glass tube with both ends unsealed, (2 cm long with a 6-mm O.D. and a 4-mm I.D.) containing 12 mg of 45/60 mesh Carbosieve B*. A plug of glass wool, preferably quartz glass wool, is placed at each end of the tube. The sampling tube is thermally desorbed in the thermal desorption apparatus as described in the analytical procedure to rid the sorbent of any background interferences. The tube is removed from the thermal desorption unit and allowed to cool. Caution: The tubes are hot when they are removed from the thermal desorption unit and should be dropped directly into a vial for cooling and storage. The sampling tube is sealed in the vial until it is used.

*Carbosieve B is a gas chromatographic column packing available from Supelco, Inc. (Bellefonte, PA).

6.3 Thermal Desorption Unit and Analysis System: A detailed description of the apparatus and instructions for installation and operation are given in Appendix A.

6.4 Flameless atomic absorption mercury analyzer with recorder set at 253.7 nm; Coleman Mercury Analysis System (MAS-50) or equivalent atomic absorption spectrophotometer.

6.5 Absorption Cell: 4.0 cm length (3.7 cm inside diameter), made of Pyrex glass with quartz windows. Satisfactory results may be obtained with cells of different path lengths and dimensions. The system used must be calibrated over the expected concentration range.

6.6 Microliter Syringes: 10-microliter for preparing standards.

6.7 Pipets: Delivery type, 1.0-mL and other convenient sizes.

6.8 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.

6.9 Thermometer.

6.10 Manometer.

6.11 Stopwatch.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 Mercuric chloride. Other stable mercury salts or conventional atomic absorption standards may be used.

7.2 Nitric acid.

7.3 Distilled or deionized water.

7.4 Stock Solution: Prepare a stock standard solution containing 1.35 mg/mL mercuric chloride in 1% nitric acid. This is equivalent to 1.0 mg/mL mercury. Conventional atomic absorption standards, any stable mercury salt, or metallic mercury (dissolved in concentrated nitric acid) may be used.

Caution: It is not recommended to use an alkyl mercury compound to prepare standards because of their volatility and extreme toxicity.

7.5 Standard Working Solution A: 0.1 mg/mL, prepared by diluting 1.00 mL of stock solution to 10 mL with 1% nitric acid.

7.6 Standard Working Solution B: 0.03 mg/mL, prepared by diluting 3.00 mL of stock solution to 100 mL with 1% nitric acid.

8. Procedure

8.1 Cleaning of Equipment. Glassware used for preparing standards should be detergent washed, thoroughly rinsed with dilute nitric acid, distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Clean lint free gloves or laboratory wipers should be used when handling the sampling tubes. After the sampling tubes have been prepared and stored, they should be stable indefinitely. Immediately before sampling, remove the sample tube from the vial.

8.2.2 If elemental mercury is expected to be present, the sample tube is preceded by a 0.8-micrometer/37-mm MCEF to collect particulate mercury and an AgCP sorbent tube to collect mercury vapor. The filter is placed in a cassette filter holder and is supported by a cellulose backup pad. The MCEF, AgCP tube, and CB tube are connected with short pieces of flexible tubing.

8.2.3 The CB sample tube should be placed nearer the sampling pump and in a vertical position during sampling to avoid channeling through the sorbent.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the sampling device.

8.2.5 A sample size of 3 liters is recommended for ceiling level determinations. A 12-liter sample is recommended for 8-hr T.W.A. determinations. Sample at a flow rate between 0.01 and 0.2 liter/minute. Do not sample at a flow rate less than 0.01 liter/minute. For ceiling measurements, sample for 15 minutes, for T.W.A., 60 minutes. Record sampling time, flow rate, and type of sampling pump used.

8.2.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.7 After sampling, disconnect the filter cassette from the sampling tubes. Return the sorbent tube(s) to the glass vial(s). Do not store the AgCP tube and CB tube in the same vial. Mark the vial to identify the type of sorbent tube. Insert cotton into the vial to prevent breakage of the tube during shipping. Gloves or wipers should be used when handling the tubes. The MCEF should be discarded after sampling, and the filter cassette holder should be cleaned for future use.

8.2.8 With each batch of ten samples, submit one CB tube from the same lot of tubes used for sample collection. This tube must

be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank.

8.2.9 Vials containing the sample tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the CB sample tubes.

8.3 Analysis of Samples

8.3.1 Preparation of Analysis System. Turn on the atomic absorption spectrophotometer and allow the instrument to stabilize. Turn on the heating tape and the nitrogen carrier. Observe the rotameter to ensure that the flow through the system is approximately 1 liter/minute. Turn on the cooling air and adjust the flow to 20 liters/minute. Turn on the recorder, and allow it to stabilize. Adjust the spectrophotometer to the desired 0 and 100% T settings. Purge the thermal desorption system before analyzing samples by heating the first desorption section for 60 seconds and allowing it to cool for 60 seconds. Heat the second section for 30 seconds, and allow the desorption unit to cool for 5 minutes before analyzing samples.

Note: The thermal desorption system must be optimized so that 100% of the mercury is desorbed from the CB tube in one heating (Appendix A).

8.3.2 Preparation of Samples. Remove the clamp between the loading mechanism and desorption unit and insert the CB sample tube. Push the sample tube into the first desorption section using the plunger of the loading mechanism and replace the clamp.

8.3.3 Desorption of Samples. Turn the switch to heat the first section of the thermal desorption unit and heat the sampling tube for 60 seconds; allow it to cool for 60 seconds. Turn the switch to heat the second section for 30 seconds. Any mercury compound desorbed from the sample tube should produce an absorption signal at this time. Allow the thermal desorption unit to cool for about 30 seconds before opening the clamp on the loading mechanism to unload the used sample tube. Allow the unit to cool 60 seconds between samples.

Caution: The sample tube is very hot when it comes out of the desorption unit. Do not touch the tube with bare hands. Drop the hot tube into a dry beaker to cool.

Note: If the used sample tube does not drop when the plunger is removed, a narrow spatula may be used to loosen the tube. The CB sample tubes are reusable.

8.3.4 The absorption signal is recorded as a very sharp peak on the recorder. The height of the sample peak is measured, and the mercury level is read from a standard curve prepared as discussed below.

9. Calibration and Standardization

9.1 A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same conditions and during the same time period as the unknown samples. Curves are established by plotting micrograms versus peak height. Standards must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the AA response.

9.2 Aliquots of 1 to 10 microliters are withdrawn from the working standards (Sections 7.5 or 7.6) by microliter syringe and injected directly onto the CB in the sample tube. Prepare at least 5 working standards to cover the range of 0.012-0.036 microgram mercury. This range is based on a 3-liter sample for ceiling determinations and a 12-liter sample for T.W.A. determinations.

9.3 Prepare a standard calibration curve by plotting micrograms of mercury versus peak height. A minimum of five standards, replicated three times at each level, should be used in preparing the calibration curve.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each peak height from the standard curve.

10.2 Corrections for the blank must be made for each sample.

micrograms = micrograms sample - micrograms blank

where:

micrograms sample = micrograms found in sample tube
micrograms blank = micrograms found in blank tube

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10.3 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.4 The concentration of organo mercury as mercury in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{micrograms (Section 10.2)}}{\text{Corrected air volume sampled (liters)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Organo (Alkyl) Mercury, prepared under NIOSH Contract No. 210-76-0123.

Appendix A

Description, Installation, and Operation of the Two-Stage Thermal Desorption Unit for the Determination of Mercury and Organo (Alkyl) Mercury

Introduction

The thermal desorption unit described here was designed for the determination of mercury collected on 4-mm I.D. sampling tubes containing silvered Chromosorb P (AgCP) and organo mercury compounds collected on 4-mm I.D. sampling tubes containing Carbosieve B. Sampling tubes are inserted into the first section of the desorption unit where the sample is thermally desorbed and the resultant mercury transferred to a second section. Mercury collected on AgCP sorbent tubes is released directly upon thermal desorption. Organo mercury compounds are decomposed forming elemental mercury upon thermal desorption. Mercury salts, used as standards with either sorbent tube, are decomposed forming mercury also. The second section contains gold granules which amalgamate all the mercury released by the first section and allow impurities to pass. Mercury is then thermally desorbed from the second section and passed into a flameless atomic absorption spectrophotometer where the amount of desorbed mercury is determined.

Description

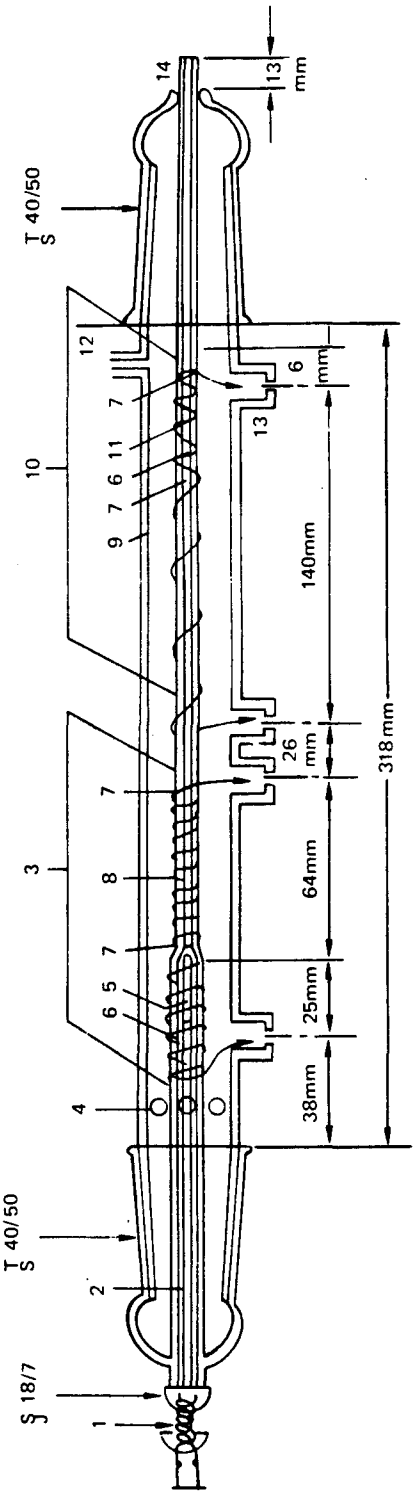
With the exception of the electrical components and the loading spring, the entire thermal desorption unit is made of either quartz or Pyrex glass. A diagram of the unit giving the critical dimensions is shown in Figure S342-A1. Each important part of the thermal desorption unit is numbered in the diagram and the numbers represent the following:

1-2. Loading mechanism (Figure S342-A2) - Made from a glass 18/7 female standard socket joint with steel spring (#1), and a plunger tube (3-mm or 4-mm O.D. quartz glass - #2). The length of the plunger is cut to reach the sample desorption section.

3. Sample desorption section - Made from 8-mm I.D. and 5-mm I.D. quartz tubing. The junction between the two sizes of tubing is tapered on the inside so that sampling tube tips fit snugly against the junction.

4. Cooling vent holes - About seven 4-mm holes are placed around the outer jacket of the unit to allow cooling air to flow from the second heating coil to the first coil.

5. Sampling tube - Sampling tubes are positioned inside the first desorption section during mercury desorption. The spring on the loading mechanism is adjusted to press the sampling tubes lightly in place.



1. LOADING MECHANISM
2. QUARTZ GLASS PLUNGER TUBE
3. SAMPLE DESORPTION SECTION
4. COOLING AIR VENT HOLES
5. SAMPLING TUBE
6. NICHROME WIRE COILS
7. QUARTZ GLASS WOOL PLUGS
8. CUPRIC OXIDE (CuO)
9. COOLING JACKET
10. SECOND DESORPTION SECTION
11. GOLD SECTION
12. COOLING AIR INTAKE
13. WIRE HOLES AND SOLDERLESS CONNECTORS
14. OUTLET

Figure S342-A1: THERMAL DESORPTION UNIT

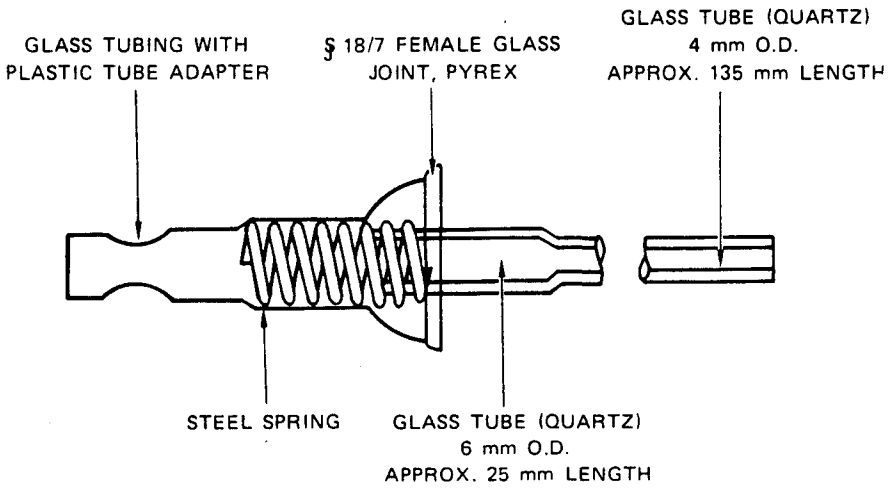


Figure S342-A2: LOADING MECHANISM

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6. Nichrome wire coils - Twenty-eight coils of 18 gauge nichrome wire are wrapped around the first desorption section to heat the sampling tubes during the thermal desorption step.

7. Quartz glass wool plugs - Quartz glass wool plugs are used to separate each section. Although the plugs should be large enough to hold the materials, they should not be packed too tightly.

8. Cupric oxide (CuO) - A 40-mm section of rod shaped CuO is placed just downstream from the sampling tubes. When heated, the CuO oxidizes organic vapors desorbed from the sampling tube. The CuO is held by a quartz glass wool plug which fits against a crimp in the glass tubing.

9. Cooling jacket - The Pyrex glass outer covering not only directs the flow of cooling air, but also acts as electrical insulation for the heating coils.

10. Second desorption section - This section is made from the 5-mm I.D. quartz glass tubing extending from the first desorption section. The contents are held in place by a crimp in the glass tube.

11. Nichrome wire coils - Thirty coils of size 20 nichrome wire are wrapped around the second desorption section. The coils are wrapped to allow most of the generated heat to concentrate over the gold granules of the second desorption section.

12. Gold section - This section consists of a 25-mm length of powdered gold mixed one-to-one with 20/40 mesh sea sand. The sand is added to the gold to prevent fusing of the gold granules and to allow better air flow through the section.

13. Cooling air intake - A 6-mm I.D. piece of glass tubing is used for connecting plastic tubing from the cooling air supply.

14. Wire lead throughs and solderless connectors - Wires to the heating coils enter the cooling jacket through 5-mm holes at the ends of glass nipples on the side of the jacket. The solderless connectors between the wires and the coils are placed inside the jacket to prevent exposing uninsulated wire outside the cooling jacket. The insulated wires to the connectors are sealed in place with a heat resistant sealer.

15. Outlet - The outlet from the desorption unit is butt connected with a Tygon overseal to a glass tube which leads to a flameless atomic absorption spectrophotometer (MAS-50). The end of the quartz tube slides through an opening at the end of the cooling jacket. The opening is kept to a minimum to limit the escape of cooling air.

Installation

A diagram of the installed thermal desorption unit system is shown in Figure S342-A3.

1. Power connections - The wires to the heating coils should be heavy enough to carry the current necessary to heat the coils (about #12). Power to the heating coils is controlled by a three position switch with an off position, an on position for the sample desorption section and on position for the gold section. Power to the switch comes from a 120 Vac Input, 20 A variable transformer set at between 20 and 30 Vac. The exact setting is determined by testing the thermal desorption unit for complete desorption of mercury from the sample tube in one heating. Complete desorption usually occurs when the CB sample tube reaches at least 300°C. Complete desorption of an AgCP sample tube usually occurs at 650°C. The time required for heating may vary slightly from what is stated in the method (60 sec). These variations are due to the spacing between heating coils and the concentration of heat near the sample tube and/or desorption sections.

2. Nitrogen Carrier - The nitrogen which passes through the thermal desorption unit is supplied by a compressed cylinder, the output of which is regulated by a needle valve at approximately 1 liter/minute. The nitrogen passes through the thermal desorption unit, through the flameless atomic absorption optical cell and into a filter containing Mersorb charcoal which collects any mercury desorbed by the desorption unit. Air from this charcoal filter then passes through a flow meter and is vented.

3. Cooling air - Cooling air for the heating coils is supplied by an air compressor. A flowmeter controls the flow rate at 20 liters/min. The air enters the desorption unit near the second desorption section.

4. Detection system - Mercury desorbed from the gold section of the thermal desorption system enters the optical cell of a flameless atomic absorption spectrophotometer through a glass tube. The glass tube connecting the desorption unit with the optical cell is maintained at 70°C using a heating tape. Power for the heating tape is supplied by a 120 Vac, 8 A variable transformer.

   Any reliable flameless atomic absorption spectrophotometer or mercury analysis system set to absorb the 253.7 nm wavelength of mercury may be used to detect the mercury vapor released from the desorption unit.

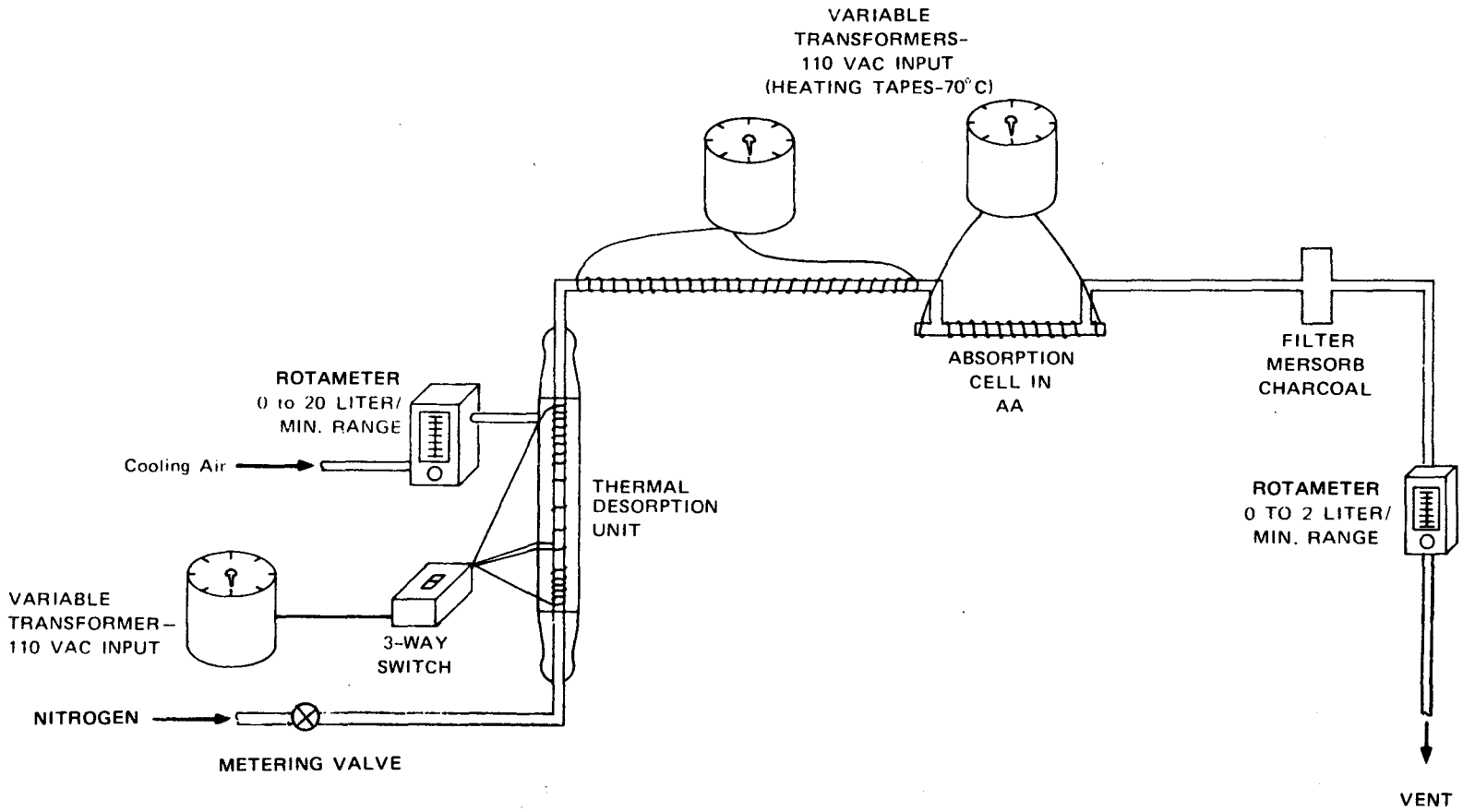

Figure S342-A3: MERCURY ANALYSIS SYSTEM

Operation

1. Turn on the atomic absorption spectrophotometer and allow to stabilize.

   Note: The time required for stabilization varies with the individual instruments.

2. Turn on the heating tape.

3. Turn on the nitrogen carrier.

4. Observe the rotameter to insure flow through the system has not been interrupted. It should be approximately 1.0 liter/min.

5. Turn on the cooling air and adjust cooling air flowmeter to 20 liters/min.

6. Turn on the recorder and allow to stabilize.

7. Adjust the spectrophotometer to the desired 0 and 100% T settings.

8. Purge the system before analyzing samples by heating the first desorption section of the desorption unit for 60 seconds, allow to cool 60 seconds, and then heating the second section for 30 seconds.

9. Allow the desorption unit to cool for five minutes before analyzing samples.

10. Remove the clamp between the loading mechanism and desorption unit and insert the sampling tube.

11. Push the sampling tube into the first desorption section of the desorption unit using the plunger of the loading mechanism and replace the clamp.

12. Switch the 3-way power switch to heat the first section of the thermal desorption unit and heat the sampling tube for the required time (usually 60 seconds).

13. After the first section is heated, allow unit to cool for 60 seconds and then switch the 3-way power switch to heat the second desorption section of the thermal desorption unit. This section is usually heated for about 30 seconds.

    Note: At this time the recorder will record the absorption signal of any mercury desorbed from the sampling tube.

14. Turn the 3-way switch to the off position.

15. Allow the thermal desorption unit to cool for about 30 seconds and open the clamp on the loading mechanism to unload the used sampling tube.

    Caution: The sampling tube is very hot when it comes out of the desorption unit. Do not touch the tube with bare hands. Drop the hot tube into a dry beaker to cool.

    Note: If the used sampling tube does not drop when the plunger is removed, turn off the air flow through the desorption unit using the shutoff valve and remove the tube with a metal rod.

16. Allow the thermal sorption unit to cool for 5 minutes. Reload the desorption unit with another sampling tube.

17. Repeat steps 11 through 16 for each analysis.

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