

NIOSH

NIOSH Manual of Analytical Methods

Second Edition

Volume 4

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

REPORT DOCUMENTATION PAGE	1. REPORT NO. 78-175	2.	3. Recipient's Accession No. PB83-105437
4. Title and Subtitle NIOSH Manual of Analytical Methods			5. Report Date August 1978
			6. NA
7. Author(s) Taylor, D.G.			8. Performing Organization Rept. No. NA
9. Performing Organization Name and Address Hazard Evaluation and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations, and Field Studies, NIOSH, Cincinnati, Ohio			10. Project/Task/Work Unit No. NA
			11. Contract(C) or Grant(G) No. (C) (G)
			13. Type of Report & Period Covered Technical Report 14.
12. Sponsoring Organization Name and Address Same as Above			
15. Supplementary Notes NA			
16. Abstract (Limit: 200 words) The fourth volume of the NIOSH Manual of Analytical Method contains 60 environmental monitoring methods. The NIOSH sampling and analytical procedures give step by step information and instructions on how to monitor for toxic chemicals found in the workplace. All but one of the methods is designed for personal air monitoring to determine exposures to individual workers. Each method is explained in 10 sections that include synopsis; working range, sensitivity and detection limit; interferences; precision and accuracy; advantages and disadvantages; apparatus; procedure; calibration and standardization; and calculations.			
17. Document Analysis a. Descriptors Analytical-method, Standards, Sampling, Standards-Completion-Program, SCP, Set-78-175 b. Identifiers/Open-Ended Terms c. COSATI Field/Group			
18. Availability Statement: Available to Public		19. Security Class (This Report) NA	21. No. of Pages
		20. Security Class (This Page)	22. Price

NIOSH MANUAL OF ANALYTICAL METHODS

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Manual Coordinator

VOLUME 4

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

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Center for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio

August 1978

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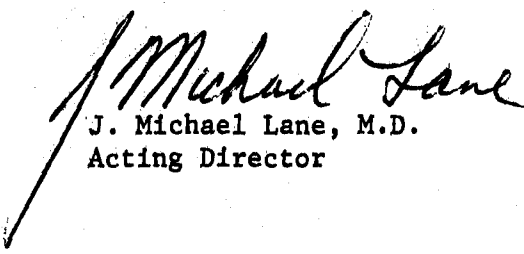
Mr. John V. Crable and Dr. David G. Taylor, respectively Chief and Assistant Chief of the Measurements Research Branch, were responsible for the development of this Manual.

DHEW (NIOSH) Publication No. 78-175

FOREWORD

This fourth volume is a supplement to the 3-volume NIOSH Manual of Analytical Methods published in 1977. It provides a single source for all of the methods developed and evaluated by NIOSH since the second edition of the manual was issued.

These personal monitoring methods are a necessary tool in evaluating the exposure of workers to toxic substances. Without them, compliance with the OSHA permissible exposure limits is not feasible. The publication of this volume brings to 400 the number of methods made available by NIOSH for monitoring the workplace.


J. Michael Lane, M.D.
Acting Director

PREFACE TO VOLUME 4

In 1977, the second edition of the NIOSH Manual of Analytical Methods was published. The second edition combined in a single source all of the NIOSH industrial hygiene monitoring methods for toxic substances. Since that time more of these methods have been developed and evaluated. This supplementary volume presents those sampling and analytical methods completed since the publication of the 3-volume second edition. These four NIOSH volumes provide a resource of nearly 400 methods for monitoring toxic substances in the workplace.

This volume can be used as a companion to the second edition. An Errata page for the second edition of the Manual has been included in this supplement. The method numbering system is the same as in the 1977 volumes. This allows the user to locate methods by NIOSH P&CAM- or S-number. In addition, a cumulative index to all four volumes is available at the end of this book to locate each method in the four-volume set. The NIOSH classification of the analytical methods is located in Volume 1 and in the American Industrial Hygiene Association Journal, 26:149 (1975). Finally, the newer methods have minor format changes. Some section titles have been modified and an acknowledgement line has been added at the end of the method to give direct credit to the author.

Copies of the previous 3 Volumes may be obtained by sending a self-addressed label with order to: The Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. Stock # Volume 1 - 017-033-00267-3 \$8.75, Volume 2 - 017-033-00260-6/\$9.75, and Volume 3 - 017-033-00261-4/\$9.00.

ABSTRACT

This fourth volume of the NIOSH Manual of Analytical Methods contains 60 environmental monitoring methods. These NIOSH sampling and analytical procedures give step-by-step information and instructions on how to monitor for toxic chemicals found in the workplace. All but one of the methods is designed for personal air monitoring to determine exposures to individual workers.

The majority of the methods have been validated using the protocol developed under the joint NIOSH/OSHA Standards Completion Program. The other methods have been only partly evaluated and are presented for your information and trial use.

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ACKNOWLEDGMENTS

All of the P&CAM-numbered methods have an author line following the references of their 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 and Alexander W. Teass and Mr. John L. Holtz is acknowledged. The help of Sandra Clark, Kay Laws, Grace Fannin, Eleanor Robers and Helen Fley in preparing the manuscript is greatly appreciated.

ERRATA TO SECOND EDITION

The following additions, changes, or corrections to methods appearing in Volume I (77-157-A), Volume II (77-157-B), and Volume III (77-157-C) of the Second Edition, NIOSH Manual of Analytical Methods are given below:

<u>Page Number; Section</u>	<u>Change</u>
<u>Volume 1</u>	
141-6; 8.3.4	"agitate for 30 seconds" <u>to</u> "agitate vigorously to evolve all the N ₂ from solution."
142-1; Box and 2.1	"0.007-0.073 ppm" <u>to</u> "0.07-0.747 mg/m ³ "
142-4; 8.2.3	"1 lpm" <u>to</u> "2.8 lpm"
142-4; 7.13	"0.1g" <u>to</u> "1.0g"
142-5; 8.3.5	"and stir" <u>to</u> "and stir vigorously to evolve all N ₂ and CO ₂ from solution."
142-6; 10.3	Replace Section 10.3 with "10.3 Calculate the concentration of MDI in the air sampled by dividing the amount found in micrograms by the volume of air sampled."
142-7; 10.4	Drop this section.
178-5; 8.2.2	"...backup and is...the first tube" <u>to</u> "...backup and is positioned immediately downstream and in tandem with the first tube."
183-1; 1.0	Add "See Ref 11.3" at end of paragraph.
183-12; 11.3	Add Reference 11.3 "T. D. Searl, F. V. Cassidy, W. H. King, and R. A. Brown, "An Analytical Method for Polynuclear Aromatic Compounds in Coke Oven Effluents by Combined Use of Gas Chromatography and Ultraviolet Absorption Spectrometry," <u>Analytical Chemistry</u> , <u>42</u> , 954 (1970)."
211-3; 8.4	"Because of the...sampling." <u>to</u> "The color takes two hours to fully develop at room temperature."
211-3; 9.4	"semi-log" <u>to</u> "linear"
239-1; Box	Change Precision to 0.11 - 0.41

239-5; line 10

Replace equation with:

$$CV_T = \left[(CV_F')^2 + (0.05)^2 \right]^{1/2}$$

where $CV_F' = \text{antilog}_{10} \left[0.595 - 0.3241(\log FB) - 0.0158(\log^2 FB) \right] - 0.12$
and FB is ..."

239-5,6; 6.1.5

Replace with the following:

6.1.5 Field Monitor (Filter and Holder).
Millipore or equivalent. The unit consists of (1) a three-section styrene plastic case for aerosol monitoring, (2) a 37-mm diameter plain white cellulose ester membrane filter, Millipore AA (pore size of 0.8 micrometer) or equivalent, (3) a support pad, and (4) two plastic sealing caps. If a large number of samples are to be taken, it may be less expensive to reuse the plastic cases. Great care must be taken in the cleaning and reassembly process. The outside mating surfaces of the field monitors may be covered with a "shrink-fit" band to provide proper sealing and a writing surface for filter identification.

239-15; 11.11

Replace with the following:

11.11 Busch, K. A., N. A. Leidel, R. W. Hornung, R. J. Smith, "Unbiased estimates of Coefficients of Variation for Asbestos Counting Determined from Johns-Manville Data," to be published August 1978 in the Proceedings of the Society for Occupational and Environmental Health Conference on "Occupational Exposures to Fibrous and Particulate Dust and Their Extension to the Environment."

239-18

Replace the old Figure 3 with the accompanying new Figure 3.

Volume 2

S8-4; 10.1

"51 mg" to "78.5 µg"

Volume 3

S293-6; 8.4.2, line 10

Spelling --desorption

NOTE: Each of the 3 volumes of the second edition has an Index in the back covering all methods in the second edition.

ZIRCONIUM OXIDE

Measurement Support Branch

Analytical Method

Analyte:	Zirconium Oxide	Method No.:	P&CAM 250
Matrix:	Airborne Dust	Range:	0.5-15 mg/m ³ in air
Procedure:	Filter Collection, Re-deposition, X-ray Diffraction	Precision:	8% (Analytical)
Date Issued:	8/1/78	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 zirconium oxide and other phases which may cause matrix interference.
- 1.4 The mass of zirconium oxide 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 20-1500 μg for pure zirconium oxide. This corresponds to an air concentration of 0.5-15 mg/m³. The range of the method is dependent on the amount of interfering substances and X-ray absorbing substances present.
- 2.2 The detection limit for pure zirconium oxide is 5 μg on a 25 mm silver filter; however, quantitative measurements cannot be made at this level.

3. Interferences

- 3.1 There are no known interferences; however, any crystalline material having a diffraction peak within $0.5^\circ 2\theta$ of the analyte diffraction peak will be an interference.

- 3.2 The presence of specific elements in the sample, e.g. iron, 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 effects of X-ray absorption by the sample may result in attenuation of the diffracted beam and correction must be made. (See Section 10).

4. Precision and Accuracy

- 4.1 The precision for the analytical method was determined to be 8% relative standard deviation over the working range 20-1500 μg pure zirconium oxide. The precision of the method is based on recovery studies at three levels: 50, 100, and 200 μg ZrO_2 /filter. Overall percent recovery was 95%.

- 4.2 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

- 5.1 The X-ray diffraction method is specific for zirconium oxide. It is non-destructive of the analyte; and, the ashing step helps eliminate organic and other volatile compounds that may interfere. The method is adaptable to automation.
- 5.2 Although the method is specific for the compound, the sensitivity is considerably poorer than that obtained for an elemental mercury determination obtained by P&CAM 175.

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 $\pm 5\%$ 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, 5 μm pore size. (Gelman VM-1 filters have been found to produce high background in the ash.)

- 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 0.80- μ m pore size: Sela's 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 asher.
- 6.8 Pyrex beakers, 50 mL.
- 6.9 Instrument calibration reference specimen, mica, Arkansas stone (alpha quartz) or other stable standard.
- 6.10 Filter storage cassettes.
- 6.11 Forceps.
- 6.12 Polyethylene wash bottle.
- 6.13 Microbalance.
- 6.14 Ultrasonic bath or probe.
- 6.15 Sonic sifter with assorted sieves including a 10- μ m sieve.
- 6.16 Assortment of pipettes, 2-25 mL.

7. Reagents

ACS Analytical Reagent Grade or Equivalent

- 7.1 Zirconium Oxide, <10 μ m particle size.
- 7.2 Glue, tape or other material necessary for attaching silver filters to filter holders.
- 7.3 Isopropanol.
- 7.4 Dessicant (Drierite).

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 l/min. A minimum sample volume of 90 L must be collected.

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 identity and all relevant sample data.

8.3.6 With each batch of ten samples, submit one filter from the same lot of filters used for sample collection and handle 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.

8.4 Sample Analysis

8.4.1 Obtain a qualitative X-ray diffraction scan (broad 2 θ

range) of the bulk dust sample to determine the presence of zirconium oxide and any matrix interference. The expected diffraction peaks are as follows:

	<u>2 Theta, Primary</u>	<u>2 Theta, Secondary</u>
Zirconium Oxide	28.16	31.20
Silver	38.12	44.28

- 8.4.2 Low Temperature Ashing of Samples. Using forceps, place 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 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 instrumental manual. After ashing add 15 mL of isopropanol to each beaker.
- 8.4.3 Ultrasonically agitate the beaker contents for 3 minutes.
- 8.4.4 Place a filter in the filtration apparatus and attach the funnel. Pour several mL 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 to a sample holder and insert in the diffractometer.
- 8.4.6 Analyze the most intense diffraction peak of zirconium oxide 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_z , 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, I , for each peak by dividing the peak intensity by that of the reference specimen. Examples for the zirconium oxide and silver peaks are:

$$\hat{I}_z = \frac{I_z}{I_r^o}$$

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

- 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 zirconium oxide standards

- 9.1.1 Dry sieve the zirconium oxide through a 10- μ m sieve using the sonic sifter.
- 9.1.2 Prepare two suspensions of zirconium oxide in isopropanol by weighing approximately 10- and 50 mg of the dry zirconium oxide to the nearest 0.01 mg in 50 mL beakers.
- 9.1.3 Measure 1.0 L of isopropanol in a volumetric flask. Add approximately 30 mL of isopropanol from the previously measured aliquot to the beaker and ultrasonically agitate the mixture for five minutes.
- 9.1.4 Add approximately one half of the remaining isopropanol to the suspension storage bottle. Place a magnetic stirrer in the bottle and stir the isopropanol.

- 9.1.5 When the ultrasonic agitation is complete quantitatively transfer the suspension to the stirred isopropanol. Rinse the beaker with several aliquots of the remaining isopropanol and add all rinsings to the suspension.
- 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 50 mg/l suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range.
- 9.1.8 Mount a 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, $\hat{I}_z^0$, for each peak measured.

10. Calculations

- 10.1 Calculate the exact weights of zirconium oxide 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_z^0 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 $\hat{I}_z^0$ axis should be approximately 0. 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, $\hat{I}_{\text{Ag}}^0$, for the silver peaks of each sample (sec. 8.4.8), and the $\hat{I}_{\text{Ag}}^0$ calculated for the clean side of the silver filter, calculate the transmittance, T , of each sample as follows:

$$T = \frac{\hat{I}_{\text{Ag}}}{\hat{I}_{\text{Ag}}^0}$$

- 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

$$R = \frac{\sin \theta_{\text{Ag}}}{\sin \theta_z}$$

and θ_{Ag} and θ_z are the angles θ (not 2θ) of the silver and zirconium oxide peaks. Table I lists $f(T)$ values for T values from 0.5 to 1.0 for common $2\theta_z$ and $2\theta_{\text{Ag}}$ combinations.

- 10.5 Calculate the weight, w , in micrograms of the ZrO_2 in each sample:

$$w = \frac{\hat{I}_z - b}{m} \times f(T)$$

- 10.6 If the sampling was conducted at a temperature and pressure near standard conditions (760 mm Hg pressure and 25°C), the

air volume need not be corrected. If other conditions existed, correct the volume in the following manner:

$$V_s = \frac{V_1}{1000} \times \frac{P}{760} \times \frac{298}{T+273}$$

where: V_s = volume of air in meters³ at 25°C and 760 mm Hg.

V_1 = volume of air in liters as measured

P = barometric pressure in mm Hg

T = temperature of the air in °C

- 10.7 Calculate the airborne concentration, C , of zirconium oxide in micrograms 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 Ref. 21, 26(1970).
- 11.2 Altree-William, S., "Quantitative X-ray Diffractometry on Milligram Samples Prepared on Silver Filters," Anal. Chem. 49, 429 (1977).

Donald D. Dollberg, Ph.D.
John Palassis
Measurements Services Section

TABLE I

Matrix Absorption Correction Factors
Zirconium Oxide/Silver Peaks, Degrees 2 θ

ZrO ₂	28.16	31.20	ZrO ₂	28.16	31.20	28.16	31.20
Ag	38.12	38.12	Ag	38.12	38.12	44.28	44.28
1.00	1.0000	1.0000	0.69	1.2696	1.2422	1.3148	1.2824
0.99	1.0068	1.0061	0.68	1.2811	1.2524	1.3283	1.2945
0.98	1.0136	1.0123	0.67	1.2928	1.2628	1.3421	1.3067
0.97	1.0206	1.0186	0.66	1.3047	1.2734	1.3561	1.3193
0.96	1.0276	1.0250	0.65	1.3168	1.2843	1.3705	1.3320
0.95	1.0348	1.0315	0.64	1.3293	1.2953	1.3852	1.3451
0.94	1.0421	1.0380	0.63	1.3420	1.3066	1.4002	1.3585
0.93	1.0495	1.0447	0.62	1.3549	1.3182	1.4156	1.3721
0.92	1.0570	1.0515	0.61	1.3682	1.3300	1.4313	1.3860
0.91	1.0646	1.0584	0.60	1.3817	1.3420	1.4473	1.4003
0.90	1.0724	1.0653					
0.89	1.0803	1.0724	0.59	1.3956	1.3543	1.4638	1.4149
0.88	1.0882	1.0796	0.58	1.4098	1.3669	1.4806	1.4298
0.87	1.0964	1.0869	0.57	1.4243	1.3798	1.4978	1.4451
0.86	1.1046	1.0944	0.56	1.4391	1.3930	1.5155	1.4607
0.85	1.1130	1.1019	0.55	1.4543	1.4065	1.5335	1.4767
0.84	1.1216	1.1096	0.54	1.4699	1.4204	1.5521	1.4932
0.83	1.1303	1.1174	0.53	1.4859	1.4345	1.5711	1.5100
0.82	1.1391	1.1253	0.52	1.5023	1.4490	1.5906	1.5272
0.81	1.1481	1.1334	0.51	1.5191	1.4639	1.6106	1.5449
0.80	1.1572	1.1416	0.50	1.5363	1.4792	1.6312	1.5631
0.79	1.1665	1.1499					
0.78	1.1760	1.1584	1.1937	1.1743			
0.77	1.1857	1.1671	1.2048	1.1842			
0.76	1.1955	1.1759	1.2161	1.1943			
0.75	1.2055	1.1848	1.2276	1.2046			
0.74	1.2157	1.1939	1.2393	1.2151			
0.73	1.2261	1.2032	1.2513	1.2258			
0.72	1.2366	1.2127	1.2635	1.2367			
0.71	1.2474	1.2223	1.2759	1.2478			
0.70	1.2584	1.2321	1.2886	1.2591			
			1.3016	1.2707			

1,2-DIBROMOETHANE

Measurements Research Branch

Analytical Method

Analyte:	1,2-Dibromoethane	Method No.:	P&CAM 260
Matrix:	Air	Range:	0.002 to 8.0 mg/m ³ for a 25-liter air sample
Procedure:	Charcoal adsorption, benzene-methanol desorption, GC-ECD analysis	Precision:	0.079 at 40 ng per sample (Analytical)
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a charcoal tube to trap the 1,2-dibromoethane vapor present.
- 1.2 The charcoal in the tube is transferred to a 10-ml volumetric flask and the analyte is desorbed with 10.0 ml of 99:1 benzene-methanol (v/v).
- 1.3 An aliquot of the desorbed sample is subjected to gas chromatographic analysis using an electron-capture detector.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The range of an electron-capture detector most useful for the quantitation of 1,2-dibromoethane depends upon the type of detector and chromatograph used. For a non-linearized ⁶³Ni electron-capture detector in a Tracor MT 220 Gas Chromatograph, the most useful range for quantitation was 20 to 400 pg of 1,2-dibromoethane per aliquot injected. This range corresponds to 40 to 80 ng of 1,2-dibromoethane per sample solution.

For a 25-liter air sample, this method is applicable to air concentrations which range from 0.002 to 8.0 mg/m³. The upper limit of the method depends upon the capacity of the charcoal tube and involves dilution of the sample solution.

2.2 The detection limit was approximately 4 pg per injection or 8 ng per sample solution.

3. Interferences

3.1 Compounds which are detected by the electron-capture detector and have retention times approximating that of 1,2-dibromoethane will interfere with the analysis.

3.2 When the amount of water in the air is so great that condensation actually occurs in the charcoal tube, vapors of 1,2-dibromoethane may not be trapped efficiently.

3.3 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.

4. Precision and Accuracy

4.1 The precision in relative standard deviation (RSD) versus the sample size for the analytical method is presented in the following table.

<u>Precision (RSD)</u>	<u>Sample Size (ng)</u>
0.032	2400
0.062	200
0.079	40

4.2 The precision and accuracy are affected by drift in detector response. Satisfactory precision can be realized by use of an appropriate internal standard.

4.3 Recoveries of analyte through desorption decrease with increasing storage times at room temperature. These decreases are more pronounced at lower levels of analyte. Storage of the charcoal tube samples at -25 °C permits satisfactory recoveries.

4.4 Dilution of the sample solution is a potential source of error. Solutions containing 1,2-dibromoethane in concentrations above the useful range of the detector must be diluted.

4.5 The capacity of the charcoal tube with respect to 1,2-dibromoethane is limited. When the sample loading in the backup section of the tube exceeds 10% of that found in the front section, the possibility of sample loss exists.

4.6 The precision of the method is dependent upon 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. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids.
- 5.2 The highly selective nature of an electron-capture detector dramatically reduces the potential number of interferences.
- 5.3 The use of an internal standard is required in order to attain good precision.
- 5.4 Recoveries of 1,2-dibromoethane from charcoal are decreased upon storage of the charcoal tube samples at room temperature, particularly at lower levels of analyte (See Section 4.3).

6. Apparatus

- 6.1 Personal sampling pump, the flow rate of which can be accurately determined at 200 ml per minute or less with the charcoal tube in line.
- 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 activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 °C prior to packing. 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 must be less than 25 torr at a flow rate of 200 ml/min.
- 6.3 Gas chromatograph equipped with an electron-capture detector. A glass tube filled with 20/40 mesh activated charcoal should be attached to the exit port in order to trap the 1,2-dibromoethane in the effluent gas stream. A glass tube with a 2-cm I.D. and a length of 25 cm was found to have little or no effect upon the retention time of 1,2-dibromoethane.
- 6.4 Gas chromatography column, 1.8 m x 4 mm I.D., constructed from borosilicate glass and packed with 3% OV-210 on 80/100 Gas Chrom Q.
- 6.5 Syringes, 10- μ l and other convenient sizes for preparing standard solutions.
- 6.6 Glass vials, 2-ml.
- 6.7 Pipets, 10.0-ml and 1.0-ml.
- 6.8 Volumetric flasks, 10.0-ml.
- 6.9 Parafilm.

7. Reagents

- 7.1 Benzene, pesticide quality
- 7.2 Methanol, pesticide quality.
- 7.3 99:1 Benzene-methanol (v/v).
- 7.4 1,2-Dibromoethane of known purity.
- 7.5 An appropriate internal standard, such as 1,1,2,2-tetrachloroethane or 1,2-dibromopropane. See Section 8.3.8.
- 7.6 A solution of internal standard in 99:1 benzene-methanol (v/v).

8. Procedure

8.1 Cleaning of Equipment

- 8.1.1 The syringes are rinsed well, first with methanol and then with benzene.
- 8.1.2 All other glassware should be cleaned with soap and water, then rinsed with the following in sequence: distilled water, pesticide quality methanol, pesticide quality benzene.

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 25 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 tube except that no air is drawn through it.

- 8.2.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling.
- 8.2.9 Low levels of 1,2-dibromoethane can not be stored on charcoal at ambient temperatures for long periods of time. Therefore, if the analysis can not be performed within 16-24 hours after sampling has been completed, the samples must be stored at -25 °C or below. Refrigerated samples may be stored for two weeks.
- 8.2.10 For shipment to the laboratory, the samples are packed firmly in an insulated container cooled with dry ice.
- 8.2.11 If appropriate, a sample of the bulk material in a glass container with a Teflon-lined cap is prepared and shipped to the laboratory in a separate container.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 10-ml volumetric flask. The separating section of polyurethane foam is removed and discarded. The charcoal in the second (smaller) section is transferred to a separate 10-ml volumetric flask. These two sections are analyzed separately.
- 8.3.2 Desorption of Samples. Prior to analysis, 10.0 ml of 99:1 benzene-methanol (v/v) is added to each 10-ml volumetric flask containing a section of charcoal. Each flask is stoppered and allowed to stand with occasional agitation over a 1-hour period.
- 8.3.3 GC conditions
- | | |
|---|-------------------------------------|
| nitrogen carrier gas flow: | 35 ml/min |
| inlet temperature: | 175 °C |
| detector temperature: | 315 °C |
| column temperature: | 50 °C |
| ⁶³ Ni detector operating mode: | DC at 90 to 95%
standing current |
- 8.3.4 Injection. By means of the solvent-flush injection technique, 5-μl aliquots of sample solutions are injected into the gas chromatograph.
- 8.3.5 After each injection, the syringe is rinsed thoroughly, first with methanol and then with benzene. Otherwise, traces of 1,2-dibromoethane will remain in the syringe and contaminate the solvent-flush solution. Periodically, an injection of solvent-flush solution only [99:1 benzene-methanol (v/v)] should be made to check the cleanliness of the syringe and the purity of the solvent-flush solution.

- 8.3.6 A preliminary analysis of the samples is run in order to determine: (a) whether the sample solutions are too concentrated for the useful range of the detector, and (b) which region of the chromatogram may be a suitable location for an internal standard peak.
- 8.3.7 If necessary, an appropriate volume of each original sample solution is diluted to 10.0 ml with 99:1 benzene-methanol (v/v). These diluted solutions should be reanalyzed in order to: (a) test whether the amount of 1,2-dibromoethane injected is now within the useful range of the detector and (b) aid in the selection of a suitable internal standard.
- 8.3.8 The use of an internal standard is required in order to compensate for changes in detector sensitivity with time. The approximate retention times of 1,2-dibromoethane and two potential internal standards [under the GC conditions described in this method] are:

Compound	Retention Time (min)	B.P. (°C)
1,2-Dibromoethane	2.2	131
1,2-Dibromopropane	2.9	140
1,1,2,2-Tetrachloroethane	4.1	146

The selection of an internal standard is based on three criteria:

- 8.4.8.1 Absence of components in the sample which would interfere with the internal standard.
- 8.4.8.2 Absence of adsorption of the internal standard by the charcoal while in 99:1 benzene-methanol (v/v) solution. If the internal standard is one other than 1,2-dibromopropane or 1,1,2,2-tetrachloroethane, then it must be tested.
- 8.4.8.3 Proximity of the internal standard peak to the 1,2-dibromoethane peak.
- 8.3.9 A stock solution of the selected internal standard in 99:1 benzene-methanol (v/v) is prepared such that 5.0 μ l of this stock solution contains approximately 400 ng of internal standard. To each diluted sample solution and each standard solution, 5.0 μ l of this internal standard stock solution is added.

8.3.10 Aliquots (5- μ l) of these solutions are injected into the gas chromatograph for quantitative analysis.

8.4 Determination of Recovery

- 8.4.1 Activated charcoal equivalent to the amount in the front (larger) section of the sampling tube is poured into a 2-ml glass vial. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of 1,2-dibromoethane in a 5- μ l aliquot of benzene solution is added directly to the charcoal with a microliter syringe. The vial is sealed immediately with Parafilm.
- 8.4.2 Six samples at each of three different levels are prepared in the above manner and allowed to stand 16-24 hours in order to assure complete adsorption of the 1,2-dibromoethane onto the charcoal. A parallel blank vial is treated in exactly the same manner except that no sample is added to it. The samples and the blank are treated with 10.0 ml of 99:1 benzene-methanol (v/v) in the manner described in Section 8.3.2.
- 8.4.3 Three control solutions are prepared by injecting the same quantity of 1,2-dibromoethane into 10.0-ml portions of 99:1 benzene-methanol (v/v) with the same syringe used in the preparation of the samples.
- 8.4.4 The samples, the blank, and the control solutions are analyzed on the same day in accordance with Section 8.3.
- 8.4.5 Recovery (R) is equal to the difference between the average quantity of 1,2-dibromoethane recovered from the samples and the quantity recovered from the blank divided by the average quantity of 1,2-dibromoethane measured in the control solutions.
- 8.4.6 The desorption efficiency obtained is dependent upon the amount of analyte collected on the charcoal. Therefore, a plot of "desorption efficiency" versus "quantity of analyte measured" is constructed. This curve is used in Section 10.2 to correct for adsorption losses.

9. Calibration and Standardization

- 9.1 A series of standards varying in concentration over the range of interest is prepared. The range of interest may be in the vicinity of 40 to 800 ng per 10.0 ml of 99:1 benzene-methanol (v/v). These standards are analyzed during the same time period as the samples.
- 9.2 In view of the low concentrations involved, the volume of a solution prepared from X number of ng of 1,2-dibromoethane and 10.0 ml of solvent is very nearly 10.0 ml and can be assumed to be 10.0 ml for the purpose of this analytical method.

- 9.3 A calibration curve is constructed daily by plotting quantity of 1,2-dibromoethane per 10.0 ml of solution versus the ratio of 1,2-dibromoethane peak area to internal standard peak area.

10. Calculations

- 10.1 Determine the quantity of 1,2-dibromoethane, W (ng), in 10.0 ml of diluted sample solution from the calibration curve.
- 10.2 Determine the total quantity of 1,2-dibromoethane, Q, in the air sample:

$$Q = \left(\frac{W \cdot F}{R} \right)_A + \left(\frac{W \cdot F}{R} \right)_B$$

where:

F -- Dilution factor. The dilution factor is equal to 10.0 ml divided by the volume of original sample solution which was diluted to 10.0 ml.

R -- Recovery (Section 8.4.5).

A -- Reference to the front section of the sampling tube.

B -- Reference to the back section of the sampling tube.

- 10.3 In the event the blank gives rise to a peak with the same retention time as that of 1,2-dibromoethane, the analyst must determine or compensate for it.

- 10.4 Determine the concentration, C ($\mu\text{g}/\text{m}^3$), of 1,2-dibromoethane in air.

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

where: V is the volume of air sampled in liters.

11. Reference

Method S104, "Ethylene Dibromide," NIOSH Manual of Analytical Methods, Second Edition, Volume 2, 1977, U. S. Government Printing Office, Washington, D.C.

James J. Sweeney
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Organic Methods Development Section

Particulate Antimony
Measurements Research Branch
Analytical Method

Analyte:	Particulate Antimony and compounds (as Sb)	Method No.:	P&CAM 261
Matrix:	Air	Range:	0.05 to 1.0 mg/m ³ for a 50-liter sample
Procedure:	Membrane Filter Collection, acid ash, graphite furnace AAS analysis		
Date Issued:	03/25/77	Precision:	3.8% (Analytical)
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Particulate matter collected from air on membrane filters is wet ashed in a mixture of nitric, perchloric and sulfuric acids and the residue is diluted with distilled water. Aliquots are introduced into the graphite furnace and the absorbance measured at 217.6 nm.

2. Working Range, Sensitivity and Detection Limit

- 2.1 The analytical range is 0.05 to 1.0 mg Sb/m³ (0.01 to 0.1 mg Sb/m³ using a purge gas interrupt mode) for a 50 liter air sample (diluted to 50 ml following ashing and using a 25 μ l aliquot for analysis). The range may be extended by using a smaller aliquot (10-20 μ l) of sample in the furnace, and/or by diluting the digested sample to a volume other than 50 ml.
- 2.2 Sensitivity varies with different instruments and graphite tubes and may vary with different sample matrices. In this laboratory, sensitivity was determined to be 0.005 μ g Sb/ml/1%A (125 pg 1%A) for a 25 μ l aliquot.
- 2.3 The absolute detection limit of this method is 97 pg (25 μ l of a 0.004 μ g Sb/ml solution).

3. Interferences

- 3.1 Flameless atomic absorption is more prone to matrix effects than are flame methods. As a consequence, it is desirable to check for interferences by the method of standard addition.

- 3.2 For the determination of antimony in the presence of lead, the 231.2 nm resonance line should be used (lead may cause a spectral interference at 217.6 nm).
4. Precision and Accuracy
- 4.1 The pooled coefficient of variation for the analysis of five calibration solutions (10 determinations each) covering the range (0.05-1.0 $\mu\text{g/ml}$) was 0.038.
- 4.2 The recoveries of antimony from filters spiked with 5.0, 12.5 and 25.0 $\mu\text{g Sb/filter}$ were $100 \pm 3.9\%$, $99.3 \pm 2.9\%$ and $98.7 \pm 3.2\%$ respectively. The pooled coefficient of variation was 0.034.
5. Advantages and Disadvantages
- 5.1 A major advantage of the graphite furnace method is that it is approximately 100 times more sensitive than conventional flame atomic absorption, thereby allowing analysis of samples with lower concentrations of antimony. The graphite furnace method requires fewer sample handling steps and exhibits a lower coefficient of variation than hydride generation techniques.
- 5.2 A disadvantage is that matrix effects are more prevalent than in flame atomic absorption. Also, volatile antimony compounds, including stibine, are not collected by the sampling method.
6. Apparatus
- 6.1 Sampling Equipment
- 6.1.1 Cellulose ester membrane filters, 0.8- μm , 37-mm diameter, Millipore type AA, or equivalent.
- 6.1.2 Filter holder for 37-mm filter, Millipore MAMP 037 A0, or equivalent.
- 6.1.3 Personal sampling pump (1.5 - 2.5 lpm), capable of delivering a flow rate of 1.5 lpm to within $\pm 5\%$, calibrated with a representative filter unit in the line.
- 6.1.4 Thermometer, manometer, and stopwatch.
- 6.2 Atomic Absorption Spectrophotometer
- 6.2.1 Atomic absorption spectrophotometer with graphite atomizer and deuterium or hydrogen continuum correction.
- 6.2.2 Hollow cathode or electrodeless discharge lamp for antimony ($\lambda = 217.6 \text{ nm}$).
- 6.2.3 Argon, high purity, in a cylinder equipped with a two-stage pressure regulator and appropriate hose connections.

6.3 Glassware (borosilicate)

6.3.1 Phillips beakers with watchglass covers, (125 ml).

6.3.2 Volumetric flasks, (50 and 100 ml).

6.3.3 Volumetric pipets, (1, 5, and 10 ml).

6.3.4 Micro-pipettes, (10, 25, 50 and 100 μ l).

6.3.5 Small test tubes (10 ml).

6.4 Variable temperature hotplate (capable of reaching 350°C).

6.5 Perchloric acid fume hood.

7. Reagents

Analytical reagent grade or equivalent. Water must be double distilled or deionized.

7.1 Nitric acid, concentrated, redistilled in glass.

7.2 Perchloric acid, 70%.

7.3 Sulfuric acid, 98%.

7.4 Ashing acid, (3:1:1, nitric:perchloric:sulfuric).

7.5 Antimony stock solution, 1000 μ g Sb/ml. Prepared commercially or by dissolving 1.0000 g Sb metal granules in hot, concentrated sulfuric acid (30 ml) and diluting to one liter with distilled water.

7.6 Dilute standard "A" (100 μ g Sb/ml). Transfer 10.0 ml of the 1000 μ g/ml stock standard to a 100 ml volumetric flask, add 5 ml concentrated, H_2SO_4 and dilute to volume. Prepare fresh monthly.

7.7 Dilute standard "B" (10 μ g Sb/ml). Transfer 1.0 ml of the 1000 μ g/ml stock standard to a 100 ml volumetric flask, add 5 ml concentrated H_2SO_4 and dilute to volume. Prepare fresh monthly.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 All glassware should be cleaned before first use with a detergent solution followed by (in order) rinsing with water, rinsing with distilled water, soaking 30 minutes in concentrated nitric acid, and thorough rinsing with distilled water.

- 8.1.2 Glassware which has been cleaned once by this method (8.1.1) and subsequently used exclusively for antimony determination may be cleaned by soaking for 30 minutes in dilute (5% w/v) nitric acid and thoroughly rinsing with distilled water.

8.2 Collection and Shipping of Samples

- 8.2.1 With a filter in place, connect the filter holder to the sampling pump and sample the air at 1.5 lpm for 30 minutes (concentrations of $0.06 - 1.1 \text{ mg/m}^3$ may be determined with this sample volume). For suspected low or high antimony concentrations, adjust the sample volume accordingly. Since it is possible for the 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 adjusted as needed. Accurately measure and record the date, flowrate, time, and/or volume.
- 8.2.2 Following sampling, replace the plastic plug on the inlet and outlet openings of the cassette and attach appropriate identification. At least one blank filter should be submitted with each group of samples; this filter is handled in the same way as the sample filters except that no air is drawn through it.
- 8.2.3 Measure and record the temperature and pressure of the atmosphere being sampled.

8.3 Analysis of Samples

- 8.3.1 Remove the filter blanks and filter samples from their containers and place in 125 ml Phillips beakers. Add 5 ml of ashing acid, cover with a watchglass, and heat at 140°C on a hotplate for 2 hours. Increase the temperature (to 200°C) and reduce the volume of solution to approximately 2 ml. If necessary to complete the ashing (a nearly colorless residual solution should result), additional small amounts (1 ml) of nitric acid may be added and evaporated before proceeding. Remove the watchglass and raise the temperature to 350°C to produce dense white fumes of sulfur trioxide. Reduce the volume to $\approx 0.5 \text{ ml}$ but do not allow the solution to evaporate to dryness. Cool, and add 1 ml H_2SO_4 .
- 8.3.2 Transfer the solution quantitatively to a 50 ml volumetric flask and dilute to volume with distilled water.
- 8.3.3 Turn on the atomic absorption spectrophotometer, antimony lamp, continuum background correction, and recorder and allow at least 20 minutes for warmup. Follow the manufacturer's recommendations for operating conditions other

than the drying, charring and atomizing times and temperatures which are as follows: dry for 30 seconds at 110°C, char for 20 seconds at 700°C, and atomize for 8 seconds at 2700°C.

8.3.4 Pipet a 25 μ l aliquot of the working standard (9.1.1) or sample (8.3.2) solution into the graphite furnace of the atomic absorption spectrophotometer, initiate the operation cycle and record the absorbance. Standard and sample solutions are run in triplicate with at least one standard analyzed for every three sample determinations.

8.4 In order to check for interferences a minimum of 2 samples and one blank from each set are analyzed by the method of standard additions and the results compared with those obtained in Section 10.1.

8.4.1 Three, 5 ml aliquots of the sample (or blank) solution are placed in small test tubes marked "I," "II" and "III." To tube "I" add an aliquot of antimony standard solution (A or B) sufficient to provide an amount of antimony equal to that estimated to be present in 5 ml of sample solution. Then add a volume of distilled water equal to volume of antimony solution just added. (For example, to 5 ml of sample containing about 0.2 μ g/ml of antimony, add 10 μ l of solution A and 10 μ l of distilled water). To tube "II" add twice as much antimony standard solution as was added to tube "I." To tube "III" add a volume of water equal to the volume of antimony standard solution that was added to tube "II." Mix the solutions thoroughly.

8.4.2. Analyze at least three aliquots of each solution as described in Section 8.3.4.

9. Calibration and Standardization

9.1 Calibration Curve

9.1.1 Prepare working standard solutions for the analytical range of the method ($\sim$ 0.05 - 1.0 μ g Sb/ml) by diluting 0.05 - 1.0 ml aliquots of standard solution A to 100 ml with distilled water plus 3 ml concentrated H_2SO_4 . A minimum of 5 working standard solutions should be used in preparing the calibration curve. (Prepare fresh daily).

9.1.2 Absorbances, if any, recorded for an acid blank (3 ml H_2SO_4 diluted to 100 ml with distilled water) are subtracted from the absorbances recorded for the working standard solutions. A calibration curve is prepared by plotting absorbances vs. concentration (μ g Sb/ml).

10. Calculations

10.1 Calibration Curve

From the peak absorbance of the samples, subtract the absorbance of the filter blank to determine the corrected sample absorbances. Compare the corrected sample absorbance with the calibration curve (9.1.2) to determine the amount of antimony, in $\mu\text{g/ml}$, in the sample solution. Convert to mg Sb/m^3 as described in Sections 10.3 and 10.4.

10.2 Method of Standard Additions

Plot the absorbance values for the sample solutions and the spiked sample solutions against an abscissa labeled " μg of Sb added/5ml." The abscissa to be plotted are the amounts (in $\mu\text{g/5ml}$) of antimony added to tubes "I," "II," and "III" ($0.0 \mu\text{g}$ for tube "III"). Draw the best straight line through the three points. The intercept of this line on the negative abscissa (0.0 absorbance units) is read as the concentration in $\mu\text{g/5 ml}$ of antimony in the sample solution (5 ml of sample solution was analyzed). The concentration is converted from $\mu\text{g/5 ml}$ to $\mu\text{g/ml}$ (e.g., $x \mu\text{g/5 ml} = (\frac{x}{5}) \mu\text{g/ml}$). Subtract the concentration, if any, in $\mu\text{g/ml}$ for the blank from the samples. Convert to mg Sb/m^3 as described in Sections 10.3 and 10.4. If the result of this determination does not agree to within 10% of the values obtained with the procedures described in Section 10.1 an interference is indicated and standard additions techniques should be utilized for sample analysis.

- 10.3 For personal sampling pumps with rotameters only, the following correction for air volume sampled 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 = sample 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

10.4 The concentration of antimony in air is calculated as follows:

$$C = \mu\text{g Sb/ml} \times \frac{V}{V_s}$$

where:

C = concentration of antimony (mg Sb/m³)

$\mu\text{g Sb/ml}$ = concentration of antimony as determined in Section 10.1 or 10.2

V = volume of digested (8.3.2) solution (in ml)

V_s = volume of air sampled in liters

11. References

- 11.1 "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin Elmer Corp., Norwalk, Conn. 1976.
- 11.2 "Analytical Methods for Atomic Absorption Spectrophotometry Using the Graphite Furnace," Perkin Elmer Corp., Norwalk, Conn. 1975.
- 11.3 NIOSH Technical Report, "Evaluation of Atomic Absorption Spectrophotometry Methods for Antimony," by R.D. Hull, May 1977.

HEXAMETHYLENETETRAMINE

Measurements Support Branch

Analytical Method

Analyte:	Hexamethylenetetramine (HMTA)	Method No.:	P&CAM 263
Matrix:	Air	Range:	0.1 $\bar{3}$ 2.4 mg/m ³
Procedure:	Filter/Impinger Collection Spectrophotometry	Precision:	5% (Analytical)
Date Issued:	8/1/78	Classification:	E(Proposed)
Date Revised:			

1. Synopsis

- 1.1 Airborne particulate hexamethylenetetramine (HMTA) is collected on a filter and HMTA vapor is collected in an impinger containing water as the absorbing reagent.
- 1.2 HMTA decomposes to formaldehyde in a sulfuric acid solution. Chromotropic acid is added and a purple monocationic chromogen is formed. The absorbance of the colored solution is measured at 580 nm and is proportional to the quantity of HMTA in the solution.
- 1.3 The chemistry of this color reaction is not known with certainty (Reference 11.1).

2. Working Range, Sensitivity, and Detection Limit

- 2.1 From 0.5 μ g HMTA/mL to 12 μ g HMTA/mL can be quantitated in a 1-cm cell without diluting the sample solution. This corresponds to an air concentration range of 0.1 mg/m³ to 2.4 mg/m³ HMTA for a 100-liter sample if a 4-mL aliquot of the 20-mL sample is analyzed. The calibration curve is linear up to approximately 1.0 absorbance unit and is usable to 1.4 absorbance units if appropriate standardization procedures are used.
- 2.2 The sensitivity is approximately 30 μ g HMTA to 1.0 absorbance unit which is equivalent to a sample solution containing 7.5 μ g/mL.
- 2.3 The detection limit is approximately 0.25 μ g HMTA which corresponds to a solution concentration of 0.06 μ g/mL and gave an absorbance reading 0.008 units greater than the reagent blank solution.

3. Interferences

The chromotropic acid procedure has very little interference from aldehydes other than formaldehyde. Saturated aldehydes and the unsaturated

aldehyde acrolein give a slight positive interference. Ethanol and higher molecular weight alcohols and olifins may be negative interferences. (Ref. 11.2). However, alcohols and aldehydes are not normally present in the same work environments as HMTA and therefore, are not serious interferences.

4. Precision and Accuracy

The method has not been tested for precision and accuracy, although the formaldehyde by chromotropic acid method (P&CAM No. 125) was checked for reproducibility by having three different analysis in three different laboratories analyze standard formaldehyde samples. The formaldehyde results agreed within ± 5 percent. A similar analytical precision is expected for HMTA.

5. Advantages and Disadvantages

5.1 No information is available on the efficiency of the collection scheme or the effect of storage on the collected air sample.

5.2 The liquid impinger/filter collection method is a disadvantage.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples consists of the following components:

6.1.1 The filter unit consists of the filter media (Section 6.2) and appropriate 37-mm 2- or 3- piece cassette filter holder.

6.1.2 The filter unit is connected to a graduated midget impinger containing deionized or distilled water as the absorbing solution using a minimum length of plastic tubing.

6.1.3 Personal Sampling Pump: A calibrated personal pump suitable for delivering a flowrate of 1.5 l/m for 8 hours is used to sample a known volume of air. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump. The pump must be calibrated using an integrating volume meter such as a dry gas or wet test meter with representative sampling components in place including filter cassette, filter and impinger containing appropriate volume of absorbing solution.

6.2 Mixed cellulose ester membrane filter, 0.8- μ pore size and 37-mm diameter. The filter is held in the cassette supported by a cellulose backup pad.

6.3 Scintillation vials with tapered polyseal caps are used for transporting samples to the laboratory.

6.4 Spectrophotometer capable of measuring the absorbance of the color-developed solution at 580 nm.

6.5 Associated laboratory glassware.

7. Reagents

All reagents must be ACS analytical reagent grade unless otherwise noted.

7.1 Chromotropic Acid Reagent. Dissolve 0.10 g of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt (Eastman Kodak Company, New York, Cat. No. P230) in water and dilute to 10 mL. Filter if the solution is cloudy and store in a brown bottle. Make up fresh weekly.

7.2 Concentrated sulfuric acid.

7.3 HMTA Standard Solution "A" (1 mg/mL). Dissolve 0.100 g hexamethylenetetramine in distilled water. Dilute to 100 mL.

7.4 HMTA Standard Solution "B" (20 µg/mL). Dilute 2.0 mL of solution "A" to 100 mL with deionized or distilled water.

8. Procedure

8.1 Cleaning of Equipment. Care must be taken to ensure the absence of probable contaminants like organic materials that can be charred by concentrated sulfuric acid. Soaking glassware for one hour in either chromic acid or a 1:1 mixture of nitric and sulfuric acids, followed by thorough rinsing with deionized or distilled water will remove all organic contaminants.

8.2 Collection and Shipping of Samples

8.2.1 Place 15 mL deionized or distilled water into each midjet impinger. Connect a filter cassette containing an appropriate filter to the inlet of the bubbler with minimum lengths of tubing. Connect the impinger to the sampling pump (via the absorption tube containing the glass-wool plug) with flexible tubing.

8.2.2 Turn on the pump to begin sample collection. Care should be taken to measure the flowrate, time and/or volume as accurately as possible. The sample should be collected at a flowrate of 1.5 l/m. A 15 liter sample can be collected in 10 minutes₃ at this sampling rate and the range 0.3 mg/m³ to 17 mg/m³ can be determined in this sample without dilution.

8.2.3 After sampling, the filter is removed from the filter cassette with tweezers and placed in a labelled scintillation vial. Remove the impinger stem and tap it gently against the inside wall of the impinger bottle to recover the sampling solution. Wash the stem with distilled or deionized water and add the wash to the impinger. Dilute impinger solution to a total volume of 20 mL with deionized or distilled water, swirl to

mix and transfer the solution to the scintillation vial containing the filter. Transport to the laboratory for analysis. Whenever possible, hand delivery of the samples is recommended.

- 8.2.4 A "blank" filter in a cassette should be handled as the other samples except that no air is drawn through this impinger or this filter.

8.3 Analysis of Samples

- 8.3.1 Shake the vial to assure solution homogeneity. Pipet a 4.0 mL aliquot from each vial into glass stoppered test tubes. A blank containing 4.0 mL of distilled water must also be run and 10% of the samples should be run in duplicate. If the HMTA content of the aliquot exceeds the limit of the method, a smaller aliquot diluted to 4.0 mL with distilled water is used.
- 8.3.2 Add 0.1 mL of 1 percent chromotropic acid reagent to each sample aliquot and mix.
- 8.3.3 Pipet 6.0 ml of concentrated sulfuric acid into each sample solution slowly and cautiously. Since the solution becomes extremely hot during the addition of the sulfuric acid, cooling the samples in a cold water bath while adding the acid is recommended. If the acid is not added slowly, some loss of sample could occur due to spattering.
- 8.3.4 Allow solutions to come to room temperature. Read at 580 nm in a suitable spectrophotometer using a 1-cm cell. The absorbance is relatively constant over a 3-hour period after color development. Determine the HMTA content of the sampling solution from a curve previously prepared from standard HMTA solutions.

9. Calibration and Standardization

- 9.1 Pipet 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0 and 2.5 mL of standard solution "B" into glass stoppered test tubes. Prepare and analyze standards and samples at the same time (See 8.3.1).
- 9.2 Dilute each standard to 4.0 mL of distilled water. These standards contain 0, 2, 6, 10, 20, 30, 40 and 50 µg HMTA, respectively.
- 9.3 Develop the color as described in the analysis procedure (Section 8.3).

10. Calculations

- 10.1 Determine the total quantity of HMTA collected as follows:

$$M = A \times \frac{20 \text{ mL}}{V_a}$$

where:

M = total μg of HMTA in the sample

A = HMTA present in the sample aliquot (in μg)

V_a = aliquot volume of the sampling solution analyzed
(in mL).

- 10.2 The concentration of HMTA in the sampled atmosphere may be calculated by using the following equation.

$$C = \frac{M}{V_s} \text{ (from Sec 10.1)}$$

where:

C = concentration of HMTA in air in mg/m^3

V_s = liters of air sampled at standard conditions (25
C, 1 atm)

11. References

- 11.1 Feigl, F., Spot Tests in Organic Analysis, Seventh Ed., American Elsevier Publishing Company, New York, 434, (1966).
- 11.2 U.S. Department of HEW, NIOSH Manual of Analytical Methods, Volume 1, Second Edition, 1977, P&CAM No. 125 "Formaldehyde in Air."
- 11.3 Kreiner, J.G., "Detection of Hexamethylenetetramine in Vulcanizates," J. Chromatogr. 88,423(1974).

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Measurements Services Section

NAPHTHYLAMINES

Measurements Research Branch

Analytical Method

Analyte:	1- and 2-Naphthylamine	Method No:	P&CAM 264
Matrix:	Air	Range:	4-70 $\mu\text{g}/\text{m}^3$ for a 50-L air sample
Procedure:	Collection on glass fiber filter and silica gel, elution with acetic acid in 2-propanol, analysis by gas chromatography.	Precision:	9% (analytical)
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a three-stage sampler consisting of a high-efficiency glass fiber filter followed by two beds of silica gel to collect the naphthylamine aerosol and/or vapor.
- 1.2 The filter and sorbent sections of the sampler are transferred to stoppered tubes and the naphthylamines are desorbed with a solution of acetic acid in 2-propanol. This desorbing solution stabilizes the naphthylamines.
- 1.3 An aliquot of this solution is injected into a gas chromatograph.
- 1.4 Peak areas are determined and compared with a calibration curve obtained from injections of standard solutions of the naphthylamines.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The range of the method is 0.2-3.5 $\mu\text{g}/\text{sample}$ (4-70 $\mu\text{g}/\text{m}^3$ for a 50-liter air sample) when using 0.5 mL of desorbing solution and 1- μL injections into the gas chromatograph.
- 2.2 The amount of naphthylamine vapor retained on the primary silica gel bed decreases as the relative humidity of the sampled air increases. Experimental data suggests that, at or below relative humidities of 80%, 100 liters of air can be sampled with little

risk of sample loss. (A small fraction of the analyte may be found in the secondary silica gel bed under these conditions.)

2.3 The limit of detection is 0.01 $\mu\text{g}/\text{sample}$.

3. Interferences

- 3.1 In solutions containing the naphthylamines at concentrations of 4 ng/ μL , the following compounds were found not to interfere when their concentrations were 8 ng/ μL : o-chloroaniline, 4,4'-methylenedianiline, 3,3'-dichlorobenzidine, 4,4'-methylenebis(2-chloroaniline), aniline, benzidine, 2-nitronaphthalene, 1-naphthol and 2-naphthol. The retention time of 1-nitronaphthalene is between those of the naphthylamines and interferes with their analyses.
- 3.2 Any compound sampled with the naphthylamines and having the same retention time as the analytes will interfere with the analysis. This type of interference often can be eliminated by changing the operating conditions of the chromatograph, e.g., by temperature programming or by changing the stationary phase.

4. Precision and Accuracy

- 4.1 Samples of 1- and 2-naphthylamine on filters or silica gel proved to be unstable at $\sim 22^\circ\text{C}$ after 3 days. Storage of samples at -15°C allowed recovery of at least 80% of the naphthylamines after 3 weeks.
- 4.2 The precision of the analytical method for 1-naphthylamine at the 0.4- $\mu\text{g}/\text{sample}$ level (8 liters at 46 $\mu\text{g}/\text{m}^3$) was 8% relative standard deviation. The precision for 2-naphthylamine at the 0.2- $\mu\text{g}/\text{sample}$ level (8 liters at 31 $\mu\text{g}/\text{m}^3$) was 9%. In both cases, the sampling rate was 0.8 L/min and the sampled air was at 30°C and 80% relative humidity.
- 4.3 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

- 5.1 The sampler is a small portable device containing no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities.
- 5.2 Desorption of the collected sample is simple, and the analysis is accomplished by a rapid instrumental technique. Interferences in the analysis can often be eliminated by changing the operating conditions of the chromatograph.
- 5.3 Relative humidity has an effect on the collection efficiency of the adsorbent (Section 2.2).

- 5.4 At a sampling flow of 0.2 L/min, the linear velocity through the 4-mm inlet of the holder is 26.5 cm/s. It is not known if this throat velocity is sufficient for the capture of all particles of analytical importance.
- 5.5 This method has not been field tested.
- 5.6 The naphthylamine samples are unstable at ambient temperature. Special precautions in shipping and storing the samples are required.

6. Apparatus

- 6.1 Personal air sampling pump that can be maintained for 8 h at a sampling flow of 0.2 L/min with the sampler in line. Each pump should be calibrated with a representative sampler in line.
- 6.2 Sampler, equivalent to that shown in Figure 1. The sampler consists of three sections: a high-efficiency glass fiber filter, followed by 100-mg and 50-mg beds of silica gel. The first section, a 13-mm Spectro Grade glass fiber filter (Gelman Instrument Co., Ann Arbor, MI) is contained in a 13-mm filter holder (SX00-013-00 Millipore Corp., Bedford, MA). The sorbent tube is a 50-mm section of Pyrex glass, 6.4-mm o.d. x 4-mm i.d. flared on one end, containing the sections of silica gel (Grade 407, 20/45 mesh, 720-760 m²/g, 0.737 g/cc; Coast Engineering Laboratories, Gardena, CA). The sorbent is held by 3.5-mm diameter 100-mesh stainless-steel screens and 4-mm o.d. Teflon rings, as shown in Figure 1. To connect the two stages, the filter holder is pressed into the flared end of the sorbent tube. The pressure drop across the sampler at 0.2 L/min is 10 torr. Plastic caps of 6 mm i.d. seal the ends of the sampler.
- 6.3 Insulated container suitable for transporting samples packed in dry ice.
- 6.4 Dry ice.
- 6.5 Gas chromatograph equipped with a flame ionization detector and injection port.
- 6.6 Glass column, 1.8-m x 2-mm i.d. x 6-mm o.d., packed with 3% OV-225 on 80/100 Supelcoport (Supelco, Inc., Bellefonte, PA).
- 6.7 Potentiometric strip chart recorder.
- 6.8 Test tubes, 1-mL, fitted with polyethylene stoppers.
- 6.9 Glass syringes, 5- and 10- μ L.
- 6.10 Pipettes of convenient volumes for the preparation of standard solutions.

- 6.11 Volumetric flasks, low actinic, of convenient volumes for the preparation of standard solutions.
- 6.12 Clinical centrifuge.
- 6.13 Analytical balance.
- 6.14 Test-tube shaker, vortex type.

7. Reagents

All reagents should be of analytical reagent quality or as noted.

- 7.1 2-Propanol, UV grade, distilled in glass.
- 7.2 Glacial acetic acid.
- 7.3 Acetone, distilled in glass.
- 7.4 Desorbing Solution: 0.05% (v/v) acetic acid in 2-propanol.
- 7.5 1-Naphthylamine, analytical standard quality.
- 7.6 2-Naphthylamine, analytical standard quality.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis is washed with detergent and rinsed with tap water, distilled water, and methyl alcohol.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling, the plastic caps are removed from the ends of the sampler and saved for resealing after sampling.
 - 8.2.2 The sorbent end of the sampler is connected to the pump with plastic or rubber tubing. The sampler is positioned vertically during sampling. Sampled air must not pass through any tubing before entering the sampler.
 - 8.2.3 The atmosphere is sampled at a flow of 0.2 L/min for no longer than 8 hours. The flow and sampling time, or the volume of sampled air, must be measured as accurately as possible.
 - 8.2.4 The temperature, pressure, and humidity of the atmosphere being sampled are measured and recorded, along with other pertinent data such as location, date, and time of sampling.
 - 8.2.5 The sampler is resealed with the plastic caps immediately after sampling.

- 8.2.6 Blank samples are obtained by handling random collection devices in the same manner as in sampling, except that no air is drawn through them.
- 8.2.7 Samples shipped to the laboratory should be packed tightly to minimize breakage and cooled with dry ice.
- 8.2.8 If samples of bulk material associated with the process under investigation are to be shipped to the laboratory, they should not be placed in the same container as the air samplers or blanks.
- 8.2.9 The samples should be stored at temperatures at or below -15°C prior to analysis. Because of the instability of the analyte, the samples should be analyzed as soon as possible after collection.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Place the glass fiber filter and the 100-mg section of silica gel in a 1-mL test tube. Place the 50-mg section of silica gel in a separate test tube; analysis of this section will indicate if breakthrough occurred at the 100-mg section. Teflon rings and stainless steel screens associated with the samplers may be analyzed with the appropriate stages. Sampler caps can be discarded.
- 8.3.2 Desorption of Samples. Add 0.5 mL of desorbing solution to each test tube. Cap the test tubes and shake them with a test tube shaker. Allow them to stand for one hour with intermittent shaking. Centrifuge for 10 min.
- 8.3.3 Gas Chromatographic Conditions

Column:	3% OV-225 on 80/100 Supelcoport in 1.8 m x 2-mm i.d. x 6-mm o.d. glass tubing
Column Temperature:	163 $^{\circ}\text{C}$
Injector Temperature:	190 $^{\circ}\text{C}$
Interface Temperature:	165 $^{\circ}\text{C}$
Helium:	24 mL/min
Hydrogen:	85 mL/min
Air:	378 mL/min
Detector:	Flame ionization

Injection Volume:	1.0 μ L
Efficiency:	2800-2900 theoretical plates
Capacity Ratio:	1-naphthylamine, 17.4; 2-naphthylamine, 20.1

8.3.4 Injection. Flush the 5- μ L syringe first with acetone (to insure its cleanliness and to wet the barrel and plunger) and then with the sample solution. Carefully draw 1 μ L of sample solution into the syringe (to minimize the intake of particulate matter) and inject the aliquot into the gas chromatograph.

8.3.5 Measurement of Peak Areas. The area of the sample peak is measured either manually or with an electronic integrator. Preliminary results are read from a standard curve prepared as discussed in Section 9.

8.4 Efficiency of Desorption

8.4.1 Importance of Determination. The efficiencies of desorption for the naphthylamines can vary from one laboratory to another and also from one batch of silica gel or filters to another. Thus, it is necessary to determine the fraction of each naphthylamine that can be recovered from these matrices. Since the efficiency of desorption may also vary with the amount of naphthylamine present, determinations should be made for at least two levels in the range of anticipated sample sizes.

8.4.2 Procedure for Determining the Efficiency of Desorption. Place the filters and silica gel from unused samplers in 1-mL test tubes. Add to each a known amount of naphthylamine in 10 μ L of 2-propanol using the same microliter syringe for each. Five filter and silica gel samples are thus prepared at each of two different levels in the range of interest. Cap the tubes and store them in the freezer overnight. Treat a parallel blank in the same manner (no analyte is added). Desorb and analyze "samples" and blanks in exactly the same manner as described in Section 8.4. Prepare two or three standards at the various levels by adding 10 μ L (same syringe as above) of the naphthylamine solution to 0.5 mL of desorbing solution. Analyze these solutions with the samples.

$$\text{Efficiency of desorption (D)} = \frac{\text{Area}_{(\text{sample})} - \text{Area}_{(\text{blank})}}{\text{Area}_{(\text{Standard})}}$$

9. Calibration and Standardization

- 9.1 For accuracy in the preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at high concentration. The initial standard is prepared by weighing a selected amount of naphthylamine (e.g. 125 mg) into a 250-ml volumetric flask (low actinic) and adding the desorbing solution to the calibration mark. Dilutions encompassing the concentration range of interest down to 0.3 ng/ μ L are then made from the stock solution. Solutions should be stored in a refrigerator when not in use to minimize degradation.

CAUTION: The naphthylamines have been identified as carcinogens. Appropriate precautions must be taken in handling these compounds to avoid personnel exposure and area contamination.

- 9.2 The standard solutions should be analyzed under the same gas chromatographic conditions and during the same time period as the samples. This will minimize inaccuracy due to day-to-day variations in the setting of instrumental conditions.
- 9.3 Calibration curves for each naphthylamine are prepared by plotting the peak areas for the standards against their concentration in μ g/0.5 mL.

10. Calculations

- 10.1 In the event that the blank produces a peak with the same retention time as the analyte, the analyst should determine the source of the interference and eliminate, or compensate for it.
- 10.2 Read the weight (M) in μ g of each naphthylamine present in the sample from the calibration curve.
- 10.3 The corrected weight (W) is determined by

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

where D is the efficiency of desorption for that sampler stage.

- 10.4 For each naphthylamine, add the weight found in the sampler stages to determine the total weight (W_t) collected.
- 10.5 The concentration of each naphthylamine in air (C , μ g/ m^3) is given by

$$C (\mu\text{g}/m^3) = \frac{W_t (\mu\text{g})}{V (\text{liters})} \times \frac{10^3 \text{ liters}}{m^3}$$

where V is the sampling volume.

11. References

R. Morales, S. M. Rappaport, R. W. Weeks, Jr., E. E. Campbell, and H. J. Ettinger, "Development of Sampling and Analytical Methods for Carcinogens: January 1-September 30, 1976" Progress Report LA-7058-PR, Los Alamos Scientific Laboratory, Los Alamos, NM, 1977. Available from the National Technical Information Service, Springfield, VA.

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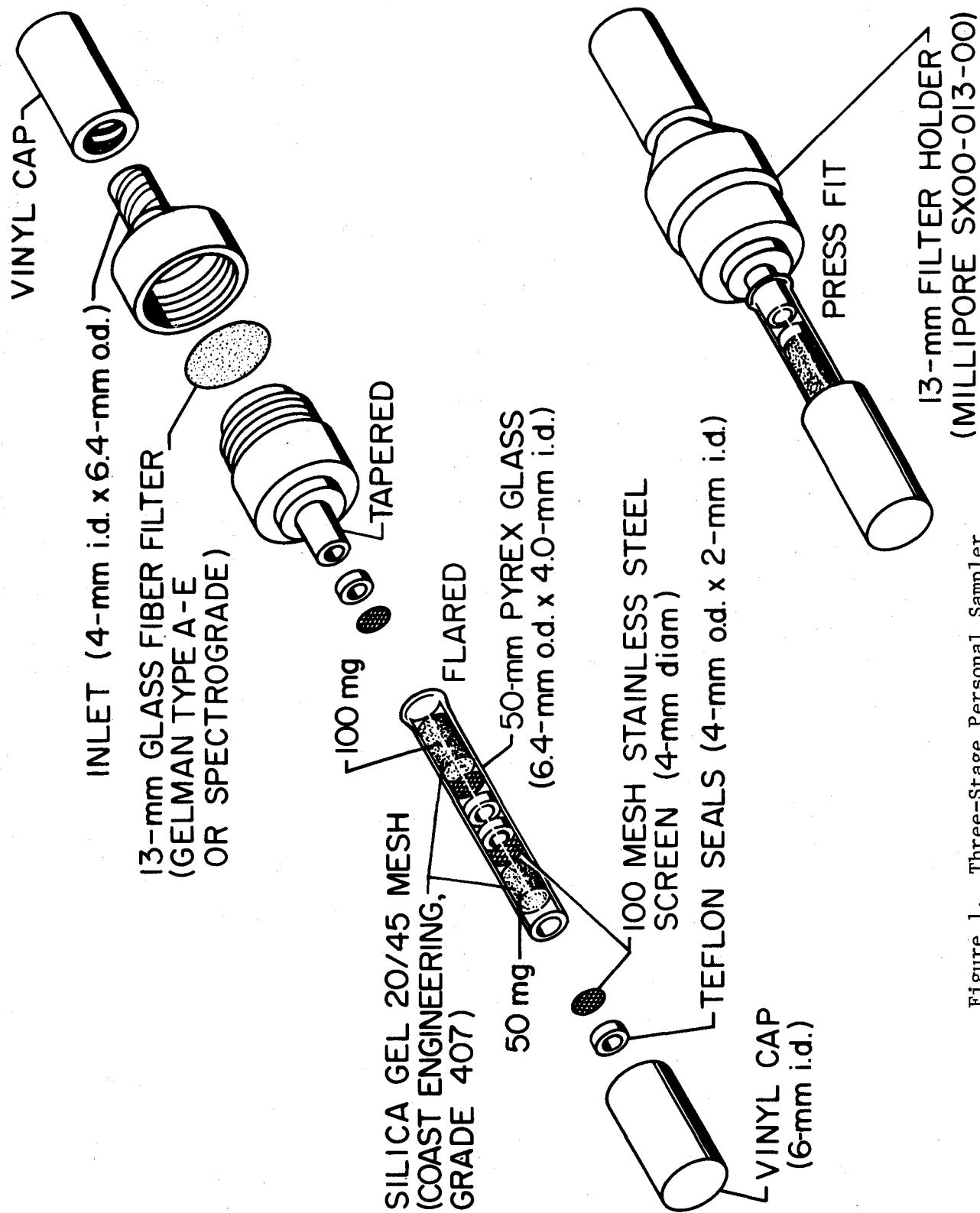


Figure 1. Three-Stage Personal Sampler

ARSINE IN AIR

Measurements Research Branch

Analytical Method

Analyte:	Arsenic	Method No:	P&CAM 265
Matrix:	Air	Range:	1-10 µg/cum
Procedure:	Charcoal Adsorption, Nitric Acid Desorption, Atomic Adsorption-HGA		
Date Issued:	8/1/78	Precision:	8.7%
Date Revised:		Classification:	E (Proposed)

1. Synopsis

- 1.1 Arsine is collected in a charcoal tube containing activated coconut shell charcoal.
- 1.2 The arsine as arsenic is desorbed from the charcoal with 0.01 M HNO_3 . Nickel is added to the solution to enhance the analytical signal.
- 1.3 The resulting solution is analyzed for arsenic by heated graphite atomization and atomic absorption spectroscopy at 193.7 nm.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method has been evaluated for a 15-liter sample containing between 12 and 110 nanograms. This corresponds to concentrations of 0.8 to 7.33 mg/m^3 in air. Because of instrument sensitivity, this method probably cannot be extended to lower concentrations.
- 2.2 The upper limit of the range of this method depends upon the adsorptive capacity of the charcoal tube. This capacity depends upon the sampling rate and concentrations of arsine and other contaminants in the air. The first section of the charcoal tube was found to hold at least 0.021 mg when a test atmosphere

containing 0.405 mg/cu m of arsine was sampled at 0.22 liters per minute for 240 minutes. At that time, the concentration of arsine in the effluent was less than 5% of the influent. (The charcoal tube contains two sections. See section 6.2). When a test atmosphere containing 2 µg/cu m of arsine was sampled at a rate of 1.0 liter per minute for 60 minutes, no analyte was detected on the second section. Because of this information, the sampling rate should be limited to 0.2 liters per minute when the concentration of arsine exceeds 10 µg/cu m. If the concentration of arsine exceeds 0.09 mg/cu m, either dilute the sample as necessary or use NIOSH Method S220.

2.3 The slope of the calibration curve is .066 absorbance units/µg Arsine. This is presumed to be the sensitivity of the method.

2.4 The detection limit was not determined.

3. Interferences

3.1 Other arsenic compounds which exist as vapors and aerosols will interfere with the analysis. It is expected that interference from particulate arsenic compounds may be eliminated by placing a filter cassette before the charcoal tube. At a sampling rate of 1.0 lpm, aerosols are inefficiently collected by the charcoal tube.

3.2 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.

3.3 When the amount of water in the air is so great that condensation actually occurs in the tube, arsine vapors may not be trapped efficiently.

4. Precision and Accuracy

4.1 The Coefficient of Variation for the total analytical and sampling method in the range of 1 to 10 µg/cu m was 0.089. This value corresponds to a 0.23 µg/cu m standard deviation at the recommended ceiling of 2.0 µg/cu m. Statistical information and details of the evaluation and experimental test procedures can be found in Reference 11.2.

4.2 On the average, the concentrations obtained at the NIOSH recommended standard level, using the overall sampling and analytical method, were about 10-15% lower than the "true"

concentrations for a limited number of laboratory experiments. Because either the "true" concentration or the concentration as measured by this method could be in error, no correction for the bias can be made.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal. The tubes are analyzed by means of an instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 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.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ 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 activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. 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 must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Atomic absorption spectrophotometer with a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and background corrector accessory. A background corrector is necessary in order to avoid false positive signals from molecular scatterings at the 193.7 nm wavelength.

- 6.4 An arsenic electrodeless discharge lamp. This lamp is recommended because it is a brighter source and enhances sensitivity.
- 6.5 An electronic integrator, or some other suitable method for measuring peak areas.
- 6.6 Volumetric flasks; 50 to 1000 ml volumetric flasks for making standards.
- 6.7 Volumetric pipets; assorted sizes for making standards.
- 6.8 Eppendorf automatic pipettor with disposable plastic tips for accurately injecting 50 microliter sample aliquots into the graphite furnace tube.
- 6.9 Assorted glassware.
- 6.10 Ultrasonic agitator.
- 6.11 Centrifuge.
- 6.12 Centrifuge tubes; stoppered.

7. Reagents

All chemicals must be ACS reagent grade or better.

- 7.1 Nitric acid, 0.01 M.
- 7.2 Nitric acid, 0.1 M.
- 7.3 Ultrapure water: Distilled water was passed through a cation and anion exchange column and finally through a Millipore cellulose nitrate filter or equivalent.
- 7.4 Sodium Hydroxide, 10 N.
- 7.5 Nickel Solution: 1000 $\mu\text{g/ml}$ as $\text{Ni}(\text{NO}_3)_2$ atomic absorption standard or equivalent.
- 7.6 Arsenic Standards
 - 7.6.1 100- $\mu\text{g/ml}$ As stock solution: 0.1322 g of dried certified reagent As_2O_3 is dissolved in 10-ml of 10-N NaOH and diluted to 1 liter with ultrapure water.

- 7.6.2 1.00- $\mu\text{g}/\text{ml}$ As Standard solution: pipet 5 ml of 100- $\mu\text{g}/\text{ml}$ As solution into a 500-ml volumetric flask and dilute to the mark with 0.01-M HNO_3 . Prepare daily.
- 7.6.3 0.01-, 0.02-, 0.05-, 0.10-, and 0.20- $\mu\text{g}/\text{ml}$ As standard solutions: using a 10-ml pipet, transfer 10 ml of 1.00 $\mu\text{g}/\text{ml}$ As standard into 1000-, 500-, 200-, 100-, and 50-ml volumetric flasks respectively and dilute to the mark with 0.01-M HNO_3 . Prepare daily.
- 7.7 Aqua regia, 5.0%. Mix by volume, a mixture of 3 or 4 parts hydrochloric acid to one part nitric acid. This mixture is diluted by a factor of 20 with Ultrapure water to make a 5% aqua regia solution.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is agitated in 5 percent aqua regia with an ultrasonic bath for 15 minutes, and finally rinsed 3 times with distilled water and twice with distilled deionized water prior to use.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in 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, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2-mm).
- 8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal tube should be placed in a vertical position during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.3.5 Sample at a rate of 1.0 liter per minute for 15 minutes to evaluate compliance with the NIOSH recommended standard of 2.0 $\mu\text{g}/\text{cu m}$. The flow rate should be known with an accuracy of at least $\pm 5\%$.

- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize the tube breakage during shipping.

8.4 Analysis of Samples

- 8.4.1 Sample Desorption. Each charcoal tube is scored with a file and broken open. The charcoal contents of each of the two sections are transferred to individual 10-ml capacity glass stoppered centrifuge tubes and analyzed separately. 1.0-ml of 0.01-M HNO_3 is pipetted into each centrifuge tube. The tube and contents are then agitated in an ultrasonic bath for 30 minutes. After centrifuging the supernatant liquid is analyzed.
- 8.4.2 Desorption efficiency tests would be experimentally difficult to perform because a small amount of arsine gas must be added to the charcoal. Therefore the experimentally determined value of 0.9¹ can be used when the charcoal used to collect the sample was from SKC lot 106 and when the samples are in the range of 1.0 to 15 $\mu\text{g}/\text{cu m}$ for 15 liter samples. When these conditions are not met, desorption efficiency must be experimentally determined.
- 8.4.3 The instrument is adjusted to read the absorption of arsenic at 193.7 nm. Follow manufacturer's recommendations for source power, background correction, and furnace alignment as well as furnace parameters such as inert gas flow and time and temperature conditions. During validation, the following heated graphite atomizer program was followed:

1. dry	40 sec @ 110 ⁰ C
2. char	15 sec @ 1200 ⁰ C
3. atomize	7 sec @ 2540 ⁰ C

8.4.4 A 50- μ l aliquot of sample is injected into the furnace followed by a 50- μ l aliquot of 1000- μ g/ml Ni as $\text{Ni}(\text{NO}_3)_2$. The absorbance is then measured. Sample loadings greater than 500 ng are diluted to a lower range.

8.4.5 A minimum of one duplicate analysis per sample should be done.

8.4.6 To obtain reliable results, samples must be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, ... etc.

9. Calibration and Standardization

9.1 To each centrifuge tube designated to contain a standard, add 100 mg SKC #106 activated charcoal. Add 1-ml of appropriate standard solution to each tube, stopper and agitate in an ultrasonic bath for 30 minutes as with samples. Repeat this procedure for each new sample batch.

9.2 Prepare a calibration curve from graduated standards by plotting absorbance against As concentration. Run samples, alternately with standards of similar concentration to minimize the effect of variations in absorbance readings.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance area of the sample by using calibration curves.

10.2 Convert micrograms arsenic to micrograms arsine using molecular weight ratio, $78/75 = 1.04$.

10.3 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where

$\mu\text{g sample}$ = μg found in front section of sample tube

$\mu\text{g blank}$ = μg found in front section of blank tube

10.4 Add the amount present in the front and backup sections of the sample tube to determine the total weight in the sample.

- 10.5 Divide the total weight in μg found by the correction factor as discussed in Section 8.6; use 0.90 for samples in the range 1.0 to 10 $\mu\text{g}/\text{cu m}$.
- 10.6 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$\text{Actual Volume Sampled} = f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

f = flow rate indicated by rotameter

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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.7 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.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.5)}}{\text{Air Volume Sampled (Liters)}}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature ($^{\circ}\text{C}$) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature ($^{\circ}\text{K}$)

11. References

- 11.1 Denyszyn, R., P. Grohse, and D. Wagoner. 1977. Report on Evaluation and Refinement of Personal Sampling Method for Arsine. Research Triangle Park, North Carolina.

- 11.2 National Institute for Occupational Safety and Health. 1977.
Method S229 for Arsine. In: NIOSH Manual of Analytical Methods,
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Charles S. McCammon
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Measurements Systems Section and
Research Triangle Institute
NIOSH Contract No. 210-76-0142

VINYLLIDENE CHLORIDE

Measurements Research Branch

Analytical Method

Analyte:	Vinlyidene Chloride*	Method No.:	P&CAM 266
Matrix:	Air	Range:	2-12 mg/m ³ in 7 liters of air
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Precision:	5% (analytical)
Date Issued:	11/21/77		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

- 1.1 A known volume of air is drawn through a charcoal tube to trap the vinylidene chloride present.
- 1.2 The charcoal in the tube is transferred to a small vial where the vinylidene chloride is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area or the height of the resulting peak is determined and compared with either the peak areas or heights obtained from injection of standards.

2. Working Range, Sensitivity and Detection Limit

- 2.1 The method was tested with sample loadings between 12 and 85 µg vinylidene chloride per charcoal tube. The samples were collected from atmospheres containing vinylidene chloride in the range of 7.6 to 10.0 mg/m³ and having a relative humidity of greater than 80%.
- 2.2 The slope of the calibration curve (response vs. weight per sample) was 0.0322 area counts/µg when analysis was done by electronic integration. When analysis was done using peak height, the slope of the calibration curve was 4.75×10^{-12} amps/µg.

*1,1-dichloroethene

- 2.3 The lowest quantifiable limit for this method was determined to be 7 μg of vinylidene chloride per sample. At this level the relative standard deviation of replicate samples was found to be less than 10% and the desorption efficiency was greater than 80%. This limit could be lower if the charcoal used is shown to give better desorption characteristics at the lower level.

3. Interferences

- 3.1 When two or more substances are known or suspected to be present in the air sampled, such information should be transmitted with the sample, because the substances may interfere with the analysis of vinylidene chloride.
- 3.2 Any substance which has the same retention time as vinylidene chloride at the operating conditions described in this method is an interference. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.
- 3.3 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 The pooled relative standard deviation of the analytical method was 4.8% for the analysis of 36 samples over the range of 12 to 85 μg vinylidene chloride per sample.
- 4.2 The concentration of the sampled air was also determined using gas phase infrared analyzer. The GC determinations averaged 5% low when compared to the results of the infrared analyzer. No desorption efficiency corrections were used.
- 4.3 The breakthrough volume and, therefore, the capacity of charcoal for vinylidene chloride decreased with increasing relative humidity. At 87% relative humidity the breakthrough volume was 10% of the breakthrough volume at 10% relative humidity. The breakthrough volume was also found to be a function of concentration of vinylidene chloride. When high relative humidity air containing 144 mg/m^3 vinylidene chloride was sampled at 0.2 liters per minute the breakthrough volume was 3.7 liters. At a vinylidene chloride concentration of 10 mg/m^3 and high relative humidity the breakthrough volume was 7.3 liters.

- 4.4 Samples of vinylidene chloride on charcoal were found to be stable at 25°C for 7 days and for 21 days if stored at 5°C for the remainder of the period.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Many of the interferences can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the capacity of the charcoal tube. When the sample value obtained for the backup section of the charcoal tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds may migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section). This can be minimized by storing the samples in a refrigerator until analysis is performed.
- 5.3 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. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.
- 5.4 The recommended GC packing will not separate vinyl chloride and carbon disulfide. Other GC packings that separate vinyl chloride and carbon disulfide do not separate vinylidene chloride and carbon disulfide. If analysis for each of these monomers is to be performed, it is advisable to use two different GC columns to analyze the samples.

6. Apparatus

- 6.1 Personal sampling pump capable of accurate performance at 0.2 liters per minute and calibrated with a representative charcoal tube in the line.
- 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 activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. 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 must be less than one inch of mercury at a flow rate of 0.2 liters per minute.

- 6.3 Gas chromatograph equipped with a flame ionization detector.
Optional: electronic integrator.
- 6.4 Silanized glass GC column (10 ft x 1/4 in o.d.) packed with Durapak OPN 100/120 mesh. Any GC column capable of separating carbon disulfide and vinylidene chloride may be used.
- 6.5 Vials, 2-ml, with serum caps containing Teflon lined silicone rubber septa.
- 6.6 Microliter syringes, 10- μ l and convenient sizes for making standards.
- 6.7 Pipet, 1.0 ml.

7. Reagents

All reagents used should be ACS Reagent Grade or better.

- 7.1 Carbon disulfide, spectroquality.
- 7.2 Vinylidene Chloride, 99%.
- 7.3 Cyclohexane.
- 7.4 Helium, Bureau of Mines grade A.
- 7.5 Hydrogen, prepurified.
- 7.6 Air, filtered and compressed.

8. Procedure

- 8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis should be washed with detergent and rinsed thoroughly with tap water and distilled water.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling the ends of the tube are broken to provide an opening (2 mm) at least one-half the internal diameter of the tube.
 - 8.2.2 The tube is connected to the sampling pump via rubber tubing. The smaller section of charcoal is the backup and is positioned nearest the sampling pump.
 - 8.2.3 The charcoal tube should be vertical during sampling to prevent channeling through the charcoal tube.

- 8.2.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.2.5 The flow rate and time or volume sampled must be measured and reported. The sample is taken at 0.2 liter per minute or less. The maximum volume sampled should not exceed 7.0 liters.
- 8.2.6 The temperature and pressure of the air being sampled is measured and reported.
- 8.2.7 Immediately after sampling the charcoal tubes are capped with the plastic caps supplied. Rubber caps should not be used.
- 8.2.8 For every 10 samples taken one charcoal tube should be handled in the same manner as the samples (break, seal and transport), except that no air is sampled through this tube. This should be labeled as a blank.
- 8.2.9 If samples are shipped to a laboratory they should be packed tightly to minimize tube breakage during shipping.
- 8.2.10 Six to twelve unopened charcoal tubes should also be shipped so desorption efficiency studies can be performed on the same type and lot of charcoal used for sampling.
- 8.2.11 Samples received at the laboratory are logged in and immediately stored in a refrigerator.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. The charcoal tubes are removed from the refrigerator and permitted to equilibrate to room temperature to prevent water condensation on the cold charcoal. Each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The front section (larger) is transferred to a small vial. The separating foam is removed from the tube and discarded. The backup section is also transferred to a small vial. The contents of each individual tube are desorbed before the next sample tube is opened.
- 8.3.2 Desorption of Samples. After the two sections of a charcoal tube are transferred to small vials, 1.00 ml of carbon disulfide is pipetted into each of the two vials. A serum cap is then crimped into place immediately after the carbon disulfide has been added. (All work with carbon disulfide should be performed in a hood because of the high toxicity of carbon disulfide). The capped samples are kept at room temperature with occasional agitation. Desorption is complete in 30 minutes. The samples should be analyzed the same day they are desorbed.

8.3.3 GC Conditions

70 ml/min helium carrier flow
50 ml/min hydrogen flow to detector
500 ml/min air flow to detector
150°C injector temperature
200°C manifold (detector) temperature
65°C (isothermal) oven temperature

Under these conditions the capacity ratio for vinylidene chloride was 5.2.

8.3.4 Injection. Inject a 5- μ l aliquot into the gas chromatograph. A syringe equipped with a Chaney adapter may be used in lieu of the solvent flush technique.

8.3.5 Measurement of Area. The area of a sample peak is measured by an electronic integrator or another suitable form of area measurement. The results are read from a standard curve prepared as discussed in Section 9.

8.3.6 Measurement of Peak Height. The product of peak height and attenuator setting is linear over the analytical range. The peak height is multiplied by the attenuator setting necessary to keep the peak on scale. Preliminary results are read from a standard curve prepared as discussed in Section 9.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound can vary between laboratories and batches of charcoal. Also, for a given batch of charcoal the desorption efficiency can vary with the weight of contaminant adsorbed. The charcoal used for the study of this method gave a desorption efficiency of 80% for a loading of 7 μ g vinylidene chloride per 100 mg bed of charcoal.

8.4.2 Procedure for Determining Desorption Efficiency

The desorption efficiency should be determined at three levels with a minimum of three samples at each level. Vinylidene chloride can be dissolved in cyclohexane to give stock solutions. The concentrations should be such that no more than 8 μ l of a stock solution will be injected onto the charcoal. Activated charcoal in an amount equivalent to that found in the larger section of the charcoal tube (100 mg) is placed in a small vial and capped. An aliquot of the stock solution is injected into the charcoal tube. Two of the levels should reflect the extremes of the analytical range while the third level is in between the

high and low levels. Each vial is allowed to stand overnight to assure complete adsorption of vinylidene chloride onto the charcoal. Standards are prepared by injecting an identical amount of cyclohexane stock solution into 1.0 ml of carbon disulfide. The samples and standards are analyzed 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. The desorption efficiency curve is constructed by plotting the amount of vinylidene chloride found in a sample versus the desorption efficiency.

9. Calibration and Standardization

CAUTION: Vinylidene chloride has been tentatively identified as a carcinogen. Precautions must be taken while handling this compound to prevent contamination of personnel and the working area.

It is convenient to express the concentration of standards in terms of $\mu\text{g}/1.0 \text{ ml}$ carbon disulfide or $\mu\text{g}/\text{sample}$. The density of vinylidene chloride is used to convert the volume of vinylidene chloride taken to mass of vinylidene chloride taken ($1.218 \text{ mg}/\mu\text{l}$). 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 samples. It is best to alternate standard then sample, during the analysis. Curves are established by plotting the concentration of the standards in $\mu\text{g}/1.0 \text{ ml}$ carbon disulfide versus peak area or peak height.

10. Calculations

10.1 The sample weight in μg is read from the standard curve.

10.2 Blank corrections are not expected 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 charcoal tube

W_S - amount found on the front section of the charcoal tube

W_b - amount (μg) found on the front section of the blank charcoal tube.

A similar procedure is followed for the backup sections.

10.3 A correction for desorption efficiency is made.

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

where: M_F - corrected amount (μg)

W_F - amount (μg) after blank correction

D - desorption efficiency corresponding to the weight W_F .

The corrected amount of the backup section M_B is similarly calculated.

10.4 The concentration, C , of vinylidene chloride in the air sampled is expressed in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{liter}$.

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

where: M_F - amount of vinylidene chloride found on front section in μg

M_B - amount of vinylidene chloride found on backup section in μg

V - volume of air sampled in liters

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

$$C(\text{ppm}) = C(\mu\text{g}/\text{l}) \times \frac{24.45}{96.9} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P - pressure of air sampled in torr

T - temperature of air sampled in $^\circ\text{C}$

24.45 - molar volume at 25°C and 760 torr in liters/mol

96.9 - molecular weight of vinylidene chloride in g/mol

11. References

- 11.1 Organic Solvents in Air, "NIOSH Manual of Analytical Methods," HEW Publication No. (NIOSH) 75-121, U.S. Government Printing Office, Washington, D.C. (1974) p. 1271.
- 11.2 L.W. Severs and K.V. Skory, "Monitoring Personnel Exposure to Vinyl Chloride, Vinylidene Chloride, and Methyl Chloride in an Industrial Environment," Amer. Ind. Hyg. Assoc. J., 36, 669 (1975).

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4-AMINOBIIPHENYL

Measurements Research Branch

Analytical Method

Analyte:	4-Aminobiphenyl	Method No:	P&CAM 269
Matrix:	Air	Range:	4-1000 $\mu\text{g}/\text{m}^3$ in a 50-liter air sample
Procedure:	Collection on glass fiber filter and silica gel, elution with 2-propanol, analysis by gas chromatography	Precision:	10%
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a three-stage sampler consisting of a high-efficiency glass fiber filter followed by two beds of silica gel to collect the 4-aminobiphenyl aerosol and/or vapor.
- 1.2 The filter and sorbent sections of the sampler are transferred to stoppered tubes and the 4-aminobiphenyl is desorbed with 2-propanol.
- 1.3 An aliquot of this solution is injected into a gas chromatograph.
- 1.4 Peak areas are electronically determined and compared with a calibration curve obtained from injections of standard solutions of 4-aminobiphenyl.

2. Range, Sensitivity and Detection Limit

- 2.1 The analytical range is 0.2-50 $\mu\text{g}/\text{sample}$ (4-1000 $\mu\text{g}/\text{m}^3$ for a 50-L air sample) when using 0.5 mL of desorbing solution and 1- μL injections into the gas chromatograph.
- 2.2 The amount of 4-aminobiphenyl vapor retained on the primary silica gel bed decreases as the relative humidity of the sampled air increases. In experiments in which atmospheres containing 600 $\mu\text{g}/\text{m}^3$ of 4-aminobiphenyl in air of 80% relative humidity and at 30 °C

were sampled, less than 4% of the analyte appeared in the secondary silica bed when 45 L was sampled. At 50% relative humidity and 30 °C, 90 L of air containing 800 $\mu\text{g}/\text{m}^3$ was sampled with no analyte detected in the secondary silica bed.

2.3 The limit of detection is 0.05 $\mu\text{g}/\text{sample}$.

3. Interferences

3.1 In solutions containing 4-aminobiphenyl at 1-2 $\text{ng}/\mu\text{L}$, the following compounds were found not to interfere when their concentrations were 1-3 $\text{ng}/\mu\text{L}$: 1-naphthol, 2-naphthol, 1-naphthylamine, 2-naphthylamine, 2-nitronaphthalene, 2-nitrobiphenyl, 4-nitrobiphenyl, and 3-aminobiphenyl. The retention time of 3-nitrobiphenyl is the same as 4-aminobiphenyl and interferes with the analysis.

3.2 Any compound sampled with 4-aminobiphenyl and having the same retention time as the analyte will interfere with the analysis. This type of interference often can be eliminated by changing the operating conditions of the chromatograph, e.g., by temperature programming or by changing the stationary phase.

4. Precision and Accuracy

4.1 The precision of the overall method is 10% relative standard deviation for samples collected at 30 °C and 80% relative humidity. This value is based on 29 samples involving volumes of 13 to 90 liters and a sampling rate of 0.2 L/min. Concentrations sampled ranged from 66 to 720 $\mu\text{g}/\text{m}^3$.

4.2 Filters spiked with 4-aminobiphenyl (0.3 and 2 μg) and stored at ~ 24 °C yielded recoveries of 55% (0.3 μg) and 93% (2 μg) after three days; and 7 and 62%, respectively, after 14 days. Spiked filters stored at -15 °C yielded recoveries of 91% (0.3 μg) and 99% (2 μg) after three days; and 71 and 94%, respectively, after 14 days. Within eight days, recoveries $\geq 75\%$ were obtained at both spike levels for filters stored at -15 °C. In the case of silica gel, recoveries $\geq 83\%$ were obtained at both spike levels after 14 days of storage either at 24 °C or -15 °C. It is recommended that field samples be shipped in dry ice and stored in a freezer until analyses can be conducted.

4.3 Analysis of the back-up silica gel section serves as a check on sample integrity. If more than 10% of the total recovered weight is found on this section, sample loss due to breakthrough may be indicated. Under these circumstances, the actual ambient concentration may be greater than the sample analysis indicates.

4.4 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

- 5.1 The sampler is a small portable device containing no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities.
- 5.2 Relative humidity has an effect on the collection efficiency of the absorbent. (Section 2.2)
- 5.3 At a flow rate of 0.2 L/min, the linear velocity through the 4-mm inlet of the holder is 26.5 cm/s. It is not known if this throat velocity is sufficient for the capture of all particles of analytical importance.
- 5.4 This method has not been field tested.
- 5.5 4-Aminobiphenyl samples are unstable at ambient temperature. Special precautions in shipping and storing the samples are required.

6. Apparatus

- 6.1 Personal air sampling pump that can be maintained for four hours at a flow rate of 0.2 L/min with the sampler in line. Each pump should be calibrated with a representative sampler in line to minimize errors in volume measurement. A bubble flow meter or other suitable flow measuring device may be used.
- 6.2 Sampler, equivalent to that shown in Figure 1. The sampler consists of three sections: a high-efficiency glass fiber filter, followed by 100-mg and 50-mg beds of silica gel. The first section, a 13-mm glass fiber filter (Spectrograde or Type A-E, Gelman Instrument Co., Ann Arbor, MI, or equivalent) is contained in a 13-mm filter holder (SX00-013-00 Millipore Corp., Bedford, MA, or equivalent). The sorbent tube is a 50-mm section of Pyrex glass, 6.4-mm o.d. x 4-mm i.d. flared on one end, containing the sections of silica gel (Grade 407, 20/45 mesh, 720-760 m²/g, 0.737 g/cc; Coast Engineering Laboratories, Gardena, CA, or equivalent). The sorbent is held by 3.5-mm diameter, 100-mesh, stainless steel screens and 4-mm o.d. Teflon rings, as shown in Figure 1. To connect the two stages, the filter holder is pressed into the flared end of the sorbent tube. The pressure drop across the sampler at 0.2 L/min is 10 torr. Flexible vinyl caps are used to seal the ends of the sampler.
- 6.3 Gas chromatograph equipped with a flame ionization detector (FID) and injection port.
- 6.4 Glass column, 1.8-m x 2-mm i.d. x 6.4-mm o.d., packed with 3% OV-225 on 80/100 mesh Supelcoport (Supelco, Inc., Bellefonte, PA, or equivalent).
- 6.5 Potentiometric strip chart recorder.

- 6.6 Test tubes, 1-mL, fitted with polyethylene stoppers.
- 6.7 Glass syringes, 5- and 10- μ L.
- 6.8 Pipettes of convenient volumes for the preparation of standard solutions.
- 6.9 Volumetric flasks of convenient volumes for the preparation of standard solutions.
- 6.10 Clinical centrifuge.
- 6.11 Analytical balance.
- 6.12 Test tube shaker, vortex type.

7. Reagents

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

- 7.1 2-Propanol, UV grade, distilled in glass.
- 7.2 Acetone, distilled in glass.
- 7.3 Methyl alcohol.
- 7.4 4-Aminobiphenyl.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis is washed with detergent and rinsed with tap water, distilled water, and methyl alcohol.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling, the vinyl caps are removed from the ends of the sampler and saved for resealing after sampling.
 - 8.2.2 The sorbent end of the sampler is connected to the pump with plastic or rubber tubing. The sampler is positioned vertically during sampling. Sampled air must not pass through any tubing before entering the sampler.
 - 8.2.3 The atmosphere is sampled at a flow rate of 0.2 L/min for no longer than 4 hours. The flow rate and sampling time, or the volume of sampled air, must be measured as accurately as possible.

- 8.2.4 The temperature, pressure, and humidity of the atmosphere being sampled are measured and recorded, along with other pertinent data such as location, date, and time of sampling.
- 8.2.5 Blank samples are obtained by handling random collection devices in the same manner as in sampling, except that no air is drawn through them.
- 8.2.6 Samples shipped to the laboratory should be packed tightly to minimize breakage.
- 8.2.7 The samples should be stored in a freezer until analyses can be conducted.
- 8.2.8 If samples of bulk material associated with the process under investigation are to be shipped to the laboratory, they should not be placed in the same container as the air samplers or blanks.

8.3 Analysis of Samples

- 8.3.1 Place the glass fiber filter and the 100-mg section of silica gel in a 1-mL tube or other suitable vial. Place the 50-mg section of silica gel in a separate test tube. Teflon rings and stainless steel screens associated with the sampler may be analyzed with the appropriate stages. Sampler caps can be discarded.
- 8.3.2 Add 0.5 mL of 2-propanol to each vial and cap it.
- 8.3.3 Allow the vials to stand for one hour, shaking them intermittently in a test tube vibrator. Centrifuge for 10 minutes.
- 8.3.4 Gas Chromatographic Conditions

Column:	3% OV-225 on 80/100 mesh Supelcoport in 1.8-m x 2-mm i.d. x 6.4-mm o.d. glass tubing.
Column Temperature:	190 °C
Injector Temperature:	210 °C
Detector Temperature:	200 °C
Helium:	22 mL/min
Hydrogen:	85 mL/min
Air:	378 mL/min

Detector:	FID; Attenuation 1 x 2 at low concentrations
Injection Volume:	1.0 μ L
Efficiency:	2600 theoretical plates
Capacity Ratio:	13.4

8.3.5 Injection: Flush the 5- μ L syringe first with acetone (to insure its cleanliness and to wet the barrel and plunger) and then with the sample solution. Carefully draw 1 μ L of sample solution into the syringe (to minimize the intake of particulate matter) and inject the aliquot into the gas chromatograph.

8.4 Efficiency of Desorption

8.4.1 Importance of Determination. The efficiency of desorption for 4-aminobiphenyl can vary from one laboratory to another and also from one batch of silica gel or filters to another. Thus, it is necessary to determine the fraction of 4-aminobiphenyl that can be recovered from these matrices. Since the efficiency of desorption may also vary with the amount of 4-aminobiphenyl present, determinations should be made for at least two levels in the range of anticipated sample sizes. If the efficiencies of desorption for the filter and primary silica gel bed do not vary by more than 5%, these two stages may be analyzed together. If greater variances are found, it may be necessary to analyze the stages individually and make appropriate corrections (Section 10.3).

8.4.2 Procedure for Determining the Efficiency of Desorption. Place the filters and silica gel from unused samplers in 1-mL test tubes. Add to each a known amount of 4-aminobiphenyl in 10 μ L of 2-propanol using the same microliter syringe for each. Five filter and silica gel samples are thus prepared at each of two different levels in the range of interest. Cap the tubes and store them in the freezer overnight. Treat a parallel blank in the same manner (no analyte is added). Prepare at least three standards at each of the various levels by adding 10 μ L (same syringe as above) of the 4-aminobiphenyl solutions to 0.5 mL of desorbent solution. Analyze the samples and standards as described in Section 8.3. The efficiency of desorption is the average gas chromatographic peak area given by the samples, corrected for the blank if necessary, divided by the average area given by the standards.

9. Calibration and Standardization

- 9.1 For accuracy in the preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at high concentration. The initial standard is prepared by weighing a selected amount of 4-aminobiphenyl (e.g., 125 mg) into a 250-mL volumetric flask and adding the desorbing solution to the calibration mark. Dilutions encompassing the concentration range of interest down to 0.3 ng/ μ L are then made from the stock solution. Solutions should be stored in a refrigerator when not in use to minimize degradation.

CAUTION: 4-AMINOBIIPHENYL HAS BEEN IDENTIFIED AS A CARCINOGEN. APPROPRIATE PRECAUTIONS MUST BE TAKEN IN HANDLING THE COMPOUND TO AVOID PERSONNEL EXPOSURE AND AREA CONTAMINATION.

- 9.2 The standard solutions should be analyzed under the same gas chromatographic conditions and during the same time period as the samples. This will minimize inaccuracy due to day-to-day variations in the setting of instrumental conditions.
- 9.3 Calibration curves for 4-aminobiphenyl are prepared by plotting the peak areas for the standards against their concentration in μ g/0.5 mL.

10. Calculations

- 10.1 In the event that the blank produces a peak with the same retention time as the analyte, the analyst should determine the source of the interference and eliminate, or compensate for it.
- 10.2 Read the weight (W_1) in μ g of 4-aminobiphenyl present in the sample from the calibration curve.
- 10.3 The corrected weight (W_2) is determined by

$$W_2 = \frac{W_1}{D}$$

where D is the efficiency of desorption for that sampler stage.

- 10.4 Add the weights found in the sampler stages to determine the total weight (W_t) collected.
- 10.5 The concentration of 4-aminobiphenyl in air (C , μ g/ m^3) is given by

$$C = \frac{W_t}{V} \times 10^3$$

where V is the volume of air sampled in liters and 10^3 is the factor to convert from liters to m^3 .

11. References

Raul Morales, J. F. Stampfer, Jr., R. E. Hermes, E. E. Campbell, and H. J. Ettinger, "Development of Sampling and Analytical Methods for Carcinogens, October 1, 1976-December 31, 1977," Progress Report LA-7375-PR, National Technical Information Service, Springfield, Virginia, 1978.

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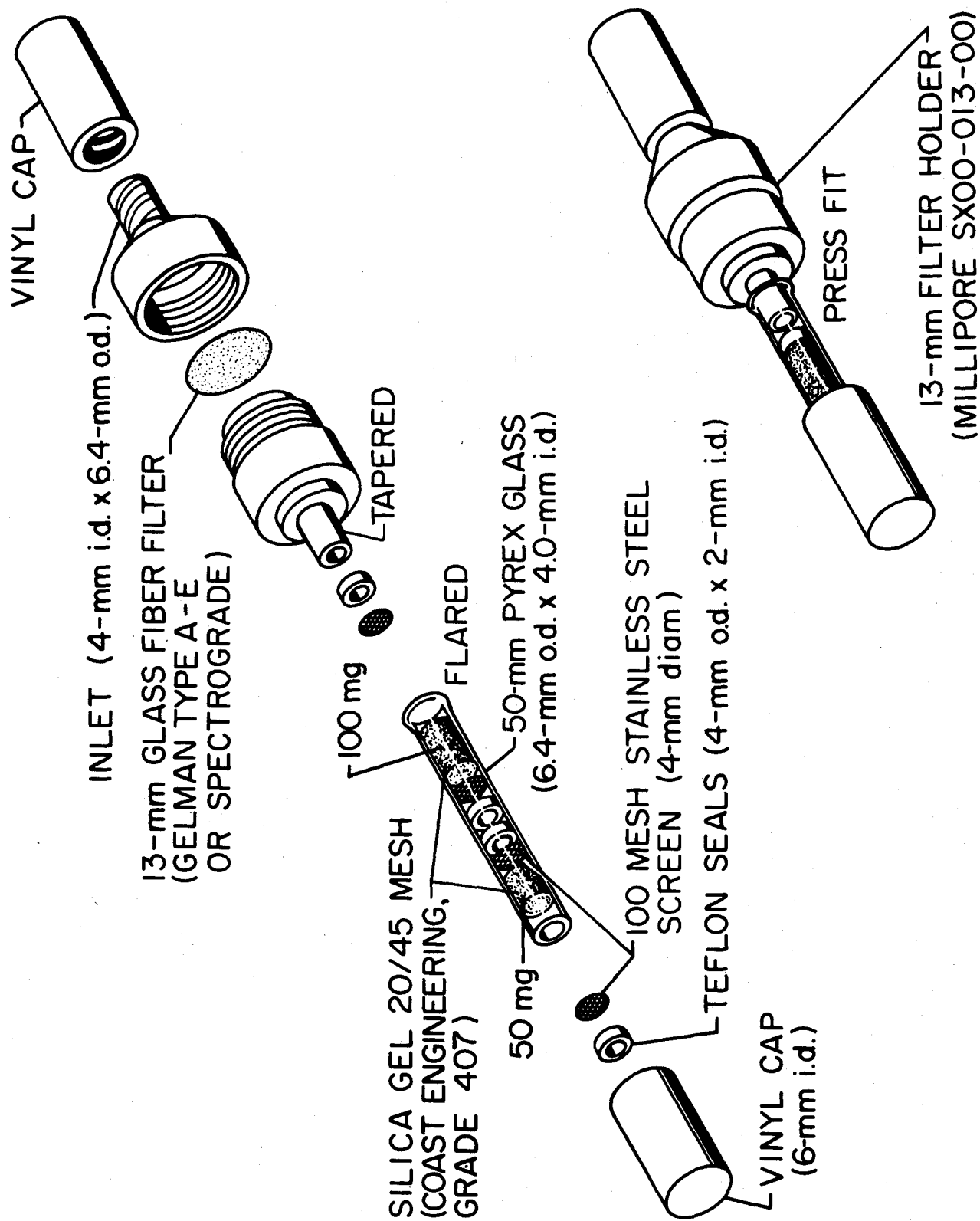


Figure 1. Three-Stage Personal Sampler

AMINOETHANOL COMPOUNDS

Measurements Research Branch

Analytical Method

Analytes:	2-Aminoethanol (Ethanolamine) 2-Diethylaminoethanol 2-Dibutylaminoethanol	Method No:	P&CAM 270
Matrix:	Air	Range:	See Paragraph 2
Procedure:	Adsorption on silica gel, elution with methanolic acid, derivatization of 2-aminoethanol, GC analysis	Precision:	2-9% (Analytical)
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

A known volume of air is drawn through a tube containing silica gel to trap the aminoethanol compounds. Concentrated HCl is added to stabilize amines collected. The sorbent sections are transferred to glass tubes and treated with methanol solution. An aliquot is alkalinized with sodium hydroxide. Benzaldehyde is added to derivatize 2-aminoethanol forming benzylidene-aminoethanol. The solution is analyzed by gas chromatography with flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

The ranges of the method for the various analytes are at least

2-Aminoethanol	0.1-15 mg/sample
2-Diethylaminoethanol	0.1-12 mg/sample
2-Dibutylaminoethanol	0.1-17 mg/sample

The lower ends of the ranges given are levels where the desorption and analysis procedure was evaluated and found to be acceptably precise (see paragraph 4.3). The upper limits are determined by the capacities of the first section of the sampling tube used to collect the sample. Amounts of individual compounds retained on 150 mg of a 42/60-mesh silica gel in 6-mm-i.d. sampling tubes at 1 L/min sampling flow rate were found to be those given above as the upper limits.

3. Interferences

- 3.1 Water vapor does not significantly affect collection efficiency.
- 3.2 Large amounts of ammonia or primary amines will reduce the amount of benzaldehyde available for reaction with 2-aminoethanol. Such interferences should be compensated for by adding additional benzaldehyde.
- 3.3 Any compound which has nearly the same retention time on the GC column as one of the analytes is an interference. Retention time data on a single GC column cannot be considered as proof of chemical identity. The presence and identity of possible interfering substances may be determined by the analysis of bulk samples from the process or environment.

4. Precision and Accuracy

- 4.1 The volume of air sampled can be measured to within $\pm 2\%$ if a pump with a calibrated volume indicator and an adequate battery is used. Volumes calculated from initially set flow rates may be less accurate ($\pm 5-10\%$) unless changes in flow rate are manually or electronically monitored and compensated.

- 4.2 Below the following levels precisions of replicate GC analyses of standards were worse than 9% relative standard deviation.

2-Aminoethanol	0.10 mg/sample
2-Diethylaminoethanol	0.08 mg/sample
2-Dibutylaminoethanol	0.02 mg/sample

At the upper limits of the method analytical precision becomes 2% relative standard deviation or better.

- 4.3 The precision (relative standard deviation) of the method based on analyses of replicate 0.1 mg samples injected by syringe into silica gel sections was

2-Aminoethanol	3%
2-Diethylaminoethanol	7%
2-Dibutylaminoethanol	2%

Replicate samples of vapor at higher sample levels had precisions ranging from 2-7%.

- 4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GC peaks of samples and standards. An electronic digital integrator with baseline correction capability is best for this purpose.
- 4.5 Collection efficiency is 100% until breakthrough of the sampling tube beds occurs (see Section 2).

- 4.6 Desorption efficiencies based on analyses of replicate 0.1 mg samples on silica gel and standards in 2 mL eluent were found to be

2-Aminoethanol	0.97 (7%)
2-Diethylaminoethanol	0.85 (22%)
2-Dibutylaminoethanol	0.93 (3%)

with the relative standard deviations given in parentheses. Measurements at higher sample levels have given desorption efficiencies consistently in the range 90-100%.

- 4.7 This method has given quantitative results equivalent to an independent method involving adsorption of 2-aminoethanol vapors in water in a bubbler and titration with standard acid. Using each method, four or five 0.030-m³ vapor in nitrogen samples were taken at 1 L/min. The following sample amounts and relative standard deviations in parenthesis were determined:

<u>Tube and Chromatography</u>	<u>Bubbler and Titration</u>
0.31 mg (7.3%)	0.35 mg (3.4%)
1.91 mg (5.0%)	1.74 mg (1.5%)

5. Advantages and Disadvantages

- 5.1 The method uses a small, portable sampling device involving no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities. Transportation to the analytical laboratory is simplified with the solid sorbent tube.
- 5.2 The sorbent tube has a high capacity even at high relative humidities. It can be used for at least eight hours to measure a workday average concentration, or for shorter times to measure excursion concentrations.
- 5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.
- 5.4 Several amines can be collected and determined simultaneously. The GC analysis distinguishes which are present and at what individual concentrations they occur. Interferences by other amines are much less likely than in colorimetric or titrimetric methods.
- 5.5 A major disadvantage is the tendency of amines to oxidize while adsorbed on surfaces exposed to air. This is overcome by addition of concentrated hydrochloric acid to the sorbent sections soon after sampling.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 Sorbent. The silica gel used should be the equivalent of Silica Gel D-08, chromatographic grade, activated and fines

free, 42/60 mesh, as produced by Coast Engineering Laboratories and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania.

- 6.1.2 Sampling Tubes. Glass tubes 7-cm-long and 6-mm-i.d., tapered and flame sealed at one end, are packed with two 150-mg sections of silica gel. Glass wool plugs are used to separate and enclose the sections. The second end is flame sealed to prevent contamination during storage prior to use.

NOTE: Sampling tubes constructed with metal parts or urethane foam plugs should not be used. Concentrated hydrochloric acid will react with these materials.

- 6.1.3 Personal Sampling Pump. Battery-operated pumps are required, capable of operation at 0.2 L/min for up to eight hours or at 1.0 L/min for up to two hours with a sampling tube in line. The pump is to be calibrated with a representative sorbent tube in line. A wet or dry test meter or bubble meter capable of measuring a flow rate of 0.2 L/min and/or 1.0 L/min to within $\pm 2\%$ may be used in setting the pump flow.
- 6.2 Gas chromatograph with a flame ionization detector. Temperature programming capability is necessary to determine more than one compound simultaneously.
- 6.3 GC column, 1.8-m x 2-mm i.d. glass, silanized and packed with 10% (by weight) Carbowax 20M and 2% KOH on 80/100-mesh Chromosorb W AW, or equivalent support.
- 6.4 Strip chart recorder compatible with the GC. An electronic digital integrator is desirable.
- 6.5 Test tubes or glass vials, 2-mL, sealed by a septum.
- 6.6 Syringes, 10- μ L.
- 6.7 Syringe for dispensing concentrated HCl, 50- μ L, with glass barrel, fluorocarbon-tipped plunger, and inert (platinum or fluorocarbon) needle.
- 6.8 Pipettes, 0.5-mL and 2-mL.
- 6.9 Volumetric flasks, 10-mL.
- 6.10 File and Forceps.
7. Reagents - All chemicals must be analytical reagent grade.
- 7.1 2-Aminoethanol (ethanolamine).
- 7.2 2-Diethylaminoethanol.
- 7.3 2-Dibutylaminoethanol.

- 7.4 Water, doubly distilled and aldehyde-free. Deionized water should not be used as it may contain formaldehyde and other impurities leached from the ion-exchange resins.
- 7.5 Concentrated hydrochloric acid (38%, 12 M).
- 7.6 Benzaldehyde.
- 7.7 Eluent solution, 4:1 methanol-water (by volume).
- 7.8 Alkalinizing solution, 0.20 N NaOH in 4:1 methanol-water (by volume).
- 7.9 Helium, Bureau of Mines Grade A.
- 7.10 Hydrogen, prepurified.
- 7.11 Air, compressed and filtered.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware is washed with detergent solution, rinsed with tap water and distilled water, and dried in an oven.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least 2 mm in diameter.
 - 8.2.2 Attach the tubing from the sampling pump to the backup end of the sampling tube. Sampled air must not pass through any hose or tubing before entering the sorbent tube.
 - 8.2.3 With the sorbent tube in a vertical position as much as is practical, sample the air at 1.0 L/min for 15 min-2 hours or at 0.2 L/min for 2-8 hours. Intermediate flow rates and other sampling periods may be used, as appropriate.
 - 8.2.4 Immediately after sampling is completed, add 20 μ L of concentrated HCl to each section of silica gel in the tube. Use a 50 μ L glass syringe with fluorocarbon-tipped plunger and inert needle, so that the acid does not contact and react with stainless steel. The silica gel will turn yellow upon addition of the acid due to iron impurities in the silica gel.
 - 8.2.5 Seal the sorbent tubes with polyethylene caps.
 - 8.2.6 Obtain a blank sample by handling one tube in the same manner as the sample tubes (break, add acid, seal, and ship) except that no air is pumped through it.

- 8.2.7 For shipping to the laboratory, pack the tubes tightly to minimize chances of breakage during transit. Tubes should not be subjected to extremes of high temperature or low pressure.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Score each tube with a file 5 mm in front of the glass wool plug that precedes the first sorbent section and break the tube there. Transfer this plug and the initial section to a 2-mL test tube or glass vial that can be septum sealed. Likewise, transfer the second plug and sorbent section to another test tube. Label each appropriately for separate analysis.
- 8.3.2 Desorption. Add 2 mL of eluent solution to each sorbent section. Seal the samples. Shake the mixtures occasionally over a period of two hours. Tests have shown that complete desorption occurs within two hours and samples are stable for at least a day.
- 8.3.3 Preparation. Transfer a 0.50-mL aliquot of each eluate to another test tube or vial. Add 0.50 mL of alkalinizing solution and mix thoroughly. Verify the basicity of the solution with litmus paper.
- 8.3.4 Reaction. If 2-aminoethanol is present in the sample, repeat the preparation step with another 0.50-mL aliquot. Add 10- μ L of benzaldehyde to the basic solution, mix thoroughly, and allow at least 20 min for reaction.
- 8.4.5 Gas Chromatograph Conditions. Typical operation conditions are:

Helium gas flow rate, 50 mL/min.
Injection port temperature, 150 °C.
Detector temperature, 250 °C.
Column temperature, 90 °C for three min, heat to 225 °C at 16 °C/min, and hold for six min.

Under these conditions, retention times are 213 sec for 2-diethylaminoethanol, 365 sec for 2-aminoethanol, 515 sec for 2-dibutylaminoethanol, and 866 sec for 2-benzylideneaminoethanol. When only one compound is present isothermal analysis is best at 90 °C (retention time, 280 sec) for 2-diethylaminoethanol, 150 °C (retention time, 180 sec) for 2-dibutylaminoethanol, or 225 °C (retention time, 195 sec) for 2-benzylideneaminoethanol.

- 8.3.6 Injection of Sample. Inject and analyze 3- μ L aliquots of each sample and standard. To eliminate difficulties arising from blowback or distillation within the 10- μ L syringe, use a solvent flush technique.

8.3.7 GC Peak Measurement. Determine the areas of the peaks of the compounds of interest from analyses of samples and standards.

8.4 Determination of Desorption Efficiency

8.4.1 Importance. Desorption efficiency for a particular compound can vary from one lot of silica gel to another and from one laboratory to another. Also, for a given lot of silica gel the desorption efficiency may vary with the amount of material adsorbed during sampling. Therefore, it is necessary to determine at least once the desorption efficiency for each aminoethanol with each lot of silica gel used for at least two levels within the normal range of samples size. If the desorption efficiencies are significantly different from quantitative recovery, they should be used to correct the measured weight of aminoethanols as described in Section 10.2 below.

8.4.2 Procedure. Place 150 mg of silica gel in a 2-mL glass-stoppered tube. The silica gel must be from the same lot as that used in collecting the sample; it can be obtained from unused sorbent tubes. With a microliter syringe, inject a known amount of the aminoethanol, either pure or in water solution, directly onto the silica gel. Also inject 20 μ L of concentrated HCl. Close the tube with the glass stopper and allow it to stand overnight to insure complete adsorption of the amine. Prepare at least three tubes for each at two different levels. These tubes are referred to as samples. Prepare a blank in the same manner, omitting the aminoethanol. Analyze the samples and blank as described in Section 8.3. Also analyze three standards prepared by adding identical amounts of the aminoethanol and 20 μ L of concentrated HCl to 2.0 mL of eluent solution. Determine the concentrations of the aminoalcohols in the blank, samples, and standards using calibration curves prepared as described in Section 9. The desorption efficiency is calculated by dividing the concentration of amine found in the sample by the concentration obtained for the corresponding standard.

9. Calibration and Standardization

9.1 Preparation of a Stock Solution. Calculate for each compound i the volume V_i (μ L) of pure liquid required for preparation of 10 mL of a stock solution, 10 μ L of which contains amounts of aminoethanols equal to those collected from volume of air V_s at concentrations X_i :

$$V_i = \frac{X_i \times V_s}{d_i} \times 1000$$

Where:

X_i - the standard concentration limit, or the anticipated average concentration, (mg/m^3) of compound i in air.

V - volume (m³) of air sampled.

d_i - density (mg/μL) of a pure compound i.

1000 - aliquot factor.

Add the calculated volumes of each compound to a 10-mL volumetric flask and dilute to the mark with 4:1 methanol-water. Neutral solutions of aminoethanols are subject to oxidation and should be prepared fresh when needed.

- 9.2 Preparation of Calibration Standards. Add 2.5 μL, 5 μL, 10 μL, 15 μL and 20 μL of the prepared standards to reaction tubes containing 2 mL eluent solutions and 10 μL concentrated hydrochloric acid. Use a 10-μL syringe to inject through septum seals. Shake these tubes. These standards correspond to 0.25, 0.5, 1, 1.5, and 2 times X_i in V_s, respectively. Other standards may be similarly prepared, if desired.
- 9.3 React and analyze standards with samples according to Section 8.3.
- 9.4 Prepare a calibration curve for each amine by plotting peak areas obtained from the analyses of standards against nominal amount (mg) in the calibration standards.

10. Calculations

- 10.1 Read the weights (mg) of each compound corresponding to each peak area from the appropriate calibration curve. Correct each value for the weight found in a blank, if any. Add the weights found in the front and backup sections of the sample tube to obtain the total weight of compound in the air volume sampled.
- 10.2 Divide the total weight by the desorption efficiency to obtain the corrected sample weight.
- 10.3 Determine the volumes (m³) of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min) and 10⁻³ m³/L. 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:

$$V_s = 10^{-3} \times f \times t \times \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

f - sample flow rate (L/min)

t - sampling time (min)

P₁ - pressure during calibration of sampling pump (torr)

P_2 - pressure of air samples (torr)
 T_1 - temperature during calibration of sampling pump ($^{\circ}\text{K}$)
 T_2 - temperature of air sampled ($^{\circ}\text{K}$)

- 10.4 Divide the total corrected weight (mg) of each compound by V_s (m^3) to obtain the concentration of the compound in the air sampled (mg/m^3).

11. References

- 11.1 G. O. Wood, R. G. Anderson, and J. W. Nickols, "Sampling and Analysis of Aminoethanols in Air," Report LA-UR-77-1398 (1977), Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. (Presented at the 1977 American Industrial Hygiene Conference, May 1977, New Orleans).
- 11.2 G. O. Wood and J. W. Nickols, "Development of Air-Monitoring Techniques Using Solid Sorbents, October 1, 1976 - December 31, 1977," Progress Report LA-7295-PR, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Also available from the National Technical Information Services, Springfield, VA. (1978).

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Particulate Tungsten and Compounds

Measurements Research Branch

Analytical Method

Analyte:	Soluble and Insoluble Particulate Tungsten and Compounds (as W)	Method No.	P&CAM 271
Matrix:	Air	Range:	0.14 to 6.8 mg/m ³ for soluble tung- sten; 0.35 to 17.4 mg/m ³ for insoluble tungsten (for a 0.72 m ³ sample)
Procedure:	Membrane filter col- lection, water extraction for soluble tungsten, acid ash for insoluble tungsten, flame AAS analysis		
Date Issued:	12/05/77	Precision:	2.9% RSD (Analytical)
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Particulate matter collected from air on cellulose ester membrane filters is extracted with deionized water and the extract analyzed for "soluble" tungsten species. The filter and residue are then extracted with hydrochloric acid (to remove interferences -- e.g., iron, cobalt), and wet ashed in nitric acid. The residue is then digested in a mixture of nitric and hydrofluoric acids and solubilized in dilute sodium hydroxide and analyzed as "insoluble" tungsten. Analysis is conducted by atomic absorption spectroscopy utilizing a nitrous oxide-acetylene flame and a wavelength of 255.1 nm.

2. Working Range, Sensitivity and Detection Limit

- 2.1 The concentration range for water soluble tungsten compounds is 0.14 to 6.9 mg/m³ and for water insoluble compounds is 0.35 to 17.4 mg/m³ for a 0.72 m³ sample. The range may be extended by diluting to a volume other than that specified or by using a less sensitive wavelength (400.8 nm) for analysis.
- 2.2 Sensitivity varies with different instruments, burners and flame stoichiometry. In this laboratory, sensitivity was determined to be 7.9 µg/ml/1%A.
- 2.3 The lowest allowable solution concentration for precise determination is 10 µg W/ml.

3. Interferences

- 3.1 The extraction (H_2O and HCl) should remove most potential inter-ferents. Sodium sulfate is used to enhance the tungsten absorbance and consequently mask the enhancement effects of other ions.
- 3.2 Metallic cobalt reduces the recovery of tungsten carbide by approximately 5%. This interference is overcome by analyzing spiked filters containing tungstic carbide and cobalt and adjusting the sample concentrations according to these known recoveries (9.3)

4. Precision and Accuracy

- 4.1 The pooled coefficient of variation for the analysis of eight calibration solutions (six determinations each) covering the range 10.2 - 523 $\mu\text{g/ml}$ was 0.029.
- 4.2 The recoveries of tungsten from filters spiked with 360, 725 and 1451 $\mu\text{g W/filter}$ of "soluble" tungsten (Na_2SO_4) were $99.6 \pm 4.5\%$, $102 \pm 2.0\%$ and $100 \pm 1.2\%$, respectively. Recoveries of "insoluble" tungsten (tungsten metal) from filters spiked with approximately 2400, 3600 and 5800 $\mu\text{g W/filter}$ were $97.5 \pm 2.7\%$, $100 \pm 4.3\%$ and $103 \pm 2.8\%$, respectively.

5. Advantages and Disadvantages

- 5.1 An advantage of this method is that it allows for the separate determination of "soluble" and "insoluble" tungsten.
- 5.2 Flame AAS is less prone to interferences than are most colorimetric methods. Also, analysis by atomic absorption spectroscopy is less time consuming than many other methods of analysis.
- 5.3 The main disadvantage of the method is that the necessary extractions and digestions involved in removing chemical interferences and allowing for differentiation of "soluble" and "insoluble" tungsten compounds make the method lengthy and time consuming.

6. Apparatus

6.1 Sampling Equipment

- 6.1.1 Cellulose ester membrane filters, 0.8 μm , 37-mm diameter. Millipore type AA, or equivalent.
- 6.1.2 Filter holder for 37-mm filter, Millipore MAWP 037 AO, or equivalent.
- 6.1.3 Personal sampling pump (1.0 - 2.0 lpm) capable of delivering a flow rate of 1.5 lpm to within $\pm 5\%$ (for 8 hours continuous operation), calibrated with a representative filter unit in the line.
- 6.1.4 Thermometer, manometer, and stopwatch.

6.2 Atomic Absorption Spectrophotometer

- 6.2.1 Atomic absorption spectrophotometer equipped with burner head for nitrous oxide-acetylene flame.
- 6.2.2 Hollow cathode lamp for tungsten ($\lambda = 255.1 \text{ nm}$).
- 6.2.3 Nitrous oxide, commercially available for atomic absorption use.
- 6.2.4 Compressed air, filtered to remove water, oil and other foreign substances.
- 6.2.5 Acetylene, commercially available for atomic absorption use.
- 6.2.6 Pressure reducing valves and appropriate hose connections for each tank of compressed gas. A heating tape, with the temperature controlled by a rheostat, is wound around the second stage of the nitrous oxide regulator and connecting hose to prevent freeze-up of the line.

6.3 Glassware (borosilicate)

- 6.3.1 Volumetric flasks (10, 25 and 100 ml)
- 6.3.2 Micro-pipettes (50 - 1000 μl)
- 6.3.3 Volumetric/transfer pipets (1-5 ml)
- 6.3.4 Side-arm test tubes (25 ml)

6.4 Büchner funnels (43 mm plate diameter)

6.5 Teflon beakers (100 ml) and beaker covers

6.6 Variable temperature hot plate (capable of reaching 200°C)

7. Reagents

Analytical reagent grade or equivalent. Water must be double distilled or deionized.

7.1 Nitric acid, concentrated, redistilled in glass.

7.2 Hydrofluoric acid, 49%

CAUTION:

All operations involving the use of hydrofluoric acid require extreme caution. Protective gloves, in addition to lab coats and safety glasses, should be worn. Also, HF dissolves glass and consequently should not be used in conjunction with glass apparatus (including pipets).

7.3 Hydrochloric acid, concentrated

7.3.1 1:1 HCl:H₂O -- to 50 ml deionized water, add 50 ml concentrated hydrochloric acid.

7.3.2 1:10 HCl:H₂O -- to 90-ml deionized water, add 10 ml concentrated hydrochloric acid.

7.4 Sodium hydroxide (about 0.5 M). Prepared by dissolving 2.0 g NaOH in boiled, deionized water and diluting to 100 ml.

7.5 Sodium sulfate stock solution (20% w/v Na₂SO₄). Prepared by dissolving 20 g Na₂SO₄ in approximately 80 ml deionized water (moderate heating and agitation may be required) and diluting to 100 ml.

7.6 Tungsten stock solution (10,000 µg W/ml). Prepare by dissolving 1.5985 g Na₂WO₄ (dried for 8 hours at 125°C to remove waters of hydration) in deionized water, adding 10 ml 0.5 M NaOH and diluting to 100 ml.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 All glassware and Teflon ware should be cleaned before first use with a detergent solution followed by (in order) rinsing with water, rinsing with distilled water, soaking 30 minutes in concentrated nitric acid, and thoroughly rinsing with distilled water.

8.1.2 Glassware which has been cleaned once by this method (8.1.1) and subsequently used exclusively for tungsten determination may be cleaned by soaking for 30 minutes in dilute (10% w/v) nitric acid and thoroughly rinsing with distilled water.

8.1.3 Teflon ware which has been cleaned once by this method (8.1.1) and subsequently used exclusively for tungsten determination may be cleaned by scrubbing with a detergent solution, rinsing with water, soaking 30 minutes in dilute (10% w/v) nitric acid and rinsing with distilled water.

8.2 Collection and Shipping of Samples

8.2.1 With a filter in place, connect the filter holder to the sampling pump and sample the air at 1.5 lpm for 8 hours. For suspected low or high tungsten concentrations, adjust the sample volume to give optimum amounts of tungsten. Since it is possible for the 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 adjusted as needed.

8.2.2 Following sampling, replace the plastic plug on the inlet and outlet openings of the cassette and attach appropriate identification. At least one blank filter should be submitted with each group of ten samples; this filter is handled in the same way as the sample filter except that no air is drawn through it.

8.2.3 Measure and record the temperature and pressure of the atmosphere being sampled.

8.3 Analysis of Samples

8.3.1 Remove the filter blanks and filter samples from their containers and place individually (contaminated side up) in Büchner funnels. Moisten the filter with 5-6 drops of water, apply vacuum (via the side-arm test tube) to firmly seat the filter, release the vacuum, add approximately 3 ml water onto the filter and allow 2 minutes before applying the vacuum. Rinse the filter with 3 ml water and transfer the contents of the test tube to a 10-ml volumetric flask. Rinse the test tube with 1 ml Na_2SO_4 (20% w/v) followed by 1 ml water and combine these rinses with the original extract. Dilute to volume. This flask contains the "soluble" tungsten which is ready for analysis.

8.3.2 Remove the filter from the funnel and place in a Teflon beaker (100 ml). Add 4.0 ml 1:1 $\text{HCl}:\text{H}_2\text{O}$ and heat 30 minutes at 110°C . Remove from the hotplate, allow to cool, and filter through a clean sampling filter (section 6.1.1) in a Büchner funnel. Rinse three times with 1:10 $\text{HCl}:\text{H}_2\text{O}$ (2 ml/rinse) and twice with deionized water (2 ml/rinse).

8.3.3 Return the filter(s) and residue to the Teflon beaker, add 12-ml nitric acid, cover with the Teflon beaker cover and ash 12 hours at 200°C . Remove the cover and allow the sample to go to dryness (110°C). If charring occurs (black residue) add 3-ml nitric acid and take to dryness again (110°C). Repeat if necessary. Add 2 ml nitric acid and 2 ml hydrofluoric acid, swirl to mix, return to the hotplate and allow to go to dryness (≈ 2.5 hours at 110°C). Add 2.5 ml NaOH (0.5 M) and heat 15 minutes (110°C). Rinse the beaker wall with 5 ml deionized water and add 2.5 ml sodium sulfate solution (20% w/v). Transfer the contents of the beaker to a 25-ml volumetric flask and rinse three times with deionized water into the flask. Dilute to volume. This flask contains the "insoluble" tungsten which is ready for analysis.

8.3.4 Turn on the atomic absorption spectrophotometer, tungsten lamp, recorder and heat tape (N_2O line) and ignite the

flame according to the instrument manufacturer's recommendations. Allow at least 15 minutes for warmup. Set the instrument to read peak absorbance at 255.1 nm with a slit width of 0.2 nm. Adjust the nitrous oxide-acetylene flame stoichiometry (rich, reducing with ≈ 3.5 cm inner red cone height) and the burner position for maximum absorbance while aspirating a standard tungsten solution (100 $\mu\text{g W/ml}$).

- 8.3.5 Aspirate standards and samples (from sections 8.3.1 and 8.3.3) into the flame to determine their respective absorbances. Analyze sample and standard solutions in triplicate with a minimum of one standard determination following every five sample determinations. Following analysis of a sample or standard solution, aspirate dilute nitric acid (1% w/v) for 5-10 seconds followed with deionized water (10-15 seconds). Removal of carbon deposits which may form on the burner head during operation is accomplished with a metal spatula or carbon rod as soon as the deposits are observed. Dismantle and clean the burner chamber (detergent solution and brush followed with deionized water rinse) after each day's use.

9. Calibration and Standardization

- 9.1 Prepare working standard solutions for the analytical range of the method (10-500 $\mu\text{g W/ml}$) by diluting 0.05 - 2.5 ml aliquots of the stock tungsten solution (10,000 $\mu\text{g W/ml}$) to 50 ml after adding 5 ml NaOH (0.5 M) and 5 ml Na_2SO_4 solution (20% w/v). A minimum of 5 working standards (prepare fresh weekly) should be used in preparing the calibration curve.
- 9.2 A reagent blank absorbance, if any, (5 ml 0.5 M NaOH and 5 ml 20% w/v Na_2SO_4 diluted to 50 ml with deionized water) is subtracted from the absorbances recorded for the working standard solutions. A calibration curve is prepared by plotting absorbance vs, concentration ($\mu\text{g W/ml}$).
- 9.3 For the determination of tungsten in tungsten carbide samples collected in the presence of cobalt less than 100% recovery may occur. This is corrected by spiking clean filters with tungsten and cobalt metal (at approximately the expected concentration) and analyzing by the procedure described (8.3.2 - 8.3.5).

10. Calculations

10.1 Calibration Curve

From the sample absorbance, subtract the filter blank absorbance to determine the corrected sample absorbance. Compare the corrected sample absorbance with the calibration curve (9.1.2)

to determine the amount of tungsten, in $\mu\text{g/ml}$, in the sample solutions. Convert to mg W/m^3 as described in Section 10.2

10.2 The concentration of tungsten in air is calculated as follows:

$$C = \mu\text{g W/ml} \times \frac{V_{\text{sol}}}{V_s}$$

where: C = concentration of tungsten (mg W/m^3)

$\mu\text{g W/ml}$ = concentration of tungsten as determined in Section 10.1

V_{sol} = volume of extracted (8.3.1) or digested (8.3.3) solution (in ml)

V_s = volume of air sampled in liters

10.3 For personal sampling pumps with rotameter only, the following correction for air volume sampled 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 = sample 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.4 The concentration of tungsten in air as determined for samples containing tungsten carbide and cobalt is calculated as follows:

$$\text{mg W/m}^3_{\text{corrected}} = C \times \frac{A}{B}$$

where:

C = concentration of tungsten as determined
in Section 10.2

A = μg tungsten recovered from spiked filter
(Sections 9.1.3 and 10.1)

[i.e., $\mu\text{g W/ml}$ (from calibration curve) times
the final solution volume (in ml).]

B = μg tungsten spiked onto filter

11. References

- 11.1 "Analytical Methods for Atomic Absorption Spectrophotometry,"
Perkin-Elmer Corp., Norwalk, Conn. 1976.
- 11.2 NIOSH Technical Report, "Analysis of Tungsten by Atomic Absorption
Spectrophotometry: A Feasibility Study," by R.D. Hull, Dec. 1977.

R. Delon Hull
Inorganic Methods Development Section

2-NITROPROPANE

Measurements Research Branch

Analytical Method

Analyte:	2-Nitropropane	Method No:	P&CAM 272
Matrix:	Air	Range:	3-36 mg/m ³ for a 3-liter sample
Procedure:	Adsorption on Chromosorb 106, desorption with ethyl acetate, GC analysis		
Date Issued:	8/1/78	Precision:	5%
Date Revised:		Classification:	E, Proposed

1. Synopsis

A known amount of air is drawn through a sorbent tube containing Chromosorb 106 to trap the organic vapors present. The Chromosorb 106 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. 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 3.1-28.3-mg/m³ at a temperature and pressure of 25°C and 745 torr, using a 3-liter sample. This corresponds to the collection of 9.3-85-μg of analyte. Smaller quantities than this could not be collected, stored, analyzed and desorbed with acceptable precision.

The upper limit of the method is dependent upon the capacity of the Chromosorb 106 to retain the analyte. A 100-mg bed of the sorbent retained 374-μg of the analyte before 5% breakthrough occurred at 10.4-liters when a test atmosphere of 36-mg/m³ of 2-nitropropane in humid air was sampled at 0.2 L/min.
(Reference 11.1)

3. Interferences

Any compound which has the same retention time as the specific compound under study 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 relative standard deviation for the total sampling and analytical method in the range 3.1-28.3-mg/m³ was 0.05. At the lower end of the analytical range, this corresponds to 0.151-mg/m³.
- 4.2 Storage stability studies on 3-liter samples of 4.67-mg/m³ 2-nitropropane in humid air indicated no stability problems.

5. Advantages and Disadvantages

- 5.1 This method was developed for monitoring personal exposures. However, it has not been field tested.
- 5.2 One disadvantage of the method is that the volume of air that can be sampled is limited by the amount of contaminant that the tube will hold before overloading. When the amount of 2-nitropropane found on the back-up section of the Chromosorb 106 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-rate 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 0.05 L/min. The pump should be calibrated with a representative Chromosorb 106 tube in line.
- 6.2 Chromosorb 106* tube. Glass tube, with both ends heat sealed, 7.0-cm long, 6-mm o.d., and 4-mm i.d., containing 100-mg front and 50-mg back-up sections of 60/80 mesh pre-extracted Chromosorb 106. The sorbent beds are separated by a 2-mm portion of urethane foam and contained at the ends by silanized glass wool plugs. The pressure drop across the tube should be approximately 7.5 torr at a flow-rate of 0.05 L/min. The glass should be rinsed with acetone and thoroughly dried before packing to prevent the Chromosorb 106 from adhering to the walls of the tube. Prior to use the Chromosorb 106 is extracted with acetone in a Soxhlet apparatus for 2 hours, allowed to air-dry, and then placed in the drying tube of the apparatus shown in Figure 1.

* Chromosorb 106 is a cross-linked polystyrene porous polymer manufactured by Johns-Manville Company.

This apparatus is connected to the carrier gas inlet port of a GC oven and exhausted into the detector manifold. 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 desiccator. Care should be taken to avoid excessive agitation of the Chromosorb 106 during handling. A static charge can be induced in the material and is not readily dissipated. The individual particles will agglomerate, making the material difficult to handle while packing the collection tubes.

- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 GC column, 20 ft long x 1/8 in i.d. stainless steel, packed with 10% FFAP on 80/100 mesh acid-washed Chromosorb W.
- 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.
- 6.9 Volumetric flasks, 10-mL and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch
- 6.11 Manometer
- 6.12 Soxhlet Extractor
- 6.13 Parafilm
- 6.14 Glass collection tubes, 7-cm x 4-mm i.d., flame sealed at one end, used for desorption experiments.

7. Reagents

- 7.1 Acetone, chromatquality
- 7.2 2-Nitropropane, 97% or purer, obtained from Fisher Chemical Company.

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 break the ends of the Chromosorb 106 tube. All tubes must be packed with Chromosorb 106 from the same manufacturer's lot.

8.2.2. Connect the Chromosorb 106 tube to the sampling pump with a piece of flexible plastic tubing. The smaller section of the Chromosorb 106 tube is used as a back-up 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 Chromosorb 106.

8.2.4. Air being sampled should not pass through any hose or tubing before entering the Chromosorb 106 tube.

8.2.5. Sample 3-liters of air. The large pressure drops across the Chromosorb 106 tubes limit the maximum useable flow-rate to 0.05 L/min. Record the collection time and the flow-rate.

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 Chromosorb 106 tube with plastic caps immediately after sampling. Rubber caps should not be used.

8.2.8. With each batch of samples, submit at least one blank tube made from the same lot of Chromosorb 106 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 caps. These samples should not be transported in the same container as the Chromosorb 106 tubes.

8.3 Analysis of Samples

8.3.1. Preparation of Samples. Remove the plastic cap from the inlet end of the Chromosorb 106 tube. Remove the glass wool plug and transfer the first (longer) section of sorbent to a 2-mL stoppered container. Remove the separating section of urethane foam and transfer the backup section of Chromosorb 106 to another stoppered container. It may be necessary to tap the tube sharply to affect complete transfer of the Chromosorb 106. 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-half 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	190
Hydrogen	33	Detector	220
Air	339	Column	91

2-Nitropropane has a retention time of approximately 20 minutes under these conditions and using the column recommended in Section 6.4. The ethyl acetate will elute from the column before the 2-nitropropane.

8.3.4. Injection. Inject a 5- μ L 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 Chromosorb 106 particles.

8.3.5. 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.

8.4. 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 106 to another. Thus, it is necessary to determine the desorption efficiency for a particular batch of Chromosorb 106.
- 8.4.2. One hundred milligrams of Chromosorb 106 is measured into a 7-cm X 4-mm i.d. glass tube, flame sealed at one end. This Chromosorb 106 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 either 1.0- $\mu\text{g}/\mu\text{l}$ or 10- $\mu\text{g}/\mu\text{l}$ of 2-nitropropane is injected directly into the Chromosorb 106 bed with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 3-liter 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 2-nitropropane onto the Chromosorb 106. 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 2-nitropropane solutions into 1.0-mL of ethyl acetate with the same syringe as used in preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D) equals the average weight of 2-nitropropane 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- $\mu\text{g}/\mu\text{L}$ of 2-nitropropane in ethyl acetate.

9.2 From the stock solution, prepare at least five standards to cover the range 10-110 μg in 1.0-mL of ethyl acetate.

9.3 Analyze the standards with the samples. Prepare a standard calibration curve by plotting concentration of 2-nitropropane in $\mu\text{g}/1.0\text{ mL}$ 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 corrected 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 (W_c).

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

10.5 The concentration (C) of 2-nitropropane in the air sampled can be expressed in $\mu\text{g}/\text{L}$.

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

where V is the volume of air sampled in liters. This number is numerically equal to the concentration of 2-nitropropane in mg/m^3 .

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

$$C' = C \times \frac{24.45}{M} \times \frac{760}{P} \times \frac{T + 273}{293}$$

where

P is the pressure of air sampled in torr

T is the temperature of air sampled in $^{\circ}\text{C}$

24.45 is the molar volume (liter/mole) at 25°C and 760 torr

M is the molecular weight (g/mole) of 2-nitropropane

760 is the standard pressure in torr

298 is the standard temperature in $^{\circ}\text{K}$

11. References

- 11.1 R. A. Glaser and J. W. Woodfin, A Method for Sampling and Analysis of 2-Nitropropane in Air, in preparation.

Robert A. Glaser, Chemist
Organic Methods Development Section

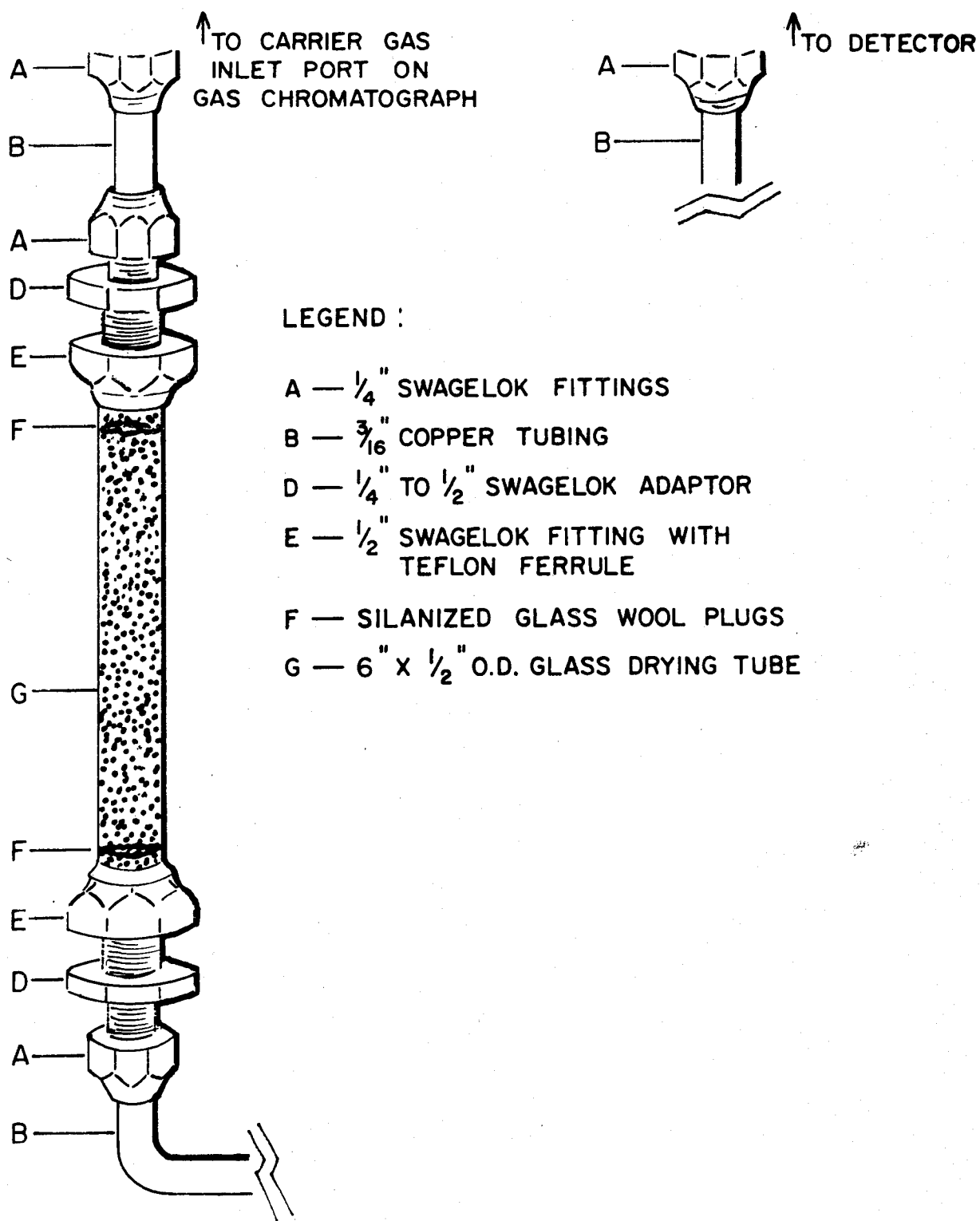


Figure 1. Batch drying apparatus for porous polymers.

4-NITROBIPHENYL

Measurements Research Branch

Analytical Method

Analyte:	4-Nitrobiphenyl	Method No:	P&CAM 273
Matrix:	Air	Range:	4-2200 $\mu\text{g}/\text{m}^3$ in a 50-liter air sample
Procedure:	Collection on glass fiber filter and silica gel, elution with 2-propanol, analysis by gas chromatography	Precision:	8%
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a three-stage sampler consisting of a high-efficiency glass fiber filter followed by two beds of silica gel to collect the 4-nitrobiphenyl aerosol and/or vapor.
- 1.2 The filter and sorbent sections of the sampler are transferred to stoppered tubes and the 4-nitrobiphenyl is desorbed with 2-propanol.
- 1.3 An aliquot of this solution is injected into a gas chromatograph.
- 1.4 Peak areas are electronically determined and compared with a calibration curve obtained from injections of standard solutions of 4-nitrobiphenyl.

2. Range, Sensitivity and Detection Limit

- 2.1 The analytical range is 0.2-110 $\mu\text{g}/\text{sample}$ (4-2200 $\mu\text{g}/\text{m}^3$ for a 50L air sample) when using 0.5 mL of desorbing solution and 1- μL injections into the gas chromatograph.
- 2.2 The amount of 4-nitrobiphenyl vapor retained on the primary silica gel bed decreases as the relative humidity of the sampled air increases. In experiments in which atmospheres containing 700 $\mu\text{g}/\text{m}^3$

of 4-nitrobiphenyl in air of 80% relative humidity and at 34 °C were sampled, less than 2% of the analyte appeared in the secondary silica bed when 45 L was sampled. At 50% relative humidity and 34 °C, 200 L of air containing 600 µg/m³ was sampled and less than 0.3% was detected in the secondary silica bed.

2.3 The limit of detection is 0.05 µg/sample.

3. Interferences

3.1 In solutions containing 4-nitrobiphenyl at 1-2 ng/µL, the following compounds were found not to interfere when their concentrations were 1-3 ng/µL: 1-naphthol, 2-naphthol, 1-naphthylamine, 2-naphthylamine, 2-nitronaphthalene, 2-nitrobiphenyl, 3-nitrobiphenyl, and 3-aminobiphenyl.

3.2 Any compound sampled with 4-nitrobiphenyl and having the same retention time as the analyte will interfere with the analysis. This type of interference often can be eliminated by changing the operating conditions of the chromatograph, e.g., by temperature programming or by changing the stationary phase.

4. Precision and Accuracy

4.1 The precision of the overall method is 8% relative standard deviation for samples collected at 34 °C and 80% relative humidity. This value is based on 43 samples involving volumes of 4 to 12 liters and a sampling rate of 0.2 L/min. Concentrations sampled ranged from 120 to 600 µg/m³.

4.2 Filters and silica gel spiked with 4-nitrobiphenyl and stored at ~24 °C yielded recoveries ≥93% when desorbed within 28 days.

4.3 Analysis of the back-up silica gel section serves as a check on sample integrity. If more than 10% of the total recovered weight is found on this section, sample loss due to breakthrough may be indicated. Under these circumstances, the actual ambient concentration may be greater than the sample analysis indicates.

4.4 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

5.1 The sampler is a small portable device containing no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities.

5.2 Relative humidity has an effect on the collection efficiency of the absorbent. (Section 2.2)

5.3 At a flow rate of 0.2 L/min, the linear velocity through the 4-mm inlet of the holder is 26.5 cm/s. It is not known if this throat velocity is sufficient for the capture of all particles of analytical importance.

5.4 This method has not been field tested.

6. Apparatus

6.1 Personal air sampling pump that can be maintained for four hours at a flow rate of 0.2 L/min with the sampler in line. Each pump should be calibrated with a representative sampler in line to minimize errors in volume measurement. A bubble flow meter or other suitable flow measuring device may be used.

6.2 Sampler, equivalent to that shown in Figure 1. The sampler consists of three sections: a high-efficiency glass fiber filter, followed by 100-mg and 50-mg beds of silica gel. The first section, a 13-mm glass fiber filter (Spectrograde or Type A-E, Gelman Instrument Co., Ann Arbor, MI, or equivalent) is contained in a 13-mm filter holder (SX00-013-00 Millipore Corp., Bedford, MA, or equivalent). The sorbent tube is a 50-mm section of Pyrex glass, 6.4-mm o.d. x 4-mm i.d. flared on one end, containing the sections of silica gel (Grade 407, 20/45-mesh, 720-760 m²/g, 0.737 g/cc; Coast Engineering Laboratories, Gardena, CA, or equivalent). The sorbent is held by 3.5-mm diameter, 100-mesh, stainless steel screens and 4-mm o.d. Teflon rings, as shown in Figure 1. To connect the two stages, the filter holder is pressed into the flared end of the sorbent tube. The pressure drop across the sampler at 0.2 L/min is 10 torr. Flexible vinyl caps are used to seal the ends of the sampler.

6.3 Gas chromatograph equipped with a flame ionization detector (FID) and injection port.

6.4 Glass column, 1.8-m x 2-mm i.d. x 6.4-mm o.d., packed with 3% OV-225 on 80/100 mesh Supelcoport (Supelco, Inc., Bellefonte, PA, or equivalent).

6.5 Potentiometric strip chart recorder.

6.6 Test tubes, 1-mL, fitted with polyethylene stoppers.

6.7 Glass syringes, 5- and 10- μ L.

6.8 Pipettes of convenient volumes for the preparation of standard solutions.

6.9 Volumetric flasks of convenient volumes for the preparation of standard solutions.

6.10 Clinical centrifuge.

6.11 Analytical balance.

6.12 Test tube shaker, vortex type.

7. Reagents

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

7.1 2-Propanol, UV grade, distilled in glass.

7.2 Acetone, distilled in glass.

7.3 Methyl alcohol.

7.4 Carbon tetrachloride.

7.5 4-Nitrobiphenyl.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis is washed with detergent and rinsed with tap water, distilled water, and methyl alcohol.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, the vinyl caps are removed from the ends of the sampler and saved for resealing after sampling.

8.2.2 The sorbent end of the sampler is connected to the pump with plastic or rubber tubing. The sampler is positioned vertically during sampling. Sampled air must not pass through any tubing before entering the sampler.

8.2.3 The atmosphere is sampled at a flow rate of 0.2 L/min for no longer than 4 hours. The flow rate and sampling time, or the volume of sampled air, must be measured as accurately as possible.

8.2.4 The temperature, pressure, and humidity of the atmosphere being sampled are measured and recorded, along with other pertinent data such as location, date, and time of sampling.

8.2.5 Blank samples are obtained by handling random collection devices in the same manner as in sampling, except that no air is drawn through them.

8.2.6 Samples shipped to the laboratory should be packed tightly to minimize breakage.

- 8.2.7 If samples of bulk material associated with the process under investigation are to be shipped to the laboratory, they should not be placed in the same container as the air samplers or blanks.

8.3 Analysis of Samples

- 8.3.1 Place the glass fiber filter and the 100-mg section of silica gel in a 1-mL tube or other suitable vial. Place the 50-mg section of silica gel in a separate test tube. Teflon rings and stainless steel screens associated with the sampler may be analyzed with the appropriate stages. Sampler caps can be discarded.

- 8.3.2 Add 0.5 mL of 2-propanol to each vial and cap it.

- 8.3.3 Allow the vials to stand for one hour, shaking them intermittently in a test tube vibrator. Centrifuge for 10 minutes.

8.3.4 Gas Chromatographic Conditions

Column:	3% OV-225 on 80/100 mesh Supelcoport in 1.8-m x 2-mm i.d. x 6.4-mm o.d. glass tubing.
Column Temperature:	190 °C
Injector Temperature:	210 °C
Detector Temperature:	200 °C
Helium:	22 mL/min
Hydrogen:	85 mL/min
Air:	378 mL/min
Detector:	FID; Attenuation 1 x 2 at low concentrations
Injection Volume:	1.0 µL
Efficiency:	2500 theoretical plates
Capacity Ratio:	15.9

- 8.3.5 Injection. Flush the 5-µL syringe first with acetone (to insure its cleanliness and to wet the barrel and plunger) and then with the sample solution. Carefully draw 1 µL of sample solution into the syringe (to minimize the intake of particulate matter) and inject the aliquot into the gas chromatograph.

8.4 Efficiency of Desorption

8.4.1 Importance of Determination. The efficiency of desorption for 4-nitrobiphenyl can vary from one laboratory to another and also from one batch of silica gel or filters to another. Thus, it is necessary to determine the fraction of 4-nitrobiphenyl that can be recovered from these matrices. Since the efficiency of desorption may also vary with the amount of 4-nitrobiphenyl present, determinations should be made for at least two levels in the range of anticipated sample sizes. If the efficiencies of desorption for the filter and primary silica gel bed do not vary by more than 5%, these two primary stages may be analyzed together. If greater variances are found, it may be necessary to analyze the stages individually and make appropriate corrections (Section 10.3).

8.4.2 Procedure for Determining the Efficiency of Desorption. Place the filters and silica gel from unused samplers in 1-mL test tubes. Add to each a known amount of 4-nitrobiphenyl in 10 μ L of carbon tetrachloride using the same microliter syringe for each. Five filter and silica gel samples are thus prepared at each of two different levels in the range of interest. Cap the tubes. Treat a parallel blank in the same manner (no analyte is added). Prepare at least three standards at each of the various levels by adding 10 μ L (same syringe as above) of the 4-nitrobiphenyl solutions to 0.5 mL of desorbing solution. Analyze the samples and standards as described in Section 8.3. The efficiency of desorption is the average gas chromatographic peak area given by the samples, corrected for the blank if necessary, divided by the average area given by the standards.

9. Calibration and Standardization

9.1 For accuracy in the preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at a high concentration. The initial standard is prepared by weighing a selected amount of 4-nitrobiphenyl (e.g., 125 mg) into a 250-mL volumetric flask and adding the desorbing solution to the calibration mark. Dilutions encompassing the concentration range of interest down to 0.3 ng/ μ L are then made from the stock solution. Solutions should be stored in a refrigerator when not in use.

CAUTION: 4-NITROBIPHENYL HAS BEEN IDENTIFIED AS A CARCINOGEN. APPROPRIATE PRECAUTIONS MUST BE TAKEN IN HANDLING THE COMPOUND TO AVOID PERSONNEL EXPOSURE AND AREA CONTAMINATION.

9.2 The standard solutions should be analyzed under the same gas chromatographic conditions and during the same time period as the samples. This will minimize inaccuracy due to day-to-day variations in the setting of instrumental conditions.

- 9.3 Calibration curves for 4-nitrobiphenyl are prepared by plotting the peak areas for the standards against their concentration in $\mu\text{g}/0.5 \text{ mL}$.

10. Calculations

- 10.1 In the event that the blank produces a peak with the same retention time as the analyte, the analyst should determine the source of the interference and eliminate or compensate for it.
- 10.2 Read the weight (W_1) in μg of 4-nitrobiphenyl present in the sample from the calibration curve.
- 10.3 The corrected weight (W_2) is determined by

$$W_2 = \frac{W_1}{D}$$

where D is the efficiency of desorption for that sampler stage.

- 10.4 Add the weights found in the sampler stages to determine the total weight (W_t) collected.
- 10.5 The concentration of 4-nitrobiphenyl in air (C , $\mu\text{g}/\text{m}^3$) is given by

$$C = \frac{W_t}{V} \times 10^3$$

where V is the volume of air sampled in liters and 10^3 is the factor to convert from liters to m^3 .

11. Reference

Raul Morales, J. F. Stampfer, Jr., R. E. Hermes, E. E. Campbell, and H. J. Ettinger, "Development of Sampling and Analytical Methods for Carcinogens, October 1, 1976-December 31, 1977," Progress Report LA-7375-PR, National Technical Information Service, Springfield, Virginia, 1978.

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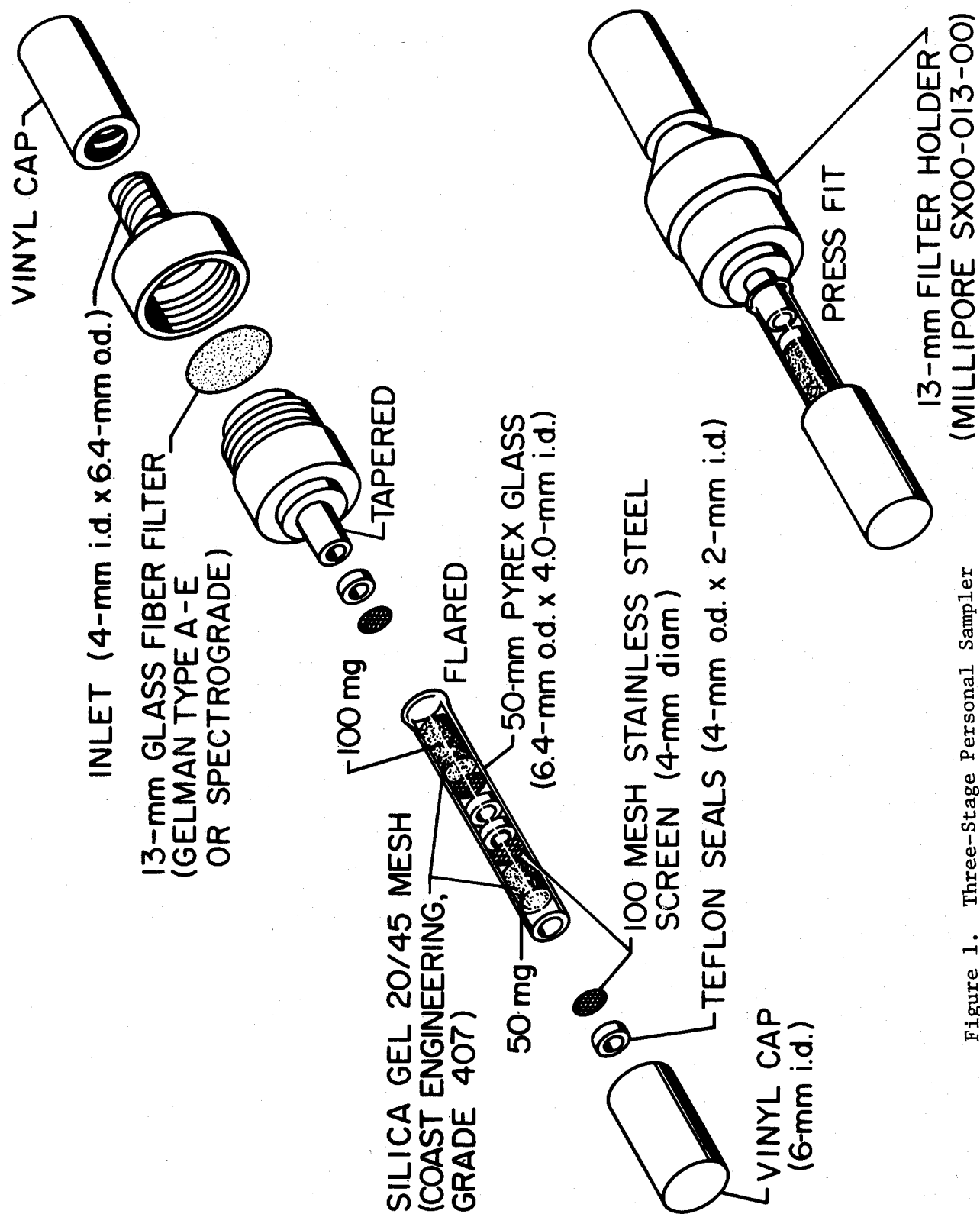


Figure 1. Three-Stage Personal Sampler

ETHYLENEDIAMINE
AND
DIETHYLENETRIAMINE

Measurements Research Branch

Analytical Method

Analytes:	Ethylenediamine (1,2-Diaminoethane) Diethylenetriamine (bis (2-aminoethyl) amine)	Method No:	P&CAM 276
Matrix:	Air	Range:	See Paragraph 2
Procedure:	Adsorption on silica gel, elution with methanolic acid, derivatization with benzaldehyde, GC analysis	Precision:	2-8% (Analytical)
Date Issued:	8/1/78		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known volume of air is drawn through a tube containing silica gel to trap vapors of the compounds. Concentrated HCl is added to stabilize amines collected. The sorbent sections are transferred to glass vials and treated with methanol solution. An aliquot is alkalized with sodium hydroxide. Benzaldehyde is added to form dibenzylidene derivatives. The solution is analyzed by gas chromatography with flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

The ranges of the method for the two analytes are at least

Ethylenediamine 0.2 - 7 mg/sample

Diethylenetriamine 0.2 - 9 mg/sample

Data relating to the lower ends of the range are given in Paragraphs 4.2, 4.3, and 4.6. The upper limits are determined by the capacities of the first section of the sampling tube used to collect the sample. Amounts of individual compounds retained on 150 mg of a 42/60-mesh silica gel in 6-mm-i.d. sampling tubes at 1 L/min sampling flow rate were found to be those given above as the upper limits.

3. Interferences

- 3.1 Water vapor does not significantly affect collection efficiency.
- 3.2 Large amounts of ammonia or primary amines will reduce the amount of benzaldehyde available for reaction with the analytes. Such interferences should be compensated for by adding additional benzaldehyde.
- 3.3 Any compound which has nearly the same retention time on the GC column as one of the analytes is an interference. Retention time data on a single GC column cannot be considered as proof of chemical identity. The presence and identity of possible interfering substances may be determined by the analysis of bulk samples from the process or environment.

4. Precision and Accuracy

- 4.1 The volume of air sampled can be measured to within $\pm 2\%$ if a pump with a calibrated volume indicator and an adequate battery is used. Volumes calculated from initially set flow rates may be less accurate ($\pm 5-10\%$) unless changes in flow rate are manually or electronically monitored and compensated.

- 4.2 Precision (relative standard deviation) of replicate GC analyses of standards was measured to be:

Ethylenediamine	5% at 0.05 mg/mL eluent
Diethylenetriamine	8% at 0.09 mg/mL eluent

These levels correspond to sample sizes of 0.1 mg and 0.2 mg, respectively. At the upper limits of the method analytical precision becomes 2% relative standard deviation or better.

- 4.3 The precision (relative standard deviation) of the method based on analyses of replicate 0.1 mg samples injected by syringe into silica gel sections or into 2 mL of eluent was 14% for both compounds.
- 4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GC peaks of samples and standards. An electronic digital integrator with baseline correction capability is best for this purpose.
- 4.5 Collection efficiency is 100% until breakthrough of the sampling tube bed occurs (see Section 2).
- 4.6 Desorption efficiencies for both compounds based on analyses of replicate 0.1 mg samples on silica gel and standards in 2 mL eluent were found to be 102% with a relative standard deviation of 20%. Measurements at higher sample levels have given desorption efficiencies consistently in the range 90-100% with better precision.

- 4.7 This method has given quantitative results equivalent to an independent method involving adsorption of ethylenediamine vapors in water in a bubbler and titration with standard acid. Using each method six 0.030-m³ vapor-in-nitrogen samples were taken at 1 L/min. The following sample amounts and relative standard deviations in parentheses were determined:

Tube and chromatography: 3.30mg (4%)

Bubbler and titration: 3.42mg (2%)

5. Advantages and Disadvantages

- 5.1 The method uses a small, portable sampling device involving no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities. Transportation to the analytical laboratory is simplified with the solid sorbent tube.
- 5.2 The sorbent tube has a high capacity even at high relative humidities. It can be used for at least eight hours to measure a workday average concentration, or for shorter times to measure excursion concentrations.
- 5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.
- 5.4 Several amines can be collected and determined simultaneously. The GC analysis distinguishes which are present and at what individual concentrations they occur. Interferences by other amines are much less likely than in colorimetric or titrimetric methods.
- 5.5 A major disadvantage is the tendency of amines to oxidize while adsorbed on surfaces exposed to air. This is overcome by addition of concentrated hydrochloric acid to the sorbent sections soon after sampling.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 Sorbent. The silica gel used should be the equivalent of Silica Gel D-08, chromatographic grade, activated and fines free, 42/60 mesh, as produced by Coast Engineering Laboratories and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania.
- 6.1.2 Sampling Tubes. Glass tubes 7-cm-long and 6-mm-i.d., tapered and flame sealed at one end, are packed with two 150-mg sections of silica gel. Glass wool plugs are used to separate and enclose the sections. The second end is flame sealed to prevent contamination during storage

prior to use. Polyethylene caps are used to seal tubes after sampling is completed.

NOTE: Sampling tubes constructed with metal parts or urethane foam plugs should not be used. Concentrated hydrochloric acid will react with these materials.

- 6.1.3 Personal Sampling Pump. Battery-operated pumps are required, capable of operation at 0.2 L/min for up to eight hours or at 1.0 L/min for up to two hours with a sampling tube in line. The pump is to be calibrated with a representative sorbent tube in line. A wet or dry test meter or bubble meter capable of measuring a flow rate of 0.2 L/min and/or 1.0 L/min to within $\pm 2\%$ may be used in setting the pump flow.
- 6.2 Gas chromatograph with a flame ionization detector. Temperature programming capability is necessary to determine more than one compound simultaneously.
- 6.3 GC column, 0.6-m x 4-mm i.d. glass, silanized and packed with 10% (by weight) silicone SE-30 on 80/100-mesh supelcoport or equivalent support.
- 6.4 Strip chart recorder compatible with the GC. An electronic digital integrator is desirable.
- 6.5 Test tubes or glass vials, 2-mL, sealed by a septum.
- 6.6 Syringes, 10- μ L.
- 6.7 Syringe for dispensing concentrated HCl, 50- μ L, with glass barrel, fluorocarbon-tipped plunger, and inert (platinum or fluorocarbon) needle.
- 6.8 Pipettes, 0.5-mL and 2-mL.
- 6.9 Volumetric flasks, 10-mL.
- 6.10 File and Forceps.
- 7. Reagents
 - All chemicals must be analytical reagent grade.
 - 7.1 Ethylenediamine.
 - 7.2 Diethylenetriamine.
 - 7.3 Water, doubly distilled and aldehyde-free. Deionized water should not be used as it may contain formaldehyde and other impurities leached from the ion-exchange resins.
 - 7.4 Concentrated hydrochloric acid (38%, 12 M).

- 7.5 Benzaldehyde.
- 7.6 Eluent solution, 4:1 methanol-water (by volume).
- 7.7 Alkalinizing solution, 0.20 N NaOH in 4:1 methanol-water (by volume).
- 7.8 Helium, Bureau of Mines Grade A.
- 7.9 Hydrogen, prepurified.
- 7.10 Air, compressed and filtered.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All glassware is washed with detergent solution, rinsed with tap water and distilled water, and dried in an oven.
 - 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least 2 mm in diameter.
 - 8.2.2 Attach the tubing from the sampling pump to the backup end of the sampling tube. Sampled air must not pass through any hose or tubing before entering the sorbent tube.
 - 8.2.3 With the sorbent tube in a vertical position as much as is practical, sample the air at 1.0 L/min for 15 min-2 hours or at 0.2 L/min for 2-8 hours. Intermediate flow rates and other sampling periods may be used, as appropriate.
 - 8.2.4 Immediately after sampling is completed, add 20 μ L of concentrated HCl to each section of silica gel in the tube. Use a 50- μ L glass syringe with fluorocarbon-tipped plunger and inert needle, so that the acid does not contact and react with stainless steel. The silica gel will turn yellow upon addition of the acid due to iron impurities in the silica gel.
 - 8.2.5 Seal the sorbent tubes with polyethylene caps.
 - 8.2.6 Obtain a blank sample by handling one tube in the same manner as the sample tubes (break, add acid, seal, and ship) except that no air is pumped through it.
 - 8.2.7 For shipping to the laboratory, pack the tubes tightly to minimize chances of breakage during transit. Tubes should not be subjected to extremes of high temperature or low pressure.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Score each tube with a file 5 mm in front of the glass wool plug that precedes the first sorbent section and break the tube there. Transfer this plug and the initial section to a 2-mL test tube or glass vial that can be septum sealed. Likewise, transfer the second plug and sorbent section to another test tube. Label each appropriately for separate analysis.
- 8.3.2 Desorption. Add 2 mL of eluent solution to each sorbent section. Seal the samples. Shake the mixtures occasionally over a period of two hours. Tests have shown that complete desorption occurs within two hours and samples are stable for at least a day.
- 8.3.3 Preparation and Reaction. Transfer a 0.50-mL aliquot of each eluate to another test tube or vial. Add 0.50 mL of alkalinizing solution and mix thoroughly. Verify the basicity of the solution with litmus paper. Add 10- μ L of benzaldehyde to the basic solution, mix thoroughly, and allow at least 20 min for reaction.
- 8.3.4 Gas Chromatograph Conditions

Helium gas flow rate, 30 mL/min.
Injection port temperature, 200 °C.
Detector temperature, 250 °C.
Column temperature, 200 °C for
1,2-(dibenzylideneamino)ethane and
235 °C for 2,2'-(dibenzylideneamino)diethylamine.

Under these conditions, retention times are 300 sec for 1,2-(dibenzylideneamino)ethane and 345 sec for 2,2'-(dibenzylideneamino)diethylamine.

- 8.3.5 Injection of Sample. Inject and analyze 3- μ L aliquots of each sample and standard. To eliminate difficulties arising from blowback or distillation within the 10- μ L syringe, use a solvent flush technique.
- 8.3.6 GC Peak Measurement. Determine the areas of the peaks of the compounds of interest from analyses of samples and standards.

8.4 Determination of Desorption Efficiency

- 8.4.1 Importance. Desorption efficiency for a particular compound can vary from one lot of silica gel to another and from one laboratory to another. Also, for a given lot of silica gel the desorption efficiency may vary with the amount of material adsorbed during sampling. Therefore, it is necessary to determine at least once the desorption

efficiency for each analyte with each lot of silica gel used for at least two levels within the normal range of samples size. If the desorption efficiencies are significantly different from quantitative recovery, they should be used to correct the measured weight of analyte as described in Section 10.2 below.

8.4.2 Procedure. Place 150 mg of silica gel in a 2-mL glass-stoppered tube. The silica gel must be from the same lot as that used in collecting the sample; it can be obtained from unused sorbent tubes. With a microliter syringe, inject a known amount of amine, either pure or in water solution, directly onto the silica gel. Also inject 20 μL of concentrated HCl. Close the tube with the glass stopper and allow it to stand overnight to insure complete adsorption of the amine. Prepare at least three tubes for each at two different levels. These tubes are referred to as samples. Prepare a blank in the same manner, omitting the amine. Analyze the samples and blank as described in Section 8.3. Also analyze three standards prepared by adding identical amounts of the amine and 20 μL of concentrated HCl to 2.0 mL of eluent solution. Determine the concentrations of the analytes in the blank, samples, and standards using calibration curves prepared as described in Section 9. The desorption efficiency is calculated by dividing the concentration of amine found in the sample by the concentration obtained for the corresponding standard.

9. Calibration and Standardization

9.1 Preparation of a Stock Solution. Calculate for each compound i the volume V_i (μL) of pure liquid required for preparation of 10 mL of a stock solution, 10 μL of which contains amounts of analytes equal to those collected from volume of air V_s at concentrations X_i .

$$V_i = \frac{X_i \times V_s}{d_i} = 1000$$

Where:

X_i - the standard concentration limit, or the anticipated average concentration, (mg/m^3) of compound i in air.

V_s - volume (m^3) of air sampled.

d_i - density ($\text{mg}/\mu\text{L}$) of a pure compound i .

1000 - aliquot factor.

Add the calculated volumes of each compound to a 10-mL volumetric flask and dilute to the mark with 4:1 methanol-water. Neutral solutions of amines are subject to oxidation and should be prepared fresh when needed.

- 9.2 Preparation of Calibration Standards. Add 2.5 μL , 5 μL , 10 μL , 15 μL and 20 μL of the prepared standard to reaction tubes containing 2 mL eluent solution and 40 μL concentrated hydrochloric acid. Use a 10- μL syringe to inject through septum seals. Shake these tubes. These standards correspond to 0.25, 0.5, 1, 1.5, and 2 times X_i in V_s , respectively. Other standards may be similarly prepared, if desired.
- 9.3 React and analyze standards with samples according to Section 8.3.
- 9.4 Prepare a calibration curve for each amine by plotting peak areas obtained from the analyses of standards against nominal amount (mg) in the calibration standards.

10. Calculations

- 10.1 Read the weights (mg) of each compound corresponding to each peak area from the appropriate calibration curve. Correct each value for the weight found in a blank, if any. Add the weights found in the front and backup sections of the sample tube to obtain the total weight of compound in the air volume sampled.
- 10.2 Divide the total weight by the desorption efficiency to obtain the corrected sample weight.
- 10.3 Determine the volumes (m^3) of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min) and $10^{-3} \text{ m}^3/\text{L}$. 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:

$$V_s = 10^{-3} \times f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}.$$

where:

- f - sample flow rate (L/min)
- t - sampling time (min)
- P_1 - pressure during calibration of sampling pump (torr)
- P_2 - Pressure of air sampled (torr)
- T_1 - temperature during calibration of sampling pump ($^{\circ}\text{K}$)
- T_2 - temperature of air sampled ($^{\circ}\text{K}$)

- 10.4 Divide the total corrected weight (mg) of each compound by V_s (m^3) to obtain the concentration of the compound in the air sampled (mg/m^3).

11. References

- 11.1 G. O. Wood, R. G. Anderson, and J. W. Nickols, "Sampling and Analysis of Aminoethanols in Air," Report LA-UR-77-1398 (1977), Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. (Presented at the 1977 American Industrial Hygiene Conference, May 1977, New Orleans).
- 11.2 G. O. Wood and J. W. Nickols, "Development of Air-Monitoring Techniques Using Solid Sorbents, October 1, 1976 - December 31, 1977," Progress Report LA-7295 -PR (1978), Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Also available from the National Technical Information Services, Springfield, VA.

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METHYLAMINE

Measurements Research Branch

Analytical Method

Analyte:	Methylamine	Method No:	P&CAM 277
Matrix:	Air	Range:	0.5-120 mg/m ³ in 100-L air sample
Procedure:	Adsorption on silica gel elution with methanolic acid, derivatization with benzaldehyde, GC analysis	Precision:	1-9% (Analytical)
Date Issued:	8/1/78		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known volume of air is drawn through a tube containing silica gel to trap methylamine vapors. Concentrated hydrochloric acid is then added to stabilize the sample. Silica gel sections are transferred to glass tubes and treated with a methanol-water solution. An aliquot is alkalinized with sodium hydroxide. Benzaldehyde is added to convert the methylamine to benzylideneaminomethane. The solution is analyzed by gas chromatography with flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The range of the method is at least 0.05-12 mg/sample.
- 2.2 The lower limit of 0.05 mg/sample is the lowest level at which the desorption and analysis procedure was found to be acceptably precise (see Paragraph 4.2) and quantitative (see Paragraph 4.6). This limit corresponds to 0.5 mg/m³ monomethylamine in a 0.1-m³ air sample.
- 2.3 The upper limit is at least 12 mg of amine per sample. This amount of methylamine was retained by the 600-mg section of silica gel in the sampling tube without breakthrough when 93L of high-humidity air containing 129 mg/m³ of methylamine was sampled. This limit corresponds to 120 mg/m³ in a 0.100-m³ air sample.

3. Interferences

- 3.1 Large amounts of ammonia or primary amines will reduce the amount of benzaldehyde available for reaction with methylamine. Such interferences should be compensated for by adding additional benzaldehyde.
- 3.2 Any compound which has nearly the same retention time on the GC column as one of the analytes is an interference. Retention time data on a single GC column cannot be considered as proof of chemical identity. The presence and identity of possible interfering substances may be determined by the analysis of bulk samples from the process or environment.

4. Precision and Accuracy

- 4.1 The volume of air sampled can be measured to within $\pm 2\%$ if a pump with a calibrated volume indicator and an adequate battery is used. Volumes calculated from initially set flow rates may be less accurate ($\pm 5-10\%$) unless changes in flow rate are manually or electronically monitored and compensated.
- 4.2 Replicate analyses of a standard solution at the level 0.05 mg/sample showed the analytical precision to be 9% relative standard deviation. At the upper limit of the method, analytical precision approached 1% relative standard deviation.
- 4.3 A sampling and analysis precision of 3% (relative standard deviation) has been measured for 10 samples, each containing 1.2 mg of methylamine collected from 4L of air with a personal sampling pump.
- 4.4 The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GC peaks of samples and standards. An electronic digital integrator with baseline correction capability is best for this purpose.
- 4.5 Collection efficiency is 100% until breakthrough of the front sampling tube bed occurs (see Paragraph 2.3).
- 4.6 Desorption efficiencies were measured to be 85% for one 42/60 mesh silica gel at the level 0.05 mg per sample and higher at higher sample levels.

5. Advantages and Disadvantages

- 5.1 The method uses a small, portable sampling device involving no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities. Transportation to the analytical laboratory is simplified with the solid sorbent tube.

- 5.2 The sorbent tube has a high capacity. It can be used for at least eight hours to measure a workday average concentration, or for shorter times to measure excursion concentrations.
- 5.3 Desorption and preparation of samples for analysis involve simple procedures and equipment.
- 5.4 Several amines can be collected and determined simultaneously. The GC analysis distinguishes which are present and at what individual concentrations they occur. Interferences by other amines are much less likely than in colorimetric or titrimetric methods.
- 5.5 A major disadvantage is the tendency of amines to oxidize while adsorbed on surfaces exposed to air. This is overcome by addition of concentrated hydrochloric acid to the sorbent sections soon after sampling.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 Sorbent. The silica gel used should be the equivalent of Silica Gel D-08, chromatographic grade, activated and fines free, 42/60 mesh, as produced by Coast Engineering Laboratories, and sold by Applied Science Laboratories, Inc. of State College, Pennsylvania.
- 6.1.2 Sampling Tubes. Glass tubes 12.5-cm long and 8-mm-i.d., packed with three sections of silica gel of weights 600 mg, 150 mg, and 150 mg, in order. These tubes are used for sampling in either direction. Sorbent sections are held in place by 7-mm-diam discs of 100-mesh Teflon screen supported by Teflon rings of 8-mm-o.d., 6-mm-i.d., and 2-mm thick. Pieces of glass tubing 12-mm long and 7-mm o.d. are located between the sorbent sections to inhibit migration of the amines and to facilitate sorbent removal. The ends of the tubes are flame-sealed after packing to prevent contamination prior to sampling. Polyethylene caps should be provided to seal the tubes after sampling has been completed. Pressure drop across such a tube containing 42/60 mesh silica gel is 6-cm of water at 0.2 L/min sampling flow rate.

Note: Sampling tubes constructed with metal parts or urethane foam plugs should not be used, as concentrated hydrochloric acid will react with these materials.

- 6.1.3 Personal Sampling Pump. A battery-operated pump capable of operation at 0.2 L/min for up to eight hours with a sampling tube in line is required. The pump is to be calibrated with a representative sorbent tube in line. A wet or dry test meter, or bubble meter, capable of measuring a flow rate of 0.2 L/min to within $\pm 2\%$ may be used in setting the pump flow.

- 6.2 Gas Chromatograph with a flame ionization detector.
- 6.3 GC column, 1.8-m x 4-mm i.d. glass, silanized and packed with 10% (by weight) silicone SE-30 on 80/100-mesh Supelcoport or equivalent support.
- 6.4 Strip chart recorder compatible with the GC. An electronic digital integrator is desirable.
- 6.5 Test tubes or glass vials, 2-mL, and 10-mL, sealed by a septum.
- 6.6 Syringes, 10- μ L.
- 6.7 Syringes for dispensing concentrated HCl, 50- μ L and 100- μ L, with glass barrel, fluorocarbon-tipped plunger, and inert (platinum or fluorocarbon) needle.
- 6.8 Pipettes, 0.5-mL and 2-mL.
- 6.9 Volumetric flasks, 10-mL.
- 6.10 File and Forceps.
- 7. Reagents
 - All chemicals must be analytical reagent grade.
 - 7.1 Methylamine, 40% in H₂O.
 - 7.2 Water, doubly distilled and aldehyde-free. Deionized water should not be used as it may contain formaldehyde and other impurities leached from the ion-exchange resins.
 - 7.3 Concentrated hydrochloric acid (38%, 12 M).
 - 7.4 Benzaldehyde.
 - 7.5 Eluent solution, 4:1 methanol-water (by volume).
 - 7.6 Alkalinizing solution, 0.20 N NaOH in 4:1 methanol-water (by volume).
 - 7.7 Helium, Bureau of Mines Grade A.
 - 7.8 Hydrogen, prepurified.
 - 7.9 Air, compressed and filtered.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All glassware is washed with detergent solution, rinsed with tap water and distilled water, and dried in an oven.
 - 8.2 Collection and Shipping of Samples

- 8.2.1 Immediately before beginning the collection of a sample, break each end of the sorbent tube so as to provide openings at least 2 mm in diameter.
- 8.2.2 Choose the direction desired for sample air flow, mark the inlet end of the tube with a permanent marker, and attach the other end to tubing from the sampling pump. Sample air must not pass through any hose or tubing before entering the sorbent tube. For low concentrations of methylamine, low humidity conditions, or short sampling periods, pump the sample air through the outer 150-mg sorbent section first; for high concentrations, high humidity, or long sampling periods, pump the sample air through the larger 600-mg sorbent section first.
- 8.2.3 With the sorbent in a vertical position as much as is practical, sample the air at 200 cm³/min for the desired period of time. The flow rate and sampling time, or the volume, must be measured as accurately as possible. The temperature and pressure of the air being sampled should be measured and recorded.
- 8.2.4 Immediately after sampling is completed, add 20 µL of concentrated HCl to each of the smaller sorbent sections and 80 µL to the larger section. The silica gel will turn yellow upon addition of the acid due to iron impurities in the silica gel. If sample desorption and analysis is to be done within one week, and the tube is not subjected to unusually high temperatures or low pressures, this acid stabilization is not necessary. In this case, the 20 µL (or 80 µL) of acid must be added to 2 mL (or 8mL) of methanol-water used for sample recovery (see Paragraph 8.3.2).
- 8.2.5 Seal the sorbent tubes with polyethylene caps.
- 8.2.6 Obtain a blank sample by handling one tube in the same manner as the sample tubes (break, add acid, seal, and ship) except that no air is pumped through it.
- 8.2.7 For shipping to the laboratory, pack the tubes tightly to minimize chances of breakage during transit. Tubes should not be subjected to extremes of high temperature or low pressure.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Score each tube with a file between the sorbent sections and break the tube into three parts. Remove the Teflon screens and transfer the smaller silica gel sections to separate 2-mL glass tubes or vials that can be tightly sealed. Repeat for the larger section and a 10-mL glass container. Label each appropriately.

8.3.2 Desorption. Add 2 mL of methanol-water eluent solution to each of the smaller silica gel sections and 8 mL to the larger one. If no acid was added to the silica gel solutions in the field, add 20 μ L of concentrated hydrochloric acid to each 2 mL of eluent and 80 μ L to each 8 mL of eluent. Seal the samples. Shake the mixtures occasionally over a period of one hour.

8.3.3 Preparation and Reaction. Transfer a 0.5-mL aliquot of each eluate to another test tube or vial. Add 0.5-mL of alkalizing solution and mix thoroughly. Verify the basicity of the solution with litmus paper. Add 10 μ L of benzaldehyde, mix thoroughly, and allow at least 5 min for reaction.

8.3.4 Gas Chromatographic Conditions. Typical operating conditions are:

Helium gas flow rate, 50 mL/min
Injection port temperature, 150 °C
Detector temperature, 200 °C
Column temperature, 100 °C

Under these conditions, unreacted benzaldehyde elutes at 190 sec and benzylideneaminomethane elutes at 425 sec.

8.3.5 Injection of Sample. Inject and analyze 3- μ L aliquots of each sample and standard. To eliminate difficulties arising from blowback or distillation within the 10- μ L syringe, use a solvent flush technique.

8.3.6 GC Peak Measurement. Determine the areas of the peaks of the compounds of interest from analyses of samples and standards.

8.4 Determination of Desorption Efficiency

8.4.1 Importance. Desorption efficiency for a particular compound can vary from one lot of silica gel to another and from one laboratory to another. Also, for a given lot of silica gel the desorption efficiency may vary with the amount of material adsorbed during sampling. Therefore, it is necessary to determine at least once the desorption efficiency for methylamine with each lot of silica gel used for at least two levels within the normal range of samples size. If the desorption efficiencies are significantly different from quantitative recovery, they should be used to correct the measured weight of analyte as described in Section 10.2 below.

8.4.2 Procedure. Place 150 mg of silica gel in a 2-mL glass-stoppered tube. The silica gel must be from the same lot

as that used in collecting the sample; it can be obtained from unused sorbent tubes. With a microliter syringe, inject a known amount of standardized 40% methylamine in water solution, directly onto the silica gel. Also inject 40 μL of concentrated HCl. Close the tube with the glass stopper and allow it to stand overnight to insure complete adsorption of the amine. Prepare at least three tubes for each at two different levels. These tubes are referred to as samples. Prepare a blank in the same manner, omitting the amine. Analyze the samples and blank as described in Section 8.3. Also analyze three standards prepared by adding identical amounts of methylamine and 40 μL of concentrated HCl to 2.0 mL of eluent solution. Determine the concentrations of methylamine in the blank, samples, and standards using calibration curves prepared as described in Section 9. The desorption efficiency is calculated by dividing the concentration of amine found in the sample by the concentration obtained for the corresponding standard.

9. Calibration and Standardization

9.1 Standardization of the 40% 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 nominally 40% methylamine solution (c_i) in g/mL.

9.2 Preparation of a Stock Solution. Calculate the volume V_i (μL) of the 40% solution required for preparation of 10 mL of a stock solution, 10 μL of which contains an amount of methylamine equal to that which would be collected from a volume of air V_s (m^3) sampled at a concentration X_i (mg/m^3):

$$V_i (\mu\text{L}) = \frac{X_i \times V_s}{C_i} \times 1000$$

where:

X_i - the standard concentration limit, or the anticipated average concentration, (mg/m^3) of compound i in air.

V_s - volume (m^3) of air sampled.

C_i - concentration ($\text{mg}/\mu\text{L} = \text{g}/\text{mL}$) of the original methylamine solution determined in Paragraph 9.1.

1000 - aliquot factor.

Add the calculated volume of 40% methylamine to a 10-mL volumetric flask and dilute to the mark with 4:1.methanol-water. Neutral solutions of amines are subject to oxidation and should be prepared fresh when needed.

- 9.3 Preparation of Calibration Standards. Add 2.5 μ L, 5 μ L, 10 μ L, 15 μ L, and 20 μ L of the prepared standard to test tubes containing 2 mL eluent solution and 40 μ L concentrated hydrochloric acid. Use a 10- μ L syringe to inject through septum seals. Shake these tubes. These standards correspond to 0.25, 0.5, 1, 1.5, and 2 times X_1 in V_s , respectively, for samples collected on the smaller tube sections and eluted with 2 mL of methanol-water. They correspond to 1, 2, 4, 6, and 8 times X_1 in V_s , respectively, for the larger section.
- 9.4 React and analyze standards with samples according to Section 8.3.
- 9.5 Prepare a calibration curve by plotting peak areas obtained from the analyses of standards against nominal amounts (mg) in the calibration standards.

10. Calculations

- 10.1 Read the weights (mg) of sample on each tube section corresponding to each measured peak area using the calibration curve. Correct each value for the weight found in a blank, if any. Add the weights found in the front and backup sections of the sample tube to obtain the total weight of compound in the air volume sampled.
- 10.2 Divide the total weight by the desorption efficiency to obtain the corrected sample weight.
- 10.3 Determine the volume V_s (m^3) of air sampled at ambient conditions based on the appropriate information, such as flow rate (L/min) multiplied by sampling time (min) and $10^{-3} m^3/L$. 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 corrected volume is:

$$V_s = 10^{-3} \times f \times t \sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$$

where:

- f - sample flow rate (L/min)
- t - sampling time (min)
- P_1 - pressure during calibration of sampling pump (torr)
- P_2 - pressure of air samples (torr)
- T_1 - temperature during calibration of sampling pump ($^{\circ}K$)
- T_2 - temperature of air sampled ($^{\circ}K$)

- 10.4 Divide the total corrected weight (mg) of methylamine by V_s (m^3) to obtain the concentration of methylamine in the air sampled (mg/m^3).

11. References

- 11.1 E. E. Campbell, G. O. Wood, and R. G. Anderson, "Development of Air-Sampling Techniques, October 1, 1973 - March 31, 1974," Progress Report LA-5634-PR (1974), Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Also available from the National Technical Information Services, Springfield, VA.
- 11.2 E. E. Campbell, G. O. Wood, and R. G. Anderson, "Development of Air-Sampling Techniques, April 1 - September 30, 1974," Progress Report LA-5973-PR (1975), Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Also available from the National Technical Information Services, Springfield, VA.
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- 11.4 G. O. Wood and R. G. Anderson, "Development of Air-Monitoring Techniques Using Solid Sorbents, April 1 - September 30, 1975," Progress Report LA-6216-PR (1976), Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Also available from the National Technical Information Services, Springfield, VA.
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- 11.7 G. O. Wood and R. G. Anderson, "Sampling and Analysis of Aliphatic Amine Vapors," Report LA-UR-74-1654 (1975), Industrial Hygiene Group, Los Alamos Scientific Laboratory, Los Alamos, New Mexico. (Presented at the 1975 American Industrial Hygiene Conference, Minneapolis, MN).

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VINYL ACETATE

Measurements Research Branch

Analytical Method

Analyte:	Vinyl Acetate	Method No.	P&CAM 278
Matrix:	Air	Range:	8-210 mg/m ³ in 1.5 liters of air
Procedure:	Adsorption on Chromo- sorb 107, thermal de- sorption, GC-FID	Precision:	8%
Date Issued:	May 10, 1978		
Date Revised:	Classification: E (Proposed)		

1. Synopsis

- 1.1 A known volume of air is drawn through a tube containing a Chromo-sorb 107 to trap the vinyl acetate present.
- 1.2 The tube is thermally desorbed into a 300 mL chamber.
- 1.3 An aliquot of the desorbed vapor is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

- 2.1 Sample loadings between 2 and 332 µg of vinyl acetate per sampling device are acceptable. Samples have been successfully collected from dynamically generated atmospheres of vinyl acetate over the concentration range of 8.2 to 206 mg/m³. The relative humidity of the sampled air was greater than 80%.

2.2 The slope of a typical calibration curve (integrator response versus mass of vinyl acetate per sample tube) was 687 (v.S)/g. The sensitivity of the flame ionization detector was 4.04×10^{-6} C/g of vinyl acetate.

2.3 The lowest quantifiable level was determined to be 0.5 μ g of vinyl acetate per 300 mg bed of Chromosorb 107. At this loading the relative standard deviation of replicate samples was better than 10%.

3. Interferences

3.1 When two or more substances are known or suspected to be present in the air sampled, such information should be transmitted with the sample, because the substances may interfere with the analysis of vinyl acetate.

3.2 Any substance which has the same retention time as vinyl acetate at the operating conditions described in this method is an interference. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

3.3 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 The pooled relative standard deviation of the sampling and analytical method was 8.1%. This reflects the precision of sampling and analysis of 50 samples of vinyl acetate collected with calibrated personal sampling pumps from humid atmospheres (>80%) over the concentration range of 8 to 200 mg/m^3 . The relative standard deviation of samples collected from atmospheres averaging 8.6 (range 8.2 to 9.0) mg/m^3 was 9.5%, from atmospheres averaging 24.3 (range 18.6 to 39.2) mg/m^3 was 8.0%, and from atmospheres averaging 181 (range 159 to 206) mg/m^3 was 5.9%.

4.2 The concentration of the sampled air was independently determined using a gas phase infrared analyzer. The samples were collected from humid air and stored at room temperature. The determination averaged 7% high, 5% high and 4% low when analyzed on days 1, 7

and 14, respectively. Thus the analyte displayed an 0.8% per day storage loss when stored at room temperature. This loss can be attributed to the analyte degrading in the presence of water, because samples spiked with 18 μg of vinyl acetate in hexane gave 98% recovery when stored for 14 days at room temperature.

- 4.3 The breakthrough volume and therefore capacity of Chromosorb 107 for vinyl acetate decreased with increasing relative humidity. Under the most adverse conditions tested, 83% relative humidity, the breakthrough volume was found to be 4.0 L when an atmosphere of vinyl acetate at 138 mg/m^3 was sampled at 0.125 L/min.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Many of the interferences can be eliminated by altering chromatographic conditions.
- 5.2 The sampling tubes are analyzed using a quick instrumental method and can be reused after the analysis is completed.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the sampling tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will be imprecise because the pump is usually calibrated for one tube only.
- 5.4 One disadvantage of the method is that the amount of sample that can be taken is limited by the capacity of the sampling device. When the amount of vinyl acetate found on the backup section exceeds 10% of the amount found on the front section, the possibility of sample loss exists. Migration from the front to the backup section is not a problem because the sections are separated and individually capped immediately after sampling.

6. Apparatus

- 6.1 Personal sampling pump capable of accurate performance at 0.1 L/min. The pump must be calibrated with a representative sampling device in line and must be fully charged prior to being used.
- 6.2 Chromosorb 107 sampling tubes. Individual front and backup tubes (Century Systems Corporation "Flare" tubes or equivalent) are used. The front section is a stainless steel tube 7.3 cm long with a 6-mm o.d., a 4-mm i.d., and a 45° flare at one end. The backup section is a chrome plated nickel tube 3 cm long with a 6-mm o.d.,

a 4-mm i.d., a 45° flare at one end and a hose connection at the other end. Each tube has a permanent metal frit in the outlet end of the tube. The front section contains 300 mg of prewashed Chromosorb 107 held in place with a removable metal frit. The backup section contains 50 mg of prewashed Chromosorb 107 held in place with a plug of silylated glass wool. The sampling device is assembled by joining the front and backup section with a nylon nut and fitting. A hollow nylon ferrule is placed between the two sections. The pressure drop across the tubes must be less than 10 inches of water at a flow rate of 0.1 L/min.

The Chromosorb 107 is washed in a Soxhlet extractor for eight hours with water, eight hours with methanol and eight hours with dichloromethane. The sorbent is then dried overnight in a vacuum oven. The tubes are loaded with sorbent and thermally purged for two minutes with helium at 150°C. After cooling in a closed container the ends are capped.

- 6.3 Thermal desorber equipped with thermostatted desorbing oven, 300-ml sample reservoir, and a 2-mL gas sampling loop (Century Systems Corporation Programmed Thermal Desorber or equivalent).
- 6.4 Gas chromatograph equipped with a flame ionization detector and electronic integrator.
- 6.5 GC column (20 ft x 1/8 in.o.d.) made of silanized stainless steel and packed with 10% FFAP on 80/100 mesh Chromosorb W AW.
- 6.6 Vials 1.5-mL, with aluminum serum cups equipped with Teflon lined silicone rubber septa.
- 6.7 Microliter syringes, 10-μl and convenient sizes for making standards.
- 6.8 Macropipette, 1000-μl, with disposable plastic tips.
- 6.9 U-tube, glass with at least one hose connection, approximately 75-mL internal volume.
- 6.10 Pump capable of drawing 200 mL/min through a front section of the sampling device.
- 6.11 Gas bag, 10 liter volume for helium purge gas.
- 6.12 Test tubes with close fitting plastic caps.
- 6.13 Ring stand with clamps.

7. Reagents

Whenever possible, reagents used should be ACS Reagent Grade or better.

- 7.1 Vinyl acetate, practical, inhibited with hydroquinone and freshly distilled before use.
- 7.2 Hexane, (UV grade).
- 7.3 Helium, Bureau of Mines Grade A.
- 7.4 Hydrogen, prepurified.
- 7.5 Air, filtered and compressed.

8. Procedure

- 8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis of vinyl acetate is washed with detergent and rinsed thoroughly with tap water and distilled water.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Immediately before sampling remove the plastic caps from the inlet and outlet ends of the sampling tube.
 - 8.2.2 Connect the tube to the sampling pump using a short piece of flexible tubing. The backup section is positioned nearest the pump. The sampling tube is kept vertical during sampling. to prevent channeling through the device.
 - 8.2.3 Air being sampled does not pass through any hose or tubing before entering the sampling device.
 - 8.2.4 The temperature, pressure, and volume of air sampled is measured and reported. The volume sampled should not exceed 3 liters sampled at a flow rate of 0.1 L/min or less. Record either the flow rate and sampling time or the initial and final stroke readings and the volumetric stroke factor.
 - 8.2.5 Immediately after sampling, disassemble the two sections, cap the sections with plastic caps, and label the sections. Do not use rubber caps.
 - 8.2.6 For every ten samples taken, handle one sampling device in the same manner as the samples (uncap, disassemble, cap, label and transport) however do not sample any air through this device. Label this device as a blank.

- 8.2.7 Samples received at the laboratory are logged in and analyzed as soon as possible. Samples stored at room temperature for 14 days exhibit an 11% loss of analyte.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. Remove the caps from either a front or a back section. Wipe the outside of the tube with a clean laboratory wiper.

- 8.3.2 Thermal Desorber Conditions. Typical operating conditions for the thermal desorber are:

Desorbing oven temperature	150°C
Desorbing rate, helium gas	70 mL/min
Transfer line temperature	160°C
Pressure equalization time	15 sec.

- 8.3.3 Gas Chromatographic Conditions. Typical operating conditions for the gas chromatograph are:

Helium carrier gas flow rate	33 mL/min
Hydrogen flow to detector	40 mL/min
Air flow to detector	435 mL/min
Injector temperature	160°C
Manifold(detector) temperature	160°C
Oven temperature	60°C

Under these conditions, the capacity ratio for vinyl acetate was 4.4.

- 8.3.4 Thermal Desorption of Samples. Wipe off the tube and insert it in the desorbing oven. Desorb with helium at atmospheric pressure. The helium is stored in the 10-L gas bag. Desorbing with air chars the Chromosorb and renders it unsuitable for reuse.
- 8.3.5 Injection. Inject a 2 mL aliquot of the desorbed vapors into the GC column. Since the desorbed vapors are stored in a reservoir, as many as five replicate injections of each sample can be made.
- 8.3.6 Measurement of Area. Measure the area of the sample peak with an electronic integrator or other suitable technique of area measurement. The results are read from a standard curve as prepared in Section 9.4.
- 8.3.7 Preparation for Next Sample. After satisfactory analysis is obtained, purge the thermal desorber with helium for two minutes.

Remove the tube from the desorbing oven, place it in a test tube and cap the test tube. When the tube is cool, remove it from the test tube and cap it with the plastic cups.

9. Calibration and Standardization

- 9.1 It is convenient to express the concentration in terms of μg of vinyl acetate per sample tube. Standard curves are prepared by loading clean sampling tubes (front sections) with known amounts of vinyl acetate. The density of vinyl acetate ($0.932 \text{ mg}/\mu\text{L}$ at 20°C) is used to convert the volume taken to mass.
- 9.2 Preparation of Standards. Pipet 1.00 mL aliquots of hexane into clean glass vials. Crimp the vials shut with an aluminum serum cap equipped with a Teflon lined silicone rubber septum. Inject either 25 , 10 , 5 or $1 \mu\text{L}$ of freshly distilled vinyl acetate into each vial. These standard solutions are freshly prepared for each analysis.
- 9.3 Loading the Standard. Support a U-tube on a ring stand. Using a short length of tubing attach the outlet end of a clean front section of a sampling tube to a small pump. The inlet end of the clean front section is attached to the side of the U-tube that has the hose connection. Use the solvent flush technique to withdraw a $2 \mu\text{L}$ aliquot of a standard solution. Turn on the pump and inject this $2 \mu\text{L}$ aliquot into the end of the μ tube farthest from the sampling tube. Sweep enough air through the U-tube (2 min at $200 \text{ mL}/\text{min}$ approximately 5 volume changes) to insure that all the vinyl acetate is loaded on the sample tube. Stop the pump, remove the sample tube cap both ends, and label. This tube now contains a known amount of vinyl acetate.
- 9.4 Standardization. Analyze each tube from Section 9.3 as per Section 8.3. The standard curve is obtained by plotting the amount of vinyl acetate loaded on a tube versus the peak area found. If conditions warrant, prepare standards at higher or lower concentrations.

10. Calculations

- 10.1 The sample weight in μg is read from the standard curve.
- 10.2 Blank corrections are not expected. 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 charcoal tube

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

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

A similar procedure is followed for the backup sections.

10.3 The concentration, C , of vinyl acetate in the air sampled is expressed in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{liter}$.

$$C = \frac{W_F + W_B}{V}$$

where: W_F = amount of vinyl acetate found on front section in μg

W_B = amount of vinyl acetate found on backup section in μg

V = volume of air sampled in liters

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

$$C(\text{ppm}) = C(\mu\text{g}/\text{L}) \times \frac{24.45}{86.1} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure of air sampled in torr

T = temperature of air sampled in $^\circ\text{C}$

24.45 = molar volume at 25°C and 760 torr in liters/mol

86.1 = molecular weight of vinyl acetate in g/mol

11. References

- 11.1 D. L. Foerst, Alexander W. Teass and Maria Risholm-Sundman, "A Sampling and Analytical Method for Vinyl Acetate in Air", (manuscript in preparation) Measurements Research Branch, NIOSH, Cincinnati, OH 1978.

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BERYLLIUM IN BIOLOGICAL TISSUE

Measurement Support Branch

Analytical Method

Analyte:	Beryllium	Method No.:	P&CAM 279
Matrix:	Biological Tissue	Range:	5-250 ng Be/g fresh tissue
Procedure:	Mixed acid ashing, dissolution in dilute sulfuric acid, furnace atomic absorption spectrophotometry.	Precision:	10% (Analytical)
Date Issued:	8/1/78		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Biological tissue samples are wet-ashed in a mixture of nitric, sulfuric and perchloric acids. After the organic matrix has been destroyed, the sample is taken to dryness, and the residue is dissolved in dilute sulfuric acid. The beryllium content of the sample is determined in the graphite furnace of an atomic absorption spectrophotometer by measuring the absorbance at 234.9 nm.

2. Working Range, Sensitivity and Detection Limit

- 2.1 Linear range of the calibration curve is 0.005-0.25 ngBe/aliquot using normal internal gas flow in the graphite furnace. This range can be extended by diluting the sample and varying the aliquot size.
- 2.2 The sensitivity of the method is dependent on graphite furnace parameters and can vary with different instruments. Under the furnace conditions given it is 2.5 pg/1% absorbance.
- 2.3 The estimated detection limit for the conditions given is 2.5 pg/aliquot.

3. Interferences

- 3.1 Perchloric acid depresses the Be signal and must be removed during sample digestion.

3.2 Calcium is a known interferent; its effect is masked by H_2SO_4 .

4. Precision and Accuracy

4.1 The precision and accuracy of this method have not been determined at this time. Spiked and unspiked NBS SRM#1577 Bovine liver and standards were carried through the ashing procedure and indicated that recovery was 100%.

4.2 The relative standard deviation of the analytical procedure is estimated to be 10%.

5. Advantages and Disadvantages

5.1 The method has the sensitivity necessary to determine beryllium in tissue samples.

5.2 Matrix effects are frequently encountered in flameless atomic absorption analysis.

5.3 The digestion procedure requires the use of a perchloric acid fume hood.

6. Apparatus

6.1 Atomic Absorption Spectrophotometer

6.1.1 Atomic absorption spectrophotometer with graphite furnace or carbon rod atomizer. Reproducible control of times and temperatures during the drying, ashing, and atomizing cycles is essential.

6.1.2 Beryllium hollow cathode lamp.

6.1.3 Purge gas, high purity argon, in a cylinder equipped with a two-stage, two-gauge pressure regulator and appropriate hose connections. The pressure on the instrument side of the regulator should be 30 psig. Nitrogen should not be used as the purge gas since cyanogen interferes in the analysis.

6.2 Glassware (borosilicate)

6.2.1 Phillips beakers with watchglass covers, 125 mL.

6.2.2 Graduated centrifuge tubes, 15 mL.

6.2.3 Volumetric flasks, 10 and 100 mL.

6.3 Micro pipettes, 10 to 50 μL .

6.4 Variable hotplate capable of reaching 250°C.

6.5 Fume hood capable of handling perchloric acid fumes.

7. Reagents

All reagents must be A.C.S. reagent grade or better. Water must be doubly distilled or deionized.

7.1 Nitric acid, concentrated, redistilled in glass.

7.2 Perchloric acid, concentrated (70-72%).

7.3 Sulfuric acid, concentrated and 3% (V/V) in double distilled or deionized water.

7.4 Beryllium standard solution (1000 µg/mL). A commercially prepared aqueous beryllium standard solution may be used; or, the solution may be prepared by dissolving 1.000 g of beryllium metal in a minimum volume of (1 + 1) HCl and diluting to 1 liter with 1%(V/V) HCl. Caution: Beryllium is potentially toxic and should be handled with care. Working standard solutions should be prepared in 3% H₂SO₄ in the range of 1 to 25 ng Be/mL. Working standards should be prepared fresh daily.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Borosilicate glassware is recommended for this method. Soak new glassware in Nochromix acid cleaning solution or chromic acid solution and rinse thoroughly with warm tap water, then soak in 10% HNO₃ for at least 30 minutes and rinse with double distilled or deionized water.

8.1.2 Clean used glassware by soaking in detergent solution and rinsing with warm tap water, then soak in 10% HNO₃ for 30 minutes and rinse with double distilled or deionized water.

8.2 Collection and Shipping of Samples

Tissue samples are collected from biopsy samples or at the time of autopsy; 500 mg should be submitted. Samples are placed in plastic containers and frozen, if possible. Bags, bottles or jars of plastic materials may be used.

8.3 Analysis of Samples

8.3.1 Place a biological tissue sample in a preweighed 125 mL

Phillips beaker, then weigh the beaker and sample to obtain the sample weight.

- 8.3.2 Add 3 mL of HNO_3 , 1 mL of HClO_4 and 1 mL of H_2SO_4 to each sample. This can be conveniently performed using a pipet with disposable plastic tips. Cover each beaker with watch glass and place the beakers on a hotplate (130 – 150°C) located in a perchloric acid fume hood. Carry reagent blanks and quality control samples through the ashing procedure with the samples. Add additional nitric acid to samples and reagent blanks to maintain oxidative conditions until the organic matrix has been destroyed and a nearly colorless solution remains. Add additional perchloric acid, if necessary.
- 8.3.3 After the organic matrix is destroyed, remove the watch glass covers, turn up the hotplate, and take the samples to dryness. Dissolve the sample residue in 3% H_2SO_4 . Warm the samples to insure complete dissolution. Transfer the samples to graduated centrifuge tubes. Rinse the Phillips beaker with 3% H_2SO_4 and add the rinse to the centrifuge tube. Dilute the sample to 5–10 mL total volume with 3% H_2SO_4 . (Alternatively, samples may be transferred to 10-mL volumetric flasks and diluted to volume with 3% H_2SO_4). Record the volume of each solution.
- 8.3.4 Operate the atomic absorption spectrophotometer according to the manufacturer's instructions, using the 234.9-nm resonance line of beryllium. Automatic background correction is desirable. If it is not available in the instrument used, estimate the non-specific absorbance by a separate analysis at 234.9 nm, using a deuterium or hydrogen lamp; subtract this value from the sample absorbance. Deliver an aliquot of 5 to 25 μL to the graphite furnace with a micropipette and read the absorbance as peak height on a recorder or an electronic peak height readout. Drying, ashing, and atomizing times and temperatures will vary according to the instrument used and other factors but are approximately as follows: dry for 20 sec at 110°C , ash for 25 sec at 500°C and atomize for 8 sec at 2800°C .

Either peak height or integrate mode may be used for this analysis. The range of standard solutions suggested is based on analysis of 10 μL aliquots.

9. Calibration and Standardization

- 9.1 Prepare working standard solutions containing 1 to 25 ng Be/mL in 3% H_2SO_4 and analyze these solutions in the same manner as samples.

9.2 Prepare a calibration curve by plotting peak height or peak area vs ng Be/aliquot. Read the amount of beryllium in an aliquot of sample solution from the calibration curve.

10. Calculations

The concentration of beryllium in a tissue sample is calculated as follows:

$$C = \frac{M}{V_a} \times \frac{V_T}{W_s} \times 1000$$

where M = ng of beryllium read from calibration curve

V_a = volume of aliquot analyzed in μ l

V_T = volume of digested solution in ml(See Sec. 8.3.3)

W_s = weight of sample analyzed in g(See Sec. 8.3.1)

11. References

- 11.1 Perkin-Elmer Corporation, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Conn., 1973.
- 11.2 Perkin-Elmer Corporation, Analytical Methods for Atomic Absorption Spectrophotometry Using the Graphite Furnace, Norwalk, Conn., 1973.
- 11.3 Bettger, R.J., et al, "Determination of Beryllium in Air Samples Using the Graphite Furnace," Atomic Absorption Newsletter, 14, 124(1975).

Michele Bolyard
Measurements Services Section

N,N-DIMETHYL-p-TOLUIDINE

Measurement Support Branch

Analytical Method

Analyte:	N,N-Dimethyl-p-toluidine	Method No.:	P&CAM 280
Matrix:	Air	Range:	9.37 to 30 mg/M ³ in a 100 L air sample
Procedure:	Adsorption on silica gel, elution by ethanol GC	Precision:	3.5% (Analytical)
Date Issued:	8/1/78		
Date Received:		Classification:	E (Proposed)

1. Synopsis

- 1.1 A known volume of air is drawn through a tube containing silica gel to trap the N,N-dimethyl-p-toluidine vapor.
- 1.2 The silica gel is transferred to a glass-stoppered tube or vial with septum cap and desorbed with ethanol.
- 1.3 An aliquot of the ethanol solution is injected into a gas chromatograph equipped with a flame ionization detector.
- 1.4 Peak areas are determined and compared with calibration curves obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method has been used for field samples in the range of 9.37 to 30.0 mg/M³ for a 100 L air sample.
- 2.2 The estimated detection limit using a flame ionization detector is 0.01 mg per sample when N,N-dimethyl-p-toluidine is desorbed with 1.0 mL ethanol and a 5.0 µl aliquot is injected into the gas chromatograms.

3. Interferences

- 3.1 Any compound which has the same or nearly the same retention time as N,N-dimethyl-p-toluidine at the gas chromatographic analytical conditions described in this method is an interference. This type of interference often can be overcome by changing the operating conditions of the gas chromatograph or selecting another column.

- 3.2 Retention time data on a single column, or even a number of columns cannot be considered as conclusive proof of chemical identity in all cases. For this reason it is important that whenever practical, a sample of the bulk compound or mixture be submitted at the same time as the sample tubes (but shipped separately) so that identification may be made by other means.

4. Precision and Accuracy

- 4.1 The precision of the overall method has not been determined. Six replicate spiked samples gave a precision of 3.5% relative standard deviation at a level of 0.469 mg/tube.
- 4.2 The accuracy of the method depends upon the collection and desorption efficiencies. If a negligible amount of N,N-dimethyl-p-toluidine is detected on the backup section, the collection efficiency of the tube is close to 100%. Desorption efficiencies at the level of 0.467 mg/tube have been found to be about 88% for the lot of silica gel tested.

5. Advantages and Disadvantages

- 5.1 The sampling method uses a small, portable device involving no liquids. Desorption of the collected sample is simple and is accomplished with a solvent of low toxicity. The analysis is accomplished by a quick instrumental method. Most analytical interferences which occur can be eliminated by altering gas chromatographic conditions. Several aromatic amines can be collected and analyzed simultaneously; this is useful where the composition of the aromatic amine vapors may not be known.
- 5.2 A major disadvantage of the method is the limitation on its precision due to the use of personal sampling pumps currently available. After initial adjustment of flow, any change in the pumping rate will affect the volume of air actually sampled. Furthermore, if the pump used is calibrated for one tube only, as is often the case, the precision of the volume of air sampled will be limited by the reproducibility of the pressure drop across the tubes.

6. Apparatus

- 6.1 One or more personal sampling pumps whose flow can be determined within 1.5% at 1 L/min for 15 minutes or 200 mL/min for 8 hours.
- 6.2 Sampling tubes 7 cm long, with a 6-mm O.D. and 4-mm I.D., consisting of two sections of 20/40 mesh silica gel. The weights of silica gel in the front and backup sections are 100 mg and 50 mg respectively separated by a 2-mm plug of urethane foam. A plug of silylated glass wool is placed in front of the absorbing section.
- 6.3 Gas chromatograph equipped with a flame ionization detector.

- 6.4 Either of two columns can be used: 4 ft. x 1/8 in. O.D., stainless steel, packed with 10% Silicone OV-25 liquid phase, on 80/100 mesh Supelcoport (or equivalent support) or 2 ft. x 1/8 in. O.D., stainless steel, packed with Chromosorb 103 (80/100) mesh.
- 6.5 Recorder and electronic integrator to determine peak height or area.
- 6.6 Glass-stoppered tubes or vials with septum caps, 2-mL and 10-mL.
- 6.7 Syringes, 10- μ L and other convenient sizes for making standards.
- 6.8 Pipettes and volumetric flasks for preparation of standard solutions.

7. Reagents

- 7.1 Ethanol, 95%
- 7.2 n-heptanol and n-octanol, reagent grade
- 7.3 N,N-dimethyl-p-toluidine
- 7.4 Helium, Bureau of Mines Grade A
- 7.5 Hydrogen, prepurified
- 7.6 Air, compressed and filtered

8. Procedure

- 8.1 Cleaning of Equipment. Wash all glassware to be used for the laboratory analysis with detergent and follow with tap water and distilled water rinses.
- 8.2 Collection and Shipping of Samples
 - 8.2.1 Each pump must be calibrated with a representative tube in the line to minimize errors associated with uncertainties in the sample volume collected.
 - 8.2.2 Immediately before sampling, break the ends of the tube so as to provide an opening of at least one-half the internal diameter of the tube.
 - 8.2.3 The tube is connected to the pump with a short piece of tubing and is positioned so that air passes through the front section and then the backup section. No sampled air is to pass through any hose or tubing before entering the sampling tube.
 - 8.2.4 The atmosphere is sampled at a flow rate of 1 L/min or less. A 100-L sample or less is recommended. The flow

rate and sampling time or air volume must be measured as accurately as possible.

- 8.2.5 The temperature, pressure, and humidity of the atmosphere being sampled are measured and recorded.
- 8.2.6 The sampling tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.
- 8.2.7 One tube should be handled in the same manner as the sample tube (break, seal, and transport) except that no air is sampled through this tube. This tube is labelled as a blank.
- 8.2.8 Capped tubes should be packed tightly before shipping to minimize tube breakage during shipping.
- 8.2.9 Samples of the bulk liquids from which the amine vapors arise should be submitted to the laboratory also, but may not be sent in the same container as the air samples or blank tubes.
- 8.2.10 Storage: After sampling, tubes should be tightly capped and not subjected to extremes of high temperature or low pressure, if avoidable.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples: By removing and discarding the glass wool plugs, the silica gel sections are transferred to glass-stoppered tubes or vials. These are analyzed separately.
- 8.3.2 Desorption of Samples: Prior to analysis, 1.0 mL ethanol containing 0.1% n-heptanol internal standard is pipetted into each flask or vial.
- 8.3.3 Typical operating conditions for the gas chromatograph are: Carrier gas flow: 50 mL/min 60 psig

Injection port temperature: 250°C
Detector temperature: 250°C
Column Temperature: 180°C isothermal
- 8.3.4 A 5 µL aliquot of the sample is injected into the gas chromatograph.
- 8.3.5 If an internal standard is not used, make injections by using the solvent flush technique.
- 8.3.6 Draw about 3.0 µL of solvent (ethanol) into the syringe.

- 8.3.7 Withdraw the needle and pull the plunger back about 0.2 μL .
- 8.3.8 Immerse the needle in the sample or standard and withdraw 4.2 μL using the air pocket as a marker. The needle volume is about 0.8 μL .
- 8.3.9 Pull the plunger back slightly, about 0.2 μL , to minimize evaporation in the tip of the needle.
- 8.3.10 If an internal standard is used, (e.g. 0.1% n-heptanol) calculate the ratio of the area of the sample or standard peak to the area of the internal standard peak to determine sample concentration in the eluent.

9. Calibration and Standardization

- 9.1 Prepare standards by adding the following amounts of N,N-dimethyl-p-toluidine to 25 ml portions of ethanol: 50 μL , 45 μL , and 80 μL . The resulting concentrations are 0.937 mg/mL, 1.69 mg/mL, and 3.00 mg/mL, respectively. When microliter pipettes are used instead of microliter syringes, take the volume indicated on the pipette, e.g., 50 μL instead of 45 μL .
- 9.2 Inject the standards under the same GC conditions and during the same time period as the unknown samples. This will minimize the effect of day-to-day variations of the flame ionization detector responses.
- 9.3 Prepare a standard curve by plotting peak area versus concentration when the external standard procedure is used, and ratio of area of sample peak to area of internal standard peak versus concentration when the internal standard procedure is used.

10. Calculations

- 10.1 Corrections for the blank must be made for each sample.

$$\text{Corrected } W_c = W_s - W_b$$

where: W_c = mg found in front section of sample tube.
 W_b = mg found in front section of blank tube.

Follow the same procedure for the backup sections.

- 10.2 Add the corrected amounts in the front and backup sections of the sample tube to determine the total measured amount in the sample.
- 10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liter at 25°C and 760 mm

V = volume of air in liters as calculated (sampling
x correct flow rate)

P = barometric pressure in mm Hg

T = temperature of air in degrees Centigrade

- 10.4 The concentration of the organic solvent can be expressed in mg/M^3 , which is numerically equal to $\mu\text{g}/\text{L}$ of air.

$$\text{mg}/\text{M}^3 = \mu\text{g}/\text{L} = \frac{W_c(\text{mg}) \times 1000 \frac{\mu\text{g}}{\text{mg}}}{V_s(\text{L})}$$

- 10.5 Another method of expressing concentration is ppm, defined as μL of compound vapor per liter of air.

$$\text{ppm} = \frac{\mu\text{L of vapor}}{V_s}$$

$$\text{ppm} = \frac{W_c(\mu\text{g})}{V_s} \times \frac{24.45 \text{ L}}{\text{Mole}} \times \frac{1}{\text{MW}}$$

where: $\text{MW} = 135.20 \text{ g}/\text{Mol}$

11. References

- 11.1 NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 1, P&CAM 168, "Aromatic Amines in Air," April 1977.

Robert W. Kurimo
Measurements Services Section

Ethylene Thiourea
Measurements Support Branch

Analytical Method

Analyte:	Ethylene Thiourea*	Method No.:	P&CAM 281
Matrix:	Air	Range:	0.03-1.5 mg/m ³ for 100-L sam- ple
Procedure:	Filter collection, ex- traction, complexation, spectrophotometry	Precision:	3% (Analytical)
Date Issued:	8/1/78		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Ethylene thiourea is collected from air on a PVC or cellulose ester membrane filter. The filter is extracted with distilled water. Pentacyanoammineferrate reagent is added to the extract to form a colored coordination complex. The absorbance of the solution is measured spectrophotometrically at 590 nm, and the concentration of ethylene thiourea is determined from a calibration curve.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The working range for this method is 0.03-1.5 mg/m³ in a 100-L sample. The entire linear working range has not been determined.
- 2.2 The sensitivity is 0.006 absorbance unit/ μ g as determined from the slope of several calibration curves.
- 2.3 The detection limit is 0.75 μ g/sample or 0.0075 mg/m³ in a 100-L sample for 0.01 absorbance, using 5-cm optical path length cells.

3. Interferences

Any compound which has an absorbance maximum in the region of the ethylene thiourea complex, will interfere by causing a higher absorbance reading.

4. Precision and Accuracy

- 4.1 The analytical precision has been determined from 21 spiked PVC and 21 cellulose ester filters ranging from 15-150 μ g/sample. The analytical relative standard deviation is 3% for PVC and 3.5% with cellulose ester filters.
- 4.2 The average percent recovery is 98.7% determined from 21 spiked PVC filters and 97.7% for 21 spiked cellulose ester filters in the 15-150 μ g/sample range.

- 4.3 Stability studies of the ethylene thiourea complex revealed a 1.5% degradation of the color in 3 hours. The complexing reagent is stable for at least two weeks when refrigerated.

5. Advantages and Disadvantages

- 5.1 The method is simple, relatively fast, has very good sensitivity and precision and requires inexpensive instrumentation.
- 5.2 The pentacyanoammineferrate reagent will complex with compounds containing the thione (C=S) moiety; this method, therefore, will be applicable to those compounds containing this moiety.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 PVC filters 5 μm in pore size, 37 mm in diameter or mixed cellulose esters filters 0.8 μm in pore size, 37 mm in diameter.
- 6.1.2 Plastic three piece 37-mm filter holders (cassettes).
- 6.1.3 A personal air sampling pump capable of operating at 1.5–2.0 liters/min.

6.2 Spectrophotometer, operating in the visible range at 590 nm.

6.3 Matched glass cells, 5-cm optical path length.

6.4 Analytical balance, capable of weighing to the nearest 0.1 mg.

6.5 Mortar and pestle.

6.6 Water bath, thermostatically controlled to $\pm 1^{\circ}\text{C}$.

6.7 Glass vials, 25-mL capacity, with teflon coated screw caps.

6.8 Beakers, assortment of 50–250 mL.

6.9 Adjustable pipettes (5–50 μL , 50–250 μL , 0.5–5 mL) with disposable tips.

6.10 Volumetric pipettes, assortment of 1–25 mL capacity.

6.11 Volumetric flasks, 25, 100, 200 and 250 mL capacity.

6.12 Miscellaneous: tweezers, microspatula, rubber suction bulb, wood applicator stick, weighing paper, filter paper, and filter funnel with stand.

7. Reagents

All reagents used should be ACS reagent grade or better.

- 7.1 Bromine liquid, Br_2 . (CAUTION: corrosive liquid, causes severe burns, vapors extremely irritating and toxic. Wear gloves and handle only in a hood).
- 7.2 Sodium nitroferricyanide (sodium nitroprusside), $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$.
- 7.3 Hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$.
- 7.4 Sodium bicarbonate, NaHCO_3 .
- 7.5 Hexane.
- 7.6 Methanol.
- 7.7 Distilled or deionized water.
- 7.8 Complexing Reagent
- 7.8.1 Weigh 0.500 g sodium nitroferricyanide in a 50-mL beaker. Add 10 mL distilled water to the beaker and swirl to dissolve.
- 7.8.2 Weigh 0.500 g hydroxylamine hydrochloride and 1.000 g sodium bicarbonate. Transfer both materials to a mortar and carefully grind them together.
- 7.8.3 The next two steps must be performed in a hood. Add the ground mixture to the sodium nitroferricyanide solution. A bubbling reaction occurs for a few minutes. When the reaction is complete, add 0.10 mL bromine (see "caution" on Section 7.1). When effervescence stops, add approximately 10 mL distilled water and filter the solution. Rinse the beaker with 4 mL distilled water and filter. Transfer filtrate to a 25 mL volumetric flask and dilute with distilled water to the mark. This reagent should be kept refrigerated.
- 7.8.4 Dilute complexing reagent. Mix one part of complexing reagent with two parts water. Prepare this solution daily when needed.
- 7.9 Ethylene thiourea (2-imidazolidinethione). Usually this material is less than 99% pure and needs to be purified by recrystallization.
- 7.9.1 CAUTION: Ethylene thiourea has been found to be an animal teratogen and carcinogen. Extra care must be taken to avoid inhalation, ingestion or skin contact with ethylene thiourea. Keep material in a labelled bottle clearly identified as "animal carcinogen," and place in a resealable thick-walled plastic bag, in a locked storage.
- 7.9.2 Recrystallization. In a 250 mL Erlenmeyer flask, weigh 3-5 g ethylene thiourea. Add 100 mL 1:1 methanol-water to dissolve the material. In a hood, heat the mixture to boiling. Cool

the flask at room temperature for five minutes. Add 5 ml hexane and shake the flask for 30 seconds. Cover the flask with a watch glass and leave undisturbed at room temperature for one hour. Filter the purified crystals, washing with 100 mL methanol-water mixture. Let the crystals air dry in the hood.

- 7.10 Ethylene thiourea 1000 µg/mL stock solution. Weigh 0.250 g of recrystallized ethylene thiourea in a beaker. Add distilled water to dissolve the material. Transfer the solution into a 250-mL volumetric flask and dilute with distilled water to the mark.

8. Procedure

- 8.1 Cleaning of Equipment. Wash all glassware with detergent solution, rinse with tap water, distilled water, and dry in an oven.
- 8.2 Calibration of Sampling Pump. The personal sampling pump should be calibrated with a representative filter assembly in the line. A wet or dry test meter or a glass rotameter capable of measuring the approximate flow rate (1.5 to 2 Lpm) to within ±5% may be used for the calibration.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Assemble the filters in the filter holder so that the air being sampled passes first through the filter and then through the filter support. Remove the small plugs from the filter holder and connect the filter holder to the sampling pump by means of an adapter and a length of flexible PVC tubing.
- 8.3.2 Sample the air at a flow rate of 1.5 to 2 Lpm. Measure the flow rate and time, or volume, as accurately as possible. A minimum sample of 200 L should be collected. The optimum sample volume will depend on the type of workroom environment being sampled. Since high concentrations of particulate material may plug the filter, the flow rate should be checked at least once every hour. On completion of sampling, reinsert the small plugs into the inlet and outlet of the filter holder. Record the temperature and pressure of the air being sampled.
- 8.3.3 With each group of samples prepare two blanks consisting of a filter holder with a representative filter that has been handled in the same manner as the sample filters, except that no air is drawn through them. The samples and the blank should be shipped promptly in a damage-proof container that allows no filter holder movement. Samples should be refrigerated as soon as possible.
- 8.4 Analysis of Samples
- 8.4.1 Extraction
1. Remove the top portion of the filter holder. Hold the

bottom portion containing the filter and filter support over a piece of weighing paper to catch any particulate material that may fall out. Remove the small plug from the bottom portion of the filter holder and insert the applicator stick through the hole. Gently raise the filter support and the filter and grasp the unexposed edge with tweezers. Very carefully pick up the filter, insert into a glass vial and push it gently to the bottom with the applicator stick. Add to the vial any particulate material remaining in the filter holder or collected on the weighing paper.

2. Pipet 7.0 mL of distilled water into the vial. This amount should completely cover the filter. Screw the cap on the vial.
3. Place vials into a 60°C water bath (thermostatically controlled) for 45 minutes. The water bath level must be above the water level of the vial. Shake each vial every 5 minutes. The use of ultrasonic bath is not recommended because it breaks up the PVC or AA filters.
4. Lift the filter with tweezers so it is above the water level in the vial and wash the filter two times with 4-mL aliquots of water using a 5-mL adjustable pipette. Position the filter over the center of the vial so the rinsings can be collected in the vial, then discard the filter.

8.4.2 Complexation

This step should be performed at the same time for both standard and field samples so that the color formation will start at the same time. This reduces color degradation discrepancies.

1. Pipet a 1.5-mL aliquot of the dilute complexing reagent into each vial.
2. Allow the vials to stand for at least 30 minutes before analysis to insure full color development. Shake the vials every 10 minutes.
3. The color of the complexed samples varies with increasing the concentration from yellow to light green to turquoise. Very high concentrations have prussian blue color; in this case, the sample must be diluted before analysis.

8.4.3 Measurement

1. Transfer the solution to a clean 5-cm optical path length glass cell. Wipe off with a lens paper any droplets left on the cell windows.

2. Place the cell in the sample compartment and measure the absorbance at 590 nm. The Reference sample contains 15-mL distilled water and 1.5-mL dilute complexing reagent in a 5-cm glass cell. Record the absorbance for each sample.

8.5 Determination of Extraction Efficiency

- 8.5.1 On a plastic test tube rack place eight filters. Using an adjustable pipette, add to the center of each filter 0, 15, 30, 45, 60, 90, 120, and 150 microliters of the 1000 µg/mL ethylene thiourea stock solution. This corresponds to quantities of 0, 15, 30, 45, 60, 90, 120 and 150 micrograms per filter. Let filters air-dry overnight at room temperature. Place each spiked filter in a vial, and mark its concentration. Follow sections 8.4.1 part 2 through 8.4.3 for preparation and analyses of the spiked samples.
- 8.5.2 The absorbance of each sample is converted to micrograms from the calibration curve (Section 10.1). Percent recovery(R) is determined as follows:

$$R = \frac{W_R}{W_A} \times 100$$

where: W_R = micrograms recovered

W_A = micrograms added

9. Calibration and Standardization

- 9.1 Prepare a 15 µg/mL ethylene thiourea standard solution by pipetting 3 mL of the 1000 µg/mL stock solution into a 200 mL volumetric flask. Dilute with distilled water to the mark.
- 9.2 Prepare standards by pipetting into clean vials 0,1,2,3,4,6,8 and 10 mL aliquots of the 15 µg/mL standard solution. Bring the total volume in each vial to 15 mL with distilled water. When the standards are complexed, they will correspond to concentrations of 0, 15, 30, 45, 60, 90, 120 and 150 µg/16.5 mL respectively. Follow section 8.4.2 and 8.4.3 to complex and analyze the standards.
- 9.3 Prepare a calibration curve by plotting absorbance vs concentration of standards in µg/16.5 mL sample.

10. Calculations

- 10.1 The concentration of ethylene thiourea in field samples can be determined graphically from the plot of absorbance vs concentration.

The concentration can also be determined using the following expression obtained from least squares analysis.

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

where: C = concentration in $\mu\text{g}/\text{sample}$
 A = absorbance value of field sample
 Y = line intercept value obtained from least squares analysis
 M = line slope value obtained from least squares analysis

- 10.2 The concentration of ethylene thiourea in air may be expressed in mg/m^3 (C_A):

$$C_A = \frac{W_F}{V_A}$$

where: W_F = weight of field sample in μg
 V_A = volume of air sampled in liters

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

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

where: F = sample 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 ($^{\circ}\text{K}$)
 T_2 = temperature of air sampled ($^{\circ}\text{K}$)

11. References

- 11.1 Grote, I.W., "A New Color Reaction for Soluble Organic Sulfur Compounds," J. Biol. Chem., 93, 25 (1931).
 11.2 Danowski, T.S., "Measurement of Thiourea in Ultrafiltrate of Serum," J. Biol. Chem., 152, 201 (1944).
 11.3 Journal of the Association of Official Agricultural Chemists, 31, 100 (1948).

John Palassis
 Measurements Services Section

Tetramethyl Thiourea
Measurement Support Branch
Analytical Method

Analyte:	Tetramethyl thiourea*	Method No.:	P&CAM 282
Matrix:	Air	Range:	0.15-1.5 mg/m ³ for 100 L sample
Procedure:	Impinger collection, complex- ation, spectrophotometry	Precision:	2% (Analytical)
Date Issued:	8/1/78		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Tetramethyl thiourea is collected from air in midget impingers containing 15 mL water. Pentacyanoammineferrate reagent is added to the sample to form a colored coordination complex. The absorbance of the solution is measured spectrophotometrically at 590 nm, and the concentration of tetramethyl thiourea is determined from a calibration curve.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The working range for this method is 0.15-1.5 mg/m³ in a 100-L sample. The entire linear working range has not been determined.
- 2.2 The sensitivity is 0.006 absorbance units/ μ g as determined from the slope of several calibration curves.
- 2.3 The detection limit, using 5-cm optical path length cells, is 3.0 μ g/sample or 0.03 mg/m³ in 100-L sample for 0.01 absorbance.

3. Interferences

Any compound which has an absorbance maximum in the region of the tetramethyl thiourea complex, will interfere by causing a higher absorbance reading.

4. Precision and Accuracy

- 4.1 The analytical precision has been determined from 35 standards (5 sets of 7 samples) ranging from 15-150 μ g/sample. The analytical relative standard deviation is 2%.
- 4.2 The collection efficiency of laboratory generated air samples has not been determined.

*1,1,3,3-tetramethyl-2-thiourea

- 4.3 Since there is no extraction step involved in the procedure, an extraction study was not performed. An extraction study with PVC filters indicates that tetramethyl thiourea cannot be extracted from PVC filters.
- 4.4 Stability study of the tetramethyl thiourea complex revealed a 4.7% degradation of the color in 2 hours. The complexing reagent is stable for at least two weeks when refrigerated.

5. Advantages and Disadvantages

- 5.1 The method is simple, relatively fast, has very good sensitivity and precision and requires inexpensive instrumentation.
- 5.2 The pentacyanoammineferrate reagent will complex with compounds containing the thione ($C=S$) moiety; this method, therefore, is applicable to those compounds containing this moiety.

6. Apparatus

6.1 Air Sampling Equipment

- 6.1.1 All glass midget impingers filled with 15 mL distilled water.
- 6.1.2 Flexible tubing, to connect impinger to the pump.
- 6.1.3 A personal air sampling pump capable of operating at 2.8 liters/min. The pump is protected from splashover or water condensation by a second empty impinger or bubbler connected in line or an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.2 Spectrophotometer. Operating in the visible range.

6.3 Matched glass cells, 5-cm optical path length.

6.4 Analytical balance, capable of weighing to the nearest 0.1 mg.

6.5 Mortar and pestle.

6.6 Test tubes, 15-mL marked with 0.1-mL graduations.

6.7 Glass vials, 25-mL capacity, with teflon coated screw caps.

6.8 Beakers, assortment of 50-250-mL.

6.9 Adjustable pipette, 0.5-5 mL with disposable tips.

6.10 Volumetric pipettes, assortment of 1-25-mL capacity.

6.11 Volumetric flasks, 25, 100, 200 and 250-mL capacity.

6.12 Miscellaneous: tweezers, microspatula, rubber suction bulb, weighing paper, filter paper, filter funnel with stand, and "Parafilm" or

equivalent.

7. Reagents

All reagents used should be ACS reagent grade or better.

7.1 Bromine liquid, Br_2 . (CAUTION: corrosive liquid, causes severe burns, vapors extremely irritating and toxic. Wear gloves and handle only in a hood).

7.2 Sodium nitroferricyanide (sodium nitroprusside), $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$.

7.3 Hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$

7.4 Sodium bicarbonate, NaHCO_3

7.5 Distilled or deionized water

7.6 Complexing Reagent

7.6.1 Weigh 0.500 g sodium nitroferricyanide in a 50-mL beaker. Add 10 mL distilled water to the beaker and swirl to dissolve.

7.6.2 Weigh 0.500 g hydroxylamine hydrochloride and 1.000 g sodium bicarbonate. Transfer both materials to a mortar and carefully grind them together.

7.6.3 The next two steps must be performed in a hood. Add the ground mixture to the sodium nitroferricyanide solution. A bubbling reaction occurs for a few minutes. When the reaction is complete, add 0.10 mL bromine (see "caution" on Section 7.1). When effervescence stops, add approximately 10 mL distilled water and filter the solution. Rinse the beaker with 4 mL distilled water and filter. Transfer filtrate to a 25-mL volumetric flask and dilute with distilled water to the mark. This reagent should be kept refrigerated.

7.6.4 Dilute complexing reagent. Mix one part of complexing reagent with two parts water. Prepare this solution daily when needed.

7.7 Tetramethyl thiourea, reagent grade.

CAUTION: Tetramethyl thiourea has been found to be an animal teratogen and carcinogen. Extra care must be taken to avoid inhalation, ingestion or skin contact with tetramethyl thiourea. Keep material in a labelled bottle clearly identified as "animal carcinogen," and place in a resealable thick-walled plastic bag, in a locked storage.

7.8 Tetramethyl thiourea 1000 $\mu\text{g}/\text{mL}$ stock solution. Weigh 0.250 g of tetramethyl thiourea in a beaker. Add distilled water to dissolve the material. Transfer the solution into a 250 mL volumetric flask and dilute with distilled water to the mark.

8. Procedure

8.1 Cleaning of Equipment. Wash all glassware with detergent solution, rinse with tap water, distilled water, and dry in an oven.

8.2 Calibration of Sampling Pump. The personal sampling pump should be calibrated in line with a representative midget impinger containing 15 mL distilled water. A wet or dry test meter or a glass rotameter capable of measuring the flow rate to within $\pm 5\%$ may be used for the calibration.

8.3 Collection and Shipping of Samples

8.3.1 Pour 15 mL distilled water into a midget impinger and connect the impinger to the vacuum pump with a short piece of flexible tubing.

8.3.2 Turn on the pump to begin sample collection. Measure the flow rate and time, or volume, as accurately as possible and record the temperature and pressure of the atmosphere being sampled. Sample at a flow rate of 2.8 L/min. Collect a sample of 200 liters or more.

8.3.3 After sampling, remove the impinger stem. Tap the stem gently against the inside wall of the impinger to recover as much of the solution as possible. Then seal the impinger with a non-reactive stopper.

8.3.4 Care should be taken to minimize spillage or loss by evaporation.

8.3.5 Whenever possible, hand deliver the samples to the laboratory. Otherwise, ship the samples in the special impinger shipping cases designed by NIOSH.

8.3.6 Handle at least one impinger in the same manner as the other samples (fill, seal, and transport), but sample no air through this impinger. Label this sample as a "blank".

8.3.7 Samples should be refrigerated as soon as received in the laboratory.

8.4 Analysis of Samples

8.4.1 Sample treatment. Transfer contents of the impinger in a clean test tube. Add water to the 15-mL mark.

8.4.2 Complexation. This step should be performed at the same time for both standard and field samples so that the color formation will start at the same time. This reduces discrepancies due to color degradation.

1. Pipet a 1.5-mL aliquot of the dilute complexing reagent into each vial or test tube. Screw a cap on the vial or

cover the opening of the test tube with parafilm.

2. Allow to stand for at least 30 minutes before analysis to insure full color development. Shake the vials or test tubes every 10 minutes.
3. The color of the complexed samples varies with increasing concentration from yellow to green to greenish blue. Extreme concentrations have prussian blue color; in this case the sample must be diluted before analysis.

8.4.3 Measurement

1. Transfer the solution to a clean 5-cm optical path length glass cell. Wipe off with a lens paper any droplets left on the cell windows.
2. Place the cell in the sample compartment and measure the absorbance at 590 nm. The Reference sample contains 15 mL distilled water and 1.5 mL dilute complexing reagent in a 5-cm glass cell. Record the absorbance for each sample.

9. Calibration and Standardization

- 9.1 Prepare a 15 µg/mL standard solution of tetramethyl thiourea by pipetting 3 mL aliquot of the 1000 µg/mL stock solution into a 200 mL volumetric flask. Dilute with distilled water to the mark.
- 9.2 Prepare standards by pipetting into clean vials 0,1,2,3,4,6,8 and 10 mL aliquots of the 15 µg/mL standard solution. Bring the total volume in each vial to 15 mL with distilled water. When the standards are complexed, they will correspond to concentrations of 0,15,30,45,60,90,120 and 150 µg/16.5 mL respectively. Follow section 8.4.2 and 8.4.3 to complex and analyze the standards.
- 9.3 Prepare a calibration curve by plotting absorbance vs concentration of standards in µg/16.5 mL sample.

10. Calculations

- 10.1 The concentration of tetramethyl thiourea in field samples can be determined graphically from the plot of absorbance vs concentration.

The concentration can also be determined using the following expression obtained from least squares analysis.

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

where: C = concentration in µg/sample

A = absorbance value of field sample
 Y = line intercept value from least squares
 M = line slope value from least squares

- 10.2 The concentration of tetramethyl thiourea in air may be expressed in mg/m^3 (C_A):

$$C_A = \frac{W_F}{V_A}$$

where: W_F = weight of field sample in μg
 V_A = volume of air sampled, in liters.

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

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

where: F = sample 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

11. References

- 11.1 Grote, I.W., "A New Color Reaction for Soluble Organic Sulfur Compounds," J. Biol. Chem., 93, 25 (1931).
 11.2 Danowski, T.S., "Measurement of Thiourea in Ultrafiltrate of Serum," J. Biol. Chem., 152, 201 (1944).
 11.3 Journal of the Association of Official Agricultural Chemists, 31, 100 (1948).

John Palassis
 Measurements Services Section

OIL MIST

Measurement Support Branch

Analytical Method

Analyte:	Oil Mist, Water Insoluble	Method No.:	P&CAM 283
Matrix:	Air	Range:	0.5 $\bar{3}$ 15 mg/m
Procedure:	Filter collection, solvent extraction, infrared spec- trophotometry	Precision:	5% (Ana- lytical)
Date Issued:	8/1/78		
Date Revised:		Classification:	D(Operational)

1. Synopsis

- 1.1 Air samples are collected using 37-mm membrane filters.
- 1.2 Oil mist is extracted from the filters with carbon tetrachloride.
- 1.3 The carbon tetrachloride solution is analyzed for oil content using infrared spectrophotometry to measure the C-H absorbance near 2940 cm^{-1} .

2. Working Range, Sensitivity, and Detection Limit

- 2.1 For a 100 liter $\bar{3}$ air sample, the working range is linear up to at least 15 mg/m^3 and can easily be extended by dilution.
- 2.2 The sensitivity is approximately 35 $\mu\text{g mL}/0.1$ absorbance unit. The sensitivity will vary somewhat depending on the actual oil being analyzed.
- 2.3 The detection limit varies slightly with oil types, but is about 2 $\mu\text{g oil/mL}$ which corresponds to 0.3 mg/m^3 for a 100-liter air sample.

3. Interferences

- 3.1 Filters must be handled with care to avoid any oil contamination since this method is sensitive to any C-H containing compound. Although the method is sensitive to hydrocarbon compounds, this should not cause a serious interference since most hydrocarbons would not be collected on a membrane filter.
- 3.2 Tobacco smoke is an interference and workers should not be allowed to use smoking materials while an oil mist sample is being collected

since the smoke will invalidate the sample.

4. Precision and Accuracy

- 4.1 The precision and accuracy have not been determined at this time.
- 4.2 The precision of the analytical procedure is estimated to be 5% RSD.

5. Advantages and Disadvantages

- 5.1 The method is simple and fast, but it can only be used for water insoluble or mineral cutting oils.
- 5.2 The instrumentation required is available in most laboratories.
- 5.3 Since the method is not specific for a particular oil, it will give a good indication of total oil mist exposure in locations where several cutting oils are in use.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the filter-collection method has the following components:
 - 6.1.1 The filter unit, consisting of the filter media (Section 6.2) supported by a backup pad and 37 mm 3-piece cassette filter holder secured with tape or a shrinkable band.
 - 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flowrate. The pump must be calibrated with a representative filter holder and filter in the line.
 - 6.1.3 Thermometer
 - 6.1.4 Manometer
 - 6.1.5 Stopwatch
- 6.2 Mixed cellulose ester membrane filter, 0.8-micrometer pore size or filter, 5.0-micrometer pore size, 37-mm diameter.
- 6.3 Infrared Spectrophotometer, double beam dispersive, with scanning capabilities in the 3400--2700 wavenumber region.
- 6.4 Glassware
 - 6.4.1 Scintillation vials with plastic-lined caps for desorption of samples.
 - 6.4.2 Volumetric flasks for preparing standards, 50 mL.

6.4.3 Transfer pipets

6.4.4 Reagent dispenser, 15 mL delivery capacity for adding solvent to samples.

6.4.5 Two 1-cm optical cells, infrared quartz with teflon stoppers mounted in demountable cell holders.

7. Reagents

7.1 Carbon tetrachloride, distilled reagent grade.

7.2 Stock Solution, 10 mg/mL - Weigh 0.500 g of oil into a 50-mL volumetric flask and dissolve with CCl_4 to volume. Working standards should be prepared in CCl_4 in the range of 1 to 100 μg oil/mL. Working standards are stable for at least one week if flasks are tightly closed.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Wash in detergent solution and follow with tap water and distilled or deionized water rinses. Dry.

8.1.2 Rinse with distilled CCl_4 and allow to dry.

CAUTION: All work with CCl_4 should be performed in a hood. All waste CCl_4 should be collected, labelled and disposed of properly.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter unit by mounting the filter disc and back-up pad in the filter cassette and securing the cassette with tape or a shrinkable band.

8.2.2 Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

8.2.3 Turn on pump to begin sample collection. The flowrate, times, and/or volume must be measured as accurately as possible. A minimum sample of 100 liters should be collected. Larger sample volumes are encouraged, provided the filters do not become loaded to the point that loose material might fall off or the filter become plugged.

8.2.4 The sample cassettes should be shipped in a suitable container to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter, nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean

filter in the cassette on top of the sample filter.

8.2.5 With each batch of samples, one filter, labeled as a blank, must be submitted. No air should be drawn through this filter.

8.2.6 An unused, undiluted sample (5-10 mL is sufficient) of the oil being used must be collected and sent to the laboratory for use as a standard material in the analysis. To prevent contamination, the bulk should not be shipped in the same container as the samples.

8.3 Analysis of Samples

8.3.1 Use tweezers to transfer sample and blank filters into individual scintillation vials exercising care to avoid contaminating the filters with oil from hands. Add 15.0 mL CCl_4 and cap the vial. Allow vials to stand for 30 minutes with occasional agitation. At this point the oil is in solution and the samples are ready for analysis.

8.3.2 Fill both cells with distilled CCl_4 and scan the region from $3400 - 2700 \text{ cm}^{-1}$. All scans should be done in absorbance mode, if available. Otherwise data must be converted to absorbance units.

8.3.3 Fill one cell with sample or blank filter extracts, one at a time and scan each solution against CCl_4 in the reference beam.

8.3.4 The absorbance at the wavenumber of the peak used to plot the calibration curve, generally about 2940 cm^{-1} , is measured and used to determine the oil concentration from the calibration curve prepared from the bulk samples (Section 8.2.6).

9. Calibration and Standardization

9.1 Appropriate dilutions of the stock solution with CCl_4 are prepared to obtain working standards in the range of 1-100 $\mu\text{g/mL}$.

9.2 The working standards are transferred to a 1-cm cell and an infrared spectrum of the region from $3400 - 2700 \text{ cm}^{-1}$ is recorded for each standard. A calibration curve is constructed by measuring the peak height of the largest absorbance peak and plotting this value vs concentration in $\mu\text{g/mL}$.

10. Calculations

10.1 Blank values, if any, should first be subtracted from each sample.

10.2 The concentration of oil in the air sampled can be calculated as mg oil/m^3 (C) as follows.

$$C = \frac{K}{V_s} \times V$$

where: K = concentration of oil from calibration curve in µg oil/
mL

V = final volume (mL) of sample analyzed including any
dilution factor.

V_s = volume of air in liters sampled at 25°C and 760 mm Hg

11. References

- 11.1 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 13th Ed., 254.
- 11.2 M. Gruenfeld, "Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectrophotometry," Environ. Sci. and Technol., 7, 636 (1973).

Michele Bolyard
Measurements Services Section

4-DIMETHYLAMINOAZOBENZENE

Measurements Research Branch

Analytical Method

Analyte:	4-Dimethylaminoazobenzene	Method No:	P&CAM 284
Matrix:	Air	Range:	4-2000 $\mu\text{g}/\text{m}^3$ in a 50-liter sample
Procedure:	Collection on glass fiber filter and Gas-Chrom P, elution with 2-propanol, analysis by gas chromatography	Precision:	7%
Date Issued:	8/1/78	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

- 1.1 A known volume of air is drawn through a two-stage sampler consisting of a high-efficiency glass fiber filter followed by a bed of Gas-Chrom P to collect the 4-dimethylaminoazobenzene aerosol and/or vapor.
- 1.2 The filter and sorbent sections of the sampler are transferred to stoppered tubes and the 4-dimethylaminoazobenzene is desorbed with 2-propanol.
- 1.3 An aliquot of this solution is injected into a gas chromatograph.
- 1.4 Peak areas are electronically determined and compared with a calibration curve obtained from injections of standard solutions of 4-dimethylaminoazobenzene.

2. Working Range, Sensitivity and Detection Limit

- 2.1 The analytical range is 0.2-100 $\mu\text{g}/\text{sample}$ (4-2000 $\mu\text{g}/\text{m}^3$ for a 50L air sample) when using 0.5 mL of desorbing solution and 1- μL injections into the gas chromatograph.
- 2.2 In experiments in which atmospheres containing 400 $\mu\text{g}/\text{m}^3$ of 4-dimethylaminoazobenzene in air of 80% relative humidity at 30°C were sampled, less than 10% of the compound was found in the sorbent bed after six hours (65 L). Tests to determine breakthrough of the

sorbent bed during the sampling periods showed no detectable 4-dimethylaminoazobenzene downstream of the sorbent bed. The compound existed primarily as an aerosol.

2.3 The limit of detection is 0.05 µg/sample.

3. Interferences

3.1 In solutions containing 4-dimethylaminoazobenzene at 3 ng/µL, the following compounds were found not to interfere when their concentrations were 3 ng/µL: azobenzene, N-methylaniline, N,N-dimethylaniline, 4-nitrobiphenyl, 4-aminobiphenyl, 4-hydroxyazobenzene and the 2'-, 3'- and 4'-methyl derivatives of 4-dimethylaminoazobenzene. 4-Aminoazobenzene has the same retention time as the analyte and does interfere.

3.2 Any compound sampled with 4-dimethylaminoazobenzene and having the same retention time as the analyte will interfere with the analysis. This type of interference often can be eliminated by changing the operating conditions of the chromatograph, e.g., by temperature programming or by changing the stationary phase.

4. Precision and Accuracy

4.1 The precision of the overall method is 7% relative standard deviation for samples collected at 30°C and 80% relative humidity. This value is based on 25 samples involving volumes of 10 to 70 liters and a sampling rate₃ of 0.2 L/min. Concentrations sampled ranged from 67 to 445 µg/m³.

4.2 Filters spiked with 0.2 µg 4-dimethylaminoazobenzene and stored at ~24°C yielded recoveries >82% when desorbed within 28 days. Filters spiked with 3.9µg yielded recoveries of 100% during that period.

4.3 If more than 10% of the total recovered weight is found on the Gas-Chron P section, sample loss may be indicated. Under these circumstances, the actual ambient concentration may be greater than the sample analysis indicates.

4.4 At a flow rate of 0.2L/min, the linear velocity through the 4-mm inlet of the holder is 26.5 cm/s. It is not known if this throat velocity is sufficient for the capture of all particles.

4.5 The accuracy of the method has not been determined.

5. Advantages and Disadvantages

5.1 The sampler is a small portable device containing no liquids. This is an advantage for sampling air in a worker's breathing zone without interfering with normal work activities.

5.2 This method has not been field tested.

6. Apparatus

- 6.1 Personal air sampling pump that can be maintained for four hours at a flow rate of 0.2 L/min with the sampler in line. Each pump should be calibrated with a representative sampler in line to minimize errors in volume measurements. A bubble flow meter or other suitable flow measuring device may be used.
- 6.2 Sampler, equivalent to that shown in Figure 1. The sampler consists of two sections: a high-efficiency glass fiber filter, followed by a 50-mg bed of Gas-Chrom P. The first section, a 13-mm glass fiber filter (Spectrograde or Type A-E, Gelman Instrument Co., Ann Arbor, MI, or equivalent) is contained in a 13-mm filter holder (SX00-013-00 Millipore Corp., Bedford, MA, or equivalent). The sorbent tube is a 50-mm section of Pyrex glass, 6.4-mm o.d. x 4-mm i.d. flared on one end, containing the section of Gas-Chrom P (Grade 407, 30/60 mesh, 1 m²/g, 0.26 g/cc; Applied Science Laboratories, State College, PA, or equivalent). The sorbent is held by 3.5-mm diameter, 100 mesh, stainless steel screens and 4-mm o.d. Teflon rings, as shown in Figure 1. To connect the two stages, the filter holder is pressed into the flared end of the sorbent tube. The pressure drop across the sampler at 0.2 L/min is ~20 torr. Flexible vinyl caps are used to seal the ends of the sampler.
- 6.3 Gas chromatograph equipped with a flame ionization detector (FID) and injection port.
- 6.4 Glass column, 1.8-m x 2-mm i.d. x 6.4-mm o.d., packed with 3% OV-225 on 80/100 mesh Supelcoport, (Supelco Inc., Bellefonte, PA, or equivalent,)
- 6.5 Potentiometric strip chart recorder.
- 6.6 Test tubes, 1-mL, fitted with polyethylene stoppers.
- 6.7 Glass syringes, 5- and 10- μ L.
- 6.8 Pipettes of convenient volumes for the preparation of standard solutions.
- 6.9 Volumetric flasks of convenient volumes for the preparation of standard solutions.
- 6.10 Clinical centrifuge.
- 6.11 Analytical balance.
- 6.12 Test tube shaker, vortex type.

7. Reagents

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

7.1 2-Propanol, UV grade, distilled in glass.

7.2 Acetone, distilled in glass.

7.3 Methyl alcohol.

7.4 Chloroform.

7.5 4-Dimethylaminoazobenzene.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis is washed with detergent and rinsed with tap water, distilled water, and methyl alcohol.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, the vinyl caps are removed from the ends of the sampler and saved for resealing after sampling.

8.2.2 The sorbent end of the sampler is connected to the pump with plastic or rubber tubing. The sampler is positioned vertically during sampling. Sampled air must not pass through any tubing before entering the sampler.

8.2.3 The atmosphere is sampled at a flow rate of 0.2 L/min for no longer than six hours. The flow rate and sampling time, or the volume of sampled air, must be measured as accurately as possible.

8.2.4 The temperature, pressure, and if possible, humidity of the atmosphere being sampled are measured and recorded, along with other pertinent data such as location, date, and time of sampling. Condition of high humidity should be noted.

8.2.5 Blank samples are obtained by handling random collection devices in the same manner as in sampling, except that no air is drawn through them.

8.2.6 Samples shipped to the laboratory should be packed tightly to minimize breakage.

8.2.7 If samples of bulk material associated with the process under investigation are to be shipped to the laboratory, they should not be placed in the same container as the air samplers or blanks.

8.3 Analysis of Samples

8.3.1 Place the glass fiber filter in a 1-mL tube. Place the 50-mg section of Gas-Chrom P in a separate test tube. Teflon rings and stainless steel screens associated with the sampler may be analyzed with the Gas-Chrom P stage. Sampler caps may be reused.

8.3.2 Add 0.5 mL of 2-propanol to each vial and cap it.

8.3.3 Allow the vials to stand for one hour, shaking them intermittently in a test tube vibrator. Centrifuge for 10 minutes.

8.3.4 Gas Chromatographic Conditions

Column:	3% OV-225 on 80/100 mesh Supelcoport in 1.8-m x 2-mm i.d. x 6.4-mm o.d. glass tubing.
Column Temperature:	218°C
Injector Temperature:	228°C
Detector Temperature:	228°C
Helium:	24 mL/min
Hydrogen:	85 mL/min
Air:	378 mL/min
Detector:	FID; Attenuation 1 x 2 at low concentrations
Injection Volume:	1.0µL
Efficiency:	3200 theoretical plates
Capacity Ratio:	18.1

8.3.5 Injection. Flush the 5 µL syringe first with acetone (to insure its cleanliness and to wet the barrel and plunger) and then with the sample solution. Carefully (to minimize the intake of particulate matter) draw 1 µL of sample solution into the syringe and inject the aliquot into the gas chromatograph.

8.3.6 Measure the peak area and read the amount of analyte from the calibration curve.

8.4 Efficiency of Desorption

- 8.4.1 Importance of Determination. The efficiency of desorption for 4-dimethylaminoazobenzene can vary from one laboratory to another and also from one batch of Gas-Chrom P or filters to another. Thus, it is necessary to determine the fraction of 4-dimethylaminoazobenzene that can be recovered from these matrices. Since the efficiency of desorption may also vary with the amount of 4-dimethylaminoazobenzene present, determinations should be made for at least two levels in the range of anticipated sample sizes.
- 8.4.2 Procedure for Determining the Efficiency of Desorption. Place the filters and Gas-Chrom P from unused samplers in 1-mL test tubes. Add to each a known amount of 4-dimethylaminoazobenzene in 10 μ L of chloroform using the same microliter syringe for each. Five filters and Gas-Chrom P samples are thus prepared at each of two different levels in the range of interest. Cap the tubes. Treat a parallel blank in the same manner (no analyte is added). Prepare at least three standards at each of the various levels by adding 10 μ L (same syringe as above) of the 4-dimethylaminoazobenzene solutions to 0.5 mL of desorbing solution. Allow them to stand overnight. Analyze the samples and standards as described in Section 8.3. The efficiency of desorption (D) is the average gas chromatographic peak area given by the samples, corrected for the blank if necessary, divided by the average area given by the standards.

9. Calibration and Standardization

- 9.1 For accuracy in preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at a high concentration. The initial standard is prepared by weighing a selected amount of 4-dimethylaminoazobenzene (e.g., 125 mg) into a 250-mL volumetric flask and adding the desorbing solution to the calibration mark. Dilutions encompassing the concentration range of interest down to 0.4ng/ μ L are then made from the stock solution. Solutions should be stored in a refrigerator when not in use.

CAUTION: 4-Dimethylaminoazobenzene Has Been Identified As A Carcinogen. Appropriate Precautions Must Be Taken In handling The Compound To Avoid Personnel Exposure And Area Contamination.

- 9.2 The standard solutions should be analyzed under the same gas chromatographic conditions and during the same time period as the samples. This will minimize inaccuracy due to day-to-day variations in the setting of instrumental conditions.
- 9.3 Calibration curves for 4-dimethylaminoazobenzene are prepared by plotting the peak areas for the standards against their concentration in μ g/0.5mL.

10. Calculations

- 10.1 In the event that the blank produces a peak with the same retention time as the analyte, the analyst should determine the source of the interference and eliminate or compensate for it.
- 10.2 Read the weight (W_1) in μg of 4-dimethylaminoazobenzene present in the sample from the calibration curve.
- 10.3 The corrected weight (W_2) is determined by

$$W_2 = \frac{W_1}{D}$$

where D is the efficiency of desorption for that sampler stage.

- 10.4 Add the weights found in the sampler stages to determine the total weight (W_t) collected.
- 10.5 The concentration of 4-dimethylaminoazobenzene in air (C , $\mu\text{g}/\text{m}^3$) is given by

$$C = \frac{W_t}{V} \times 10^3$$

where V is the volume of air sampled in liters and 10^3 is the factor to convert from liters to m^3 .

11. Reference

Raul Morales, J.F. Stampfer, Jr., R. E. Hermes, E.E. Campbell, and H.J. Ettinger, "Development of Sampling and Analytical Methods for Carcinogens, October 1, 1976 - December 31, 1977," Progress Report LA-7375-PR, National Technical Information Service, Springfield, Virginia, 1978.

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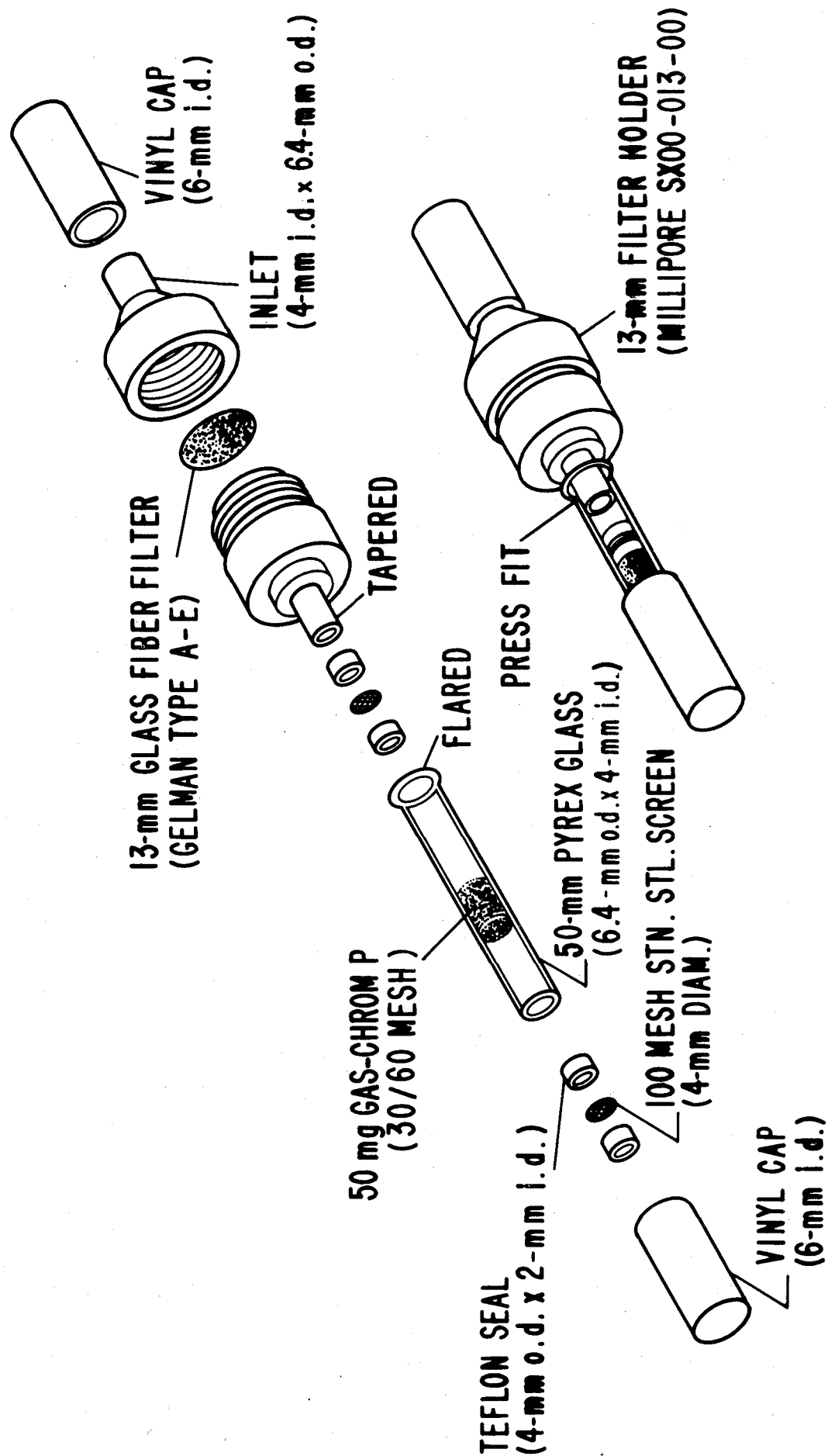


Figure 1. Two-Stage Personal Sampler for 4-Dimethylaminoazobenzene

SCP METHODS

S24-i

Diphenyl
(Biphenyl)

Analyte:	Biphenyl	Method No.:	S24
Matrix:	Air	Range:	0.64-2.4 mg/cu m
OSHA Standard:	0.2 ppm (1 mg/cu m)	Precision ($\overline{CV}_T$):	0.068
Procedure:	Adsorption on Tenax GC, desorption with carbon tetrachloride, GC	Validation Date:	11/25/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass tube containing Tenax GC to trap biphenyl vapors.
- 1.2 Biphenyl is desorbed from the Tenax GC with carbon tetrachloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.642-2.35 mg/cu m at an atmospheric temperature of 24.5°C and atmospheric pressure of 760 mm Hg, using a 30-liter sample. This sample size is based on the capacity of the Tenax GC to collect vapors of biphenyl in air at high relative humidity. 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 Tenax GC. This capacity may vary with the concentrations of biphenyl and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 20 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough occurred after 130 minutes at an average sampling rate of 0.532 liter/minute and relative humidity greater than 84% and temperature of 24°C. The breakthrough test was conducted at an average concentration of 2.49 mg/cu m.

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 biphenyl 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 0.642-2.35 mg/cu m was 0.068. This value corresponds to a 0.07 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 On the average, the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 7.3% lower than the "true" concentrations for 18 samples. 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. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.24 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 One disadvantage of the method is that 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 biphenyl found on the backup section of the Tenax GC tube 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 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.

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.
- 6.2 Tenax GC Tubes: Glass tube with both ends unsealed, 6.0-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 35/60 mesh Tenax GC separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 20 mg of Tenax GC, and the

backup section contains 10 mg. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be less than 10 mm of mercury at a flow rate of 0.50 liter per minute. Immediately prior to packing, the empty glass tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. The Tenax GC tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to usage, Tenax GC* is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch to batch differences in production. A quantity of Tenax GC is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Tenax GC is added to the sorbent and mixed, and a vacuum is applied. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C under 25 inches mercury vacuum for four hours.

- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (1.8 m long x 4-mm I.D. glass) packed with 5% OV-17 on 80/100 mesh Chrom W.
- 6.5 An electronic integrator or some other suitable method of determining peak areas.
- 6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

- 7.1 Acetone, reagent grade.
- 7.2 Biphenyl, reagent grade.

* Tenax GC is a solid adsorbent manufactured by Enka N.V. (Holland). It is available through many domestic distributors.

- 7.3 Carbon tetrachloride, reagent grade.
- 7.4 Hexane, reagent grade.
- 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, thoroughly rinsed with tap water and distilled water, and dried.
- 8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative Tenax GC tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tube. All tubes must be packed with Tenax GC from the same manufacturer's lot.
 - 8.3.2 The smaller section of Tenax GC is used as a backup and should be positioned nearer the sampling pump.
 - 8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tube.
 - 8.3.5 A sample size of 30 liters is recommended. Sample at a flow rate of 0.50 liter/minute or less. Do not sample at a flow rate less than 0.01 liter/minute. Record the sampling time, flow rate, and type of sampling pump used.
 - 8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
 - 8.3.7 The Tenax GC tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
 - 8.3.8 With each 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 Tenax GC tubes should be provided for desorption efficiency determinations.

- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the Tenax GC tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Tenax GC tube. Remove the glass wool plug and transfer the first (larger) section of Tenax GC to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Tenax GC to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to effect complete transfer of the Tenax GC.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of CCl_4 is pipetted into each sample container. All work with CCl_4 should be performed in a hood because of its high toxicity. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the biphenyl is desorbed.

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

50 ml/min (60 psig) nitrogen carrier gas flow
50 ml/min (24 psig) hydrogen gas flow to detector
500 ml/min (50 psig) air flow to detector
225°C injector manifold temperature
250°C detector manifold temperature
135°C column temperature

A retention time of approximately 6 minutes is to be expected for biphenyl under these conditions and using the column recommended in Section 6.4. The carbon tetrachloride will elute from the column before the biphenyl.

- 8.4.4 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. Three 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. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Tenax GC.

- 8.4.5 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.

8.5 Determination of Desorption Efficiency

- 8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC 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 Tenax GC.
- 8.5.2 Tenax GC equivalent to the amount in the first section of the sampling tube (20 mg) is measured into a 2-ml glass sample container and capped. This Tenax GC must be from the same batch as that used in obtaining the samples. If extra sampling tubes are available, biphenyl may be spiked onto the front section of the tube and then transferred to a 2-ml glass container. A known amount of a hexane solution of biphenyl containing 9.45 mg/ml is injected directly into the Tenax GC with a microliter syringe, and the sample container is capped. The amount injected is equivalent to that present in a 30-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to ensure complete adsorption of the biphenyl onto the Tenax GC. 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 8.4.

Two or three standards are prepared by injecting the same volume of the biphenyl-hexane solution into 1.0 ml of carbon tetrachloride with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

$$D.E. = \frac{\text{Average Weight recovered (micrograms)}}{\text{Weight added (micrograms)}}$$

The desorption efficiency is dependent on the amount of biphenyl collected on the Tenax GC. Plot the desorption efficiency versus weight of biphenyl found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms/1.0 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 FID response.

- 9.1 Prepare several stock standard solutions of biphenyl in carbon tetrachloride.
- 9.2 From the above stock solutions, appropriate aliquots are withdrawn and dilutions are made in carbon tetrachloride. Prepare at least 5 working standards to cover the range of 3.8-113 micrograms/ml. This range is based on a 30-liter sample.
- 9.3 Prepare a standard calibration curve by plotting concentration of biphenyl in micrograms/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 because the standard curve is based on micrograms/1.0 ml carbon tetrachloride 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.

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

where:

$$\begin{aligned} \text{micrograms sample} &= \text{micrograms found in front section of sample tube} \\ \text{micrograms blank} &= \text{micrograms found in front section of blank tube} \end{aligned}$$

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 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected micrograms/sample.

$$\text{Corrected micrograms/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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
t = sampling time
P₁ = pressure during calibration of sampling pump (mm Hg)
P₂ = pressure of air sampled (mm Hg)
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K)

10.6 The concentration of biphenyl in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected micrograms (Section 10.4)}}{\text{Corrected air volume (liters) (Section 10.5)}}$$

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 (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight of biphenyl
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 Diphenyl, prepared under NIOSH Contract No. 210-76-0123.

Methyl Chloride

Analyte:	Methyl Chloride	Method No.: S99
Matrix:	Air	Range: 59-220 ppm (8-hr. T.W.A.) 143-580 ppm (Peak)
OSHA Standard:	100 ppm (8-hr. T.W.A.) 200 ppm (Ceiling) 300 ppm (Peak)	Precision (CV_T): 0.052
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date: 3/18/77

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through two tubes in series containing activated coconut charcoal to trap the gaseous methyl chloride.
- 1.2 Methyl chloride is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 58.9-222 ppm for the time weighted average (T.W.A.) concentration and over the range of 143.4-582 ppm for the peak concentration. For the T.W.A. concentration, a sample size of 1.5 liters was collected. For the peak concentration, a sample size of 500 ml was collected. Both methods were validated at an atmospheric temperature of 25°C and atmospheric pressure of 760 mm Hg. The sample sizes used are based on the capacity of the charcoal to collect vapors of methyl chloride in air at a relative humidity of greater than 80%. 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 charcoal. This capacity may vary with the concentrations of methyl chloride and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 600 mg of charcoal) reaches 5% of the concentration in the test gas mixture. At a temperature of 22°C and relative humidity of 82%, breakthrough occurred in 135 minutes when a test concentration of 200 ppm was sampled at a flow rate of 0.0235 liter/minute. Breakthrough occurred in 24.4 minutes when a test concentration of 692 ppm at relative humidity of 84% was sampled at a flow rate of 0.105 liter/minute.

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 compound that has the same retention time as methyl chloride 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 (CV_T) for the total analytical and sampling method in the range of 58.9-222 ppm was 0.052. CV_T is based on the data for the T.W.A. concentrations. This value corresponds to a 5.2 ppm standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level for an 8-hour T.W.A. sample were 5.2% higher than the "true" concentrations for 17 samples. At the peak concentrations, the average concentrations obtained were 1% higher than the "true" concentrations for 18 samples. 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 318 ppm indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and uses a solid sorbent. 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 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 methyl chloride found on the backup charcoal tube exceeds 10% of that found in the front sections, the probability of sample loss exists.
- 5.3 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.

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.
- 6.2 Charcoal Tubes: Two charcoal tubes are used in this method. One charcoal tube is used to collect the samples, and a smaller charcoal tube is used as a backup. The charcoal tubes are connected in series with Tygon tubing. The larger charcoal tube is a glass tube, approximately 10-cm long with a 8-mm O.D. and a 6-mm I.D. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal; the back 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 25 mm of mercury at a flow rate of 0.05 liter per minute. The smaller charcoal tube is 7-cm long with a 6-mm O.D. and a 4-mm I.D. The smaller charcoal tube contains 100 mg of charcoal in the front section and 50 mg in the backup section.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 102.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Microliter Syringes: 10-microliter for injection of samples into the gas chromatograph.
- 6.7 Gas Tight Syringes: 0.1, 0.25, 0.50, and 1.0 ml sizes for preparing standards.
- 6.8 Pipets: 3.0-ml delivery pipets.
- 6.9 Serum Bottles: 15-ml glass bottles with 20-mm O.D. mouth.
Septa: 20-mm rubber septa with Teflon lining.
Aluminum tear-away seals to fit serum bottles.
- 6.10 Hand crimper for sealing septa to serum bottles.
- 6.11 Stopwatch.
- 6.12 Manometer.

7. Reagents

- 7.1 Methylene chloride, chromatographic quality, methyl chloride-free.
- 7.2 Methyl chloride, 99.5%.

- 7.3 Nitrogen, purified.
- 7.4 Hydrogen, prepurified.
- 7.5 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 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative charcoal tubes in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.4)

8.3 Collection and Shipping of Samples

- 8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube.
- 8.3.2 Connect the larger charcoal tube in series with the smaller charcoal tube by connecting the backup section of the larger charcoal tube to the front section of the small charcoal tube with flexible vinyl tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearer the pump. Air should flow through the large charcoal tube before entering the small charcoal tube.
- 8.3.3 Both charcoal tubes should be vertical during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.
- 8.3.5 For peak concentration measurement, a sample size of 0.5 liter is recommended. Sample for 5 minutes at a flow rate of 0.10 liter per minute.

For T.W.A. concentration measurement, a sample size of 1.5 liters is recommended. Sample at a flow rate of 0.025 liter per minute.

Record sampling flow rates, collection time, and the type of sampling pump used.

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

- 8.3.7 The charcoal tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the large charcoal tube with the corresponding backup charcoal tube.
- 8.3.8 With each batch of ten samples, submit one set of tubes (a larger charcoal tube and a smaller backup tube) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks. A minimum of 18 charcoal tubes from the same batch of tubes should be provided for desorption efficiency tests during sample analysis.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

Upon receipt of the samples in the laboratory, the samples should be refrigerated if analysis cannot be done immediately.

- 8.4.1 Desorption of Methyl Chloride. Pipet 3.0 ml of methylene chloride into the 15-ml serum bottle. Remove the plastic caps from both ends of the larger charcoal tube. Remove the plug of urethane foam from the outlet end of the tube. Transfer the 200-mg portion of charcoal to the serum bottle. Next, remove the glass wool plug from the inlet end of the tube and transfer the 400-mg section of charcoal to the same bottle. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. It is important that the transfer of the charcoal be carried out as quickly as possible once the methylene chloride has been added to the bottle. The backup charcoal tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.
- 8.4.2 Gently shake the sample. The extract is now ready for analysis. Analyses should be completed within one day after the methyl chloride is desorbed. Prepare standards as in Section 8.5.3. Fresh standards should be prepared daily (throughout the day if possible).
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

40 ml/min (60 psig) nitrogen carrier gas flow rate
65 ml/min (24 psig) hydrogen gas flow rate to detector
500 ml/min (50 psig) air flow rate to detector
200°C injector temperature
260°C detector temperature
100°C column temperature

A retention time of approximately 3.0 minutes is to be expected for the analyte under these conditions and using the column recommended in Section 6.4. The methylene chloride will elute from the column after the methyl chloride.

- 8.4.4 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. Three 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 microliter 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. It is not advisable to use an automatic sample injector for methyl chloride in methylene chloride.
- 8.4.5 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.

8.5 Determination of Desorption Efficiency

- 8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal 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 charcoal.
- 8.5.2 Known amounts of methyl chloride are sorbed from the gas phase on the charcoal in the tubes as described below:

The apparatus to be used for spiking charcoal with known amounts of methyl chloride consists of a union tee connected to a source of purified nitrogen, a charcoal tube, and a septum for introducing methyl chloride from a gas tight syringe. A known amount of methyl chloride is injected slowly through the septum where nitrogen at a flow rate of approximately 30 ml/min carries methyl chloride into the charcoal tube. The nitrogen is allowed to flow through the tube for an

additional 1 minute after discharge of the contents of the syringe through the septum. The charcoal tube is capped with plastic caps.

The amount sorbed is equivalent to that present in an air sample at the selected level and flow rate. This requires 0.075, 0.15, and 0.30 ml of methyl chloride for 0.5X, 1X, and 2X the OSHA T.W.A. and ceiling levels, respectively. The atmospheric temperature, pressure, and relative humidity at which the tubes are prepared should be recorded.

Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of methyl chloride onto the charcoal in the tube. 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.

8.5.3 Desorption and analysis experiments are done on the contents of the larger charcoal tube as described in Section 8.4.1.

In preparation of the standards, 3.0 ml of methylene chloride is added to a 15-ml serum bottle. The bottle is then sealed using a Teflon-lined septum and aluminum seal. An appropriate amount of methyl chloride gas is bubbled slowly into the methylene chloride, by means of a gas tight syringe.

The syringe needle should be immersed in the methylene chloride during discharge of methyl chloride from the syringe. The bottle should be shaken gently after removal of the syringe needle. Standards should be prepared at the same time that the sample analysis is done, and analyzed with the samples.

The weight (mg) of methyl chloride in each standard and sample is calculated by the formula in Section 9.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{Average weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of methyl chloride collected on the charcoal. Plot the desorption efficiency versus weight of methyl chloride found. This curve is used to correct for losses, as described in Section 10.4.

9. Calibration and Standards

A series of standards, varying in concentration over the range of interest, is prepared as described in Section 8.5.3 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.

It is convenient to express concentration of standards in terms of mg/3.0 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The number of mg in the standard is calculated as follows:

$$\text{mg} = V \times \frac{\text{M.W.}}{24.45} \times \frac{298}{T + 273} \times \frac{P}{760}$$

where:

V = ml of methyl chloride used to prepare the standard
 T = temperature (°C) at which the sample was prepared
 P = pressure (mm Hg) at which the sample was prepared
 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
 M.W. = molecular weight of methyl chloride (50.49 g/mole)
 298 = standard temperature (°K)
 760 = standard pressure (mm Hg)

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/3.0 ml methylene chloride 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. It may be necessary to run blanks on several lots of methylene chloride to determine which reagent is not contaminated with methyl chloride.

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

where:

mg sample = mg found in both sections of sample tube
 mg blank = mg found in both sections of blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to get 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 first tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

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
t = sampling time
P₁ = pressure during calibration of sampling pump (mm Hg)
P₂ = pressure of air sampled (mm Hg)
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K)

10.6 The concentration of methyl chloride in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of methyl chloride
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.3 Backup Data Report for Methyl Chloride, prepared under NIOSH Contract No. 210-76-0123.
- 11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Ethyl chloride

Analyte:	Ethyl chloride	Method No.: S105
Matrix:	Air	Range: 1590-6500 mg/cu m
OSHA Standard:	1000 ppm (2600 mg/cu m)	Precision ($\overline{CV}_T$): 0.096
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC/FID	Validation Date: 1/20/78

1. Principle of the Method

- 1.1 A known volume of air is drawn through a large charcoal tube to trap the ethyl chloride gas 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 charcoal in each tube is transferred to a serum vial and sealed with a septum and a laquered aluminum seal. The ethyl chloride is desorbed with carbon disulfide 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. Range and Sensitivity

- 2.1 This method was validated over the range of 1586-6500 mg/cu m at an atmospheric temperature of 24.5°C and atmospheric pressure of 770.8 mm Hg using a 3-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity at the 2S test level determined at 90% relative humidity. This method is capable of measuring much 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 charcoal tube. This capacity varies with the concentrations of ethyl chloride and other substances in the air (see Section 5.2).

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, temperature, 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 method in the range 1586-6500 mg/cu m was 0.0955. This value corresponds to a 248.3 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 concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.4% lower than the "true" concentrations 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, no recovery correction should be applied to the final result.
- 4.3 The data are based on validation experiments using the internal standard method.

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 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. The sample capacity of the charcoal tube is dependent on humidity. When an atmosphere at 90% relative humidity containing 5560 mg/cu m of ethyl chloride was sampled at a flow rate of 0.0576 liter per minute, 5% breakthrough was observed after 74 minutes (capacity = 4.26 liters or 23.69 mg).

To minimize the probability of overloading the sampling tube, the sample size recommended is less than 2/3 the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard level.

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

6. Apparatus

6.1 Sampling Equipment

- 6.1.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate (Reference 11.3).
- 6.1.2 Sampling Tubes. The sampling train consists of two separate charcoal tubes connected in series. The tubes are glass tubes with both ends flame-sealed, 10-cm long with an 8-mm O.D. and a 6-mm I.D. The front tube contains 400 mg of 20/40 mesh activated coconut charcoal; the backup tube, 200 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. 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.

This sampling train can be prepared by modifying commercially available charcoal tubes as follows. For the front tube--break off exit end of a large tube and using pointed tweezers remove the urethane foam plug and the backup charcoal section; push in snugly remaining plug and charcoal to minimize channeling. For the backup tube--similarly break off inlet end of a second large tube and remove retaining plug and the front charcoal section; again push together remaining plug and charcoal. The front tube is connected to the backup tube with a minimal piece of plastic or rubber tubing.

Note that this sampling tube scheme is necessary to minimize probable sample migration effects upon storage.

- 6.1.3 Thermometer.
- 6.1.4 Barometer.
- 6.1.5 Stopwatch.
- 6.2 Gas chromatograph equipped 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 Glass serum vials for desorption, 3-ml, molded to take 13-mm rubber septa and 13-mm aluminum seals.

6.5.1 Rubber septa, 13-mm.

6.5.2 Lacquered aluminum seals or caps, 13-mm.

6.5.3 Hand crimper, 13-mm, or equivalent for properly sealing the vial assembly.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

6.6 Microliter syringes, 500-microliter and other convenient sizes for making internal standard stock solution.

6.7 Gas-tight syringes, 10-ml and other convenient sizes for making standards.

6.8 Syringe, 5.0-ml capacity for adding the carbon disulfide used for desorption.

6.9 Syringe needle, 1.5-inch, 22-gauge or other convenient size.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Carbon disulfide, chromatographic quality.

7.2 Ethyl chloride, 99.7%.

7.3 Nonane or other suitable internal standard. The appropriate solution of the internal standard is prepared in carbon disulfide.

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 Pumps. Each personal pump must be calibrated with a representative sampling train in the line assembled as noted in Section 6.1.2. 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, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube (3-mm). Prepare and assemble as described in Section 6.1.2. Connect the front 400-mg tube to the 200-mg backup tube with a short piece of tubing.
- 8.3.2 The tube containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal sampling train should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the front charcoal tube.
- 8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate of 0.05 liter per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The front charcoal tube should be separated from the backup tube immediately after sampling. Both tubes must be labeled appropriately and capped with the supplied plastic caps.
- 8.3.8 One set of charcoal tubes (a 400-mg tube and a 200-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 batch of 10 samples.
- 8.3.9 Unused, capped charcoal tubes should accompany the samples. These tubes are used in desorption efficiency studies in conjunction with these samples because desorption efficiency varies from one batch of charcoal to another. Record the batch number of the charcoal used.
- 8.3.10 Capped charcoal 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 charcoal tube is scored with a file and broken open. The glass wool is removed and discarded. The charcoal in the front tube is transferred to a 3-ml serum vial and the vial is sealed with the rubber septum and the aluminum cap with the aid of the crimper. The charcoal in the backup tube is transferred to another serum vial and handled in a similar manner.

8.4.2 Desorption of Sample. Immediately before desorption, lift up or remove the removable portion of the aluminum cap to expose a portion of the septum without destroying the seal. Insert a syringe needle through the septum keeping the tip of the needle just below the surface of the septum in the vial. (This needle serves as a vent to prevent pressure buildup in the vial when carbon disulfide is added.) Add 2.0 ml of carbon disulfide or 2.0 ml of internal standard stock solution into the sample-containing vial with the aid of a syringe. After the carbon disulfide addition, remove the needle being used as a vent. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

If an automatic sample injector is used, transfer the sample solution from the desorption vial to the automatic sample injector vial with the aid of a syringe. Seal the sample injector vial with the Teflon-lined septum and screw cap.

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. 190°C manifold temperature (detector)
6. 110°C column temperature

A retention time of approximately 3.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6. The retention time for the internal standard, nonane, is approximately 4.5 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 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 below.

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 charcoal 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 charcoal 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 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 ethyl chloride found in the samples. The desorption efficiency must be determined for each concentration level of ethyl chloride found in the samples analyzed.

The analytical samples are prepared as follows: Activated charcoal (400 mg), from the same lot used in collecting samples, is packed into glass tubes (10 cm x 8 mm O.D. x 6 mm I.D.). If the commercially available charcoal tubes are used, break off both ends and remove the backup sections. These tubes are labeled and weighed. The appropriate volume of ethyl chloride is slowly injected directly onto the charcoal with a gas-tight syringe. These tubes are weighed again, capped immediately, and stored. The weight (mg) of ethyl chloride added is calculated by taking the difference between the two weights.

For the validation studies conducted to determine the precision and accuracy of this method, six tubes at each of three concentration levels (0.5, 1, and 2X the OSHA standard) were prepared by adding an amount of ethyl chloride equivalent to that present in a 3-liter sample at the selected level. This required the addition of 1.5, 3, and 6 ml of ethyl chloride gas into charcoal tubes. The tubes were allowed to stand at least over-

night to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the analytical samples. A parallel blank tube was treated in the same manner except that no sample was added to it. Desorption and analysis experiments were performed on the analytical samples as described in Sections 8.4.2 to 8.4.5.

The desorption efficiency (D.E.) equals the average in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is expected to be dependent on the amount of ethyl chloride collected on the charcoal. Plot the desorption efficiency versus weight of ethyl chloride found. This curve is used in Section 10.4 to correct for adsorption losses. If the desorption efficiency is greater than 95% no correction should be applied.

9. Calibration and Standards

- 9.1 Seal a 3-ml serum vial, using a rubber septum and aluminum cap with the aid of a crimper.
- 9.2 Insert a syringe needle through the septum keeping the tip just below the surface of the septum, in order to provide a vent. With the aid of a syringe, inject 2.0 ml of carbon disulfide (or 2.0 ml of internal standard solution) into the vial. Remove the needle used as a vent.
- 9.3 Immediately before adding the ethyl chloride gas, withdraw an amount of air from the sealed vial equal to the volume of the gas to be added. Label and weigh the vial and record the weight. An appropriate amount of ethyl chloride is bubbled slowly into the carbon disulfide using a gas-tight syringe. The syringe needle should be immersed in the carbon disulfide during discharge of the ethyl chloride from the syringe.
- 9.4 The vial is weighed again and the weight (mg) of the ethyl chloride is calculated by taking the difference between the weight before and after the addition of ethyl chloride gas.
- 9.5 The concentration of standards can be expressed in terms of mg ethyl chloride per 2 ml of carbon disulfide. This unit is convenient because samples are desorbed in 2 ml of carbon disulfide.

- 9.6 A series of standards, varying in concentration over the range of interest, is prepared as described above 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/2 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 40% of the concentration at the OSHA standard. The analyte concentration in mg per 2.0 ml is plotted versus the area ratio of the analyte to that of the internal standard.

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 carbon disulfide 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:

$$\begin{aligned}\text{mg sample} &= \text{mg found in front (400-mg) sample tube} \\ \text{mg blank} &= \text{mg found in front (400-mg) blank tube}\end{aligned}$$

A similar procedure is followed for the backup tube.

- 10.3 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front 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 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (See Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

- 10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{64.52} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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
 64.52 = molecular weight of ethyl chloride
 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. 017-033-0231-2.
- 11.2 Backup Data Report for Ethyl chloride, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Chlorodiphenyl, 42% chlorine

Analyte:	Chlorodiphenyl, 42% chlorine	Method No.: S120
Matrix:	Air	Range: 0.51-2.7 mg/cu m
OSHA Standard:	1 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.092
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date: 12/24/76

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass fiber filter connected in series with a midget bubbler containing 15 ml of iso-octane to collect chlorodiphenyl, 42% chlorine.
- 1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial, and an aliquot of the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.507-2.747 mg/cu m at an atmospheric temperature of 23.5°C and atmospheric pressure of 766 mm Hg, using a 235-liter sample.
- 2.2 The upper limit of the range of the method is dependent on the capacity of the glass fiber filter connected in series to the midget bubbler and the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

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. This is particularly important, because chlorodiphenyl, 42% chlorine, is a mixture.
- 3.2 Chlorodiphenyl, 42% chlorine, gives a characteristic envelope shaped gas chromatographic curve for a number of unresolved peaks. Any other compound that has the same retention time as chlorodiphenyl, 42% chlorine, at the operating conditions described in this method is 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 0.507-2.747 mg/cu m was 0.092. This value corresponds to a standard deviation of 0.09 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 Collected samples are analyzed by means of a quick, instrumental method.
- 5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.
- 5.3 Another disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.4 Chlorodiphenyl, 42% chlorine, is a mixture of isomers. Under the gas chromatographic conditions used for validation an "envelope" of peaks was analyzed. The quantitation of area is difficult unless an integrator is used. It is likely that samples may give slightly different shaped envelopes than standards.
- 5.5 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.
- 5.6 Scintillation vials are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the vials during shipping.

6. Apparatus

- 6.1 Filter unit: The filter unit consists of a 37-mm diameter glass fiber filter (Gelman Type AE or equivalent) and a polystyrene 37-mm two-piece cassette filter holder. The filter is held in the two-piece filter holder, supported by a stainless steel support screen. The filter must be free of organic binders. Filter holders made of Tenite should not be used. Secure the cassette holder together with tape or a shrinkable band.
- 6.2 A glass midget bubbler containing 15 ml of iso-octane.

- 6.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.4 Manometer.
- 6.5 Thermometer.
- 6.6 Scintillation vials: 20 ml, with Teflon cap liners (22-mm) for proper seal. Add 15 ml of distilled water into each vial and mark the liquid level. Pour out the water and dry each vial.
- 6.7 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor Coulson Conductivity Detector or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge. The gas chromatograph must be equipped with a temperature programmer.
- 6.8 Column (1.5 m x 2-mm I.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.9 An electronic integrator or some other suitable method for measuring areas of the envelope of unresolved peaks.
- 6.10 Microliter syringes: 25-microliter for making GC injections.
- 6.11 Volumetric flasks: Convenient sizes for preparing standard solutions.
- 6.12 Pipets: 15-ml pipets for measuring the collection medium, and other convenient sizes for preparing standard solutions.

7. Reagents

- 7.1 Chlorodiphenyl, 42% chlorine.
- 7.2 Iso-octane, nanograde.
- 7.3 Nitrogen, purified.
- 7.4 Hydrogen, prepurified.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.
- 8.2 Calibration of Personal Sampling Pump. Each personal sampling pump

must be calibrated with a representative filter cassette and bubbler 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 cassette holder and close firmly.
- 8.3.2 Pipet 15 ml of iso-octane into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked at least every 15 minutes. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the solution at the end of sampling should be 12 ml or less.
- 8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.
- 8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
- 8.3.5 A sample size of 270 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.
- 8.3.6 Turn the pump on and begin sample collection. 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.
- 8.3.7 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.
- 8.3.8 After sampling remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.
- 8.3.9 Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding the rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

- 8.3.10 The glass fiber filter should be removed from the cassette filter holder and placed in the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vials with appropriate caps with Teflon liners.
- 8.3.11 Carefully record the sample identity, all relevant sampling data, and the type of sampling pump used.
- 8.3.12 With each batch of ten samples submit one filter and bubbler from the same lot of filters and bubblers used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.
- 8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit. These samples must not be sent through the mail. The Department of Transportation Regulations do not permit the shipment of these samples in containers that will prevent breakage and leakage of these samples.

8.4 Analysis of Samples

- 8.4.1 Each sample is analyzed separately. Before injection of the sample into the GC, swirl the contents in the vials to ensure thorough mixing.
- 8.4.2 Appropriate blanks must be analyzed at the same time as the samples.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
- 220°C inlet temperature
 - column temperature program from 120°C-220°C as described below.
 - 150 ml/min nitrogen carrier gas flow
 - 150 ml/min hydrogen gas flow to detector furnace
 - 820°C detector furnace temperature
 - 250°C transfer temperature
 - 250°C vent temperature
- 8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, a solvent flush injection technique should be used. The 25- μ l syringe is first flushed with solvent several times to wet the barrel and plunger. Three 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 1.0 microliter to separate the sol-

vent 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 15-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 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The sample is injected slowly over a time period of 10 seconds. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 30 seconds was adequate to elute the solvent. After 30 seconds, close the vent and begin temperature programming at a rate of 7.5°C per minute. The initial temperature should be 120°C and the final temperature should be 220°C. The final temperature is held for 5 minutes. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

- 8.4.5 Measurement of area. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area. The area of the envelope 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.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample size 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/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

- 9.1 Prepare a stock standard solution by weighing 1 gram of the analyte and add to a 100-ml volumetric flask. Make to volume with acetone and mix thoroughly. Acetone is preferred as a solvent for the stock standard solution, because the analyte dissolves readily in acetone at this concentration.

- 9.2 From the 10 microgram/microliter stock standard, appropriate aliquots are used to prepare at least five working standards to cover the range of 0.030-0.810 mg/15 ml. This range is based on a 270-liter air sample. Prepare all working standards in iso-octane.
- 9.3 Prepare a standard calibration curve by plotting concentration in mg/15 ml versus areas of peak envelopes.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane, 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 sample.

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

where:

$$\text{mg sample} = \text{mg found in sample filter and bubbler}$$

$$\text{mg blank} = \text{mg found in blank filter and bubbler}$$

- 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:

$$f = \text{flow rate sampled}$$

$$t = \text{sampling time}$$

$$P_1 = \text{pressure during calibration of sampling pump (mm Hg)}$$

$$P_2 = \text{pressure of air sampled (mm Hg)}$$

$$T_1 = \text{temperature during calibration of sampling pump (°K)}$$

$$T_2 = \text{temperature of air sampled (°K)}$$

- 10.4 The concentration of chlorodiphenyl, 42% chlorine, in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.2 Backup Data Report for Chlorodiphenyl, 42% chlorine, prepared under NIOSH Contract No. 210-76-0123.

n-Butylamine

Analyte:	n-Butylamine	Method No.:	S138
Matrix:	Air	Range:	8.1 - 35.5 mg/cu m
OSHA Standard:	5 ppm (15 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.092
Procedure:	Adsorption on sulfuric acid-treated silica gel, desorption with 50% methanol, GC/FID		
		Validation Date:	7/8/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a sulfuric acid-treated silica gel tube to trap the organic vapors present. The sampling tube consists of front and backup adsorbing sections.
- 1.2 The treated silica gel in each section is transferred to a vial and the n-butylamine is desorbed with 50% methanol and analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 8.09-35.5 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 769 mm Hg using a 15-liter sample volume. When an atmosphere at 90% relative humidity containing 34.4 mg/cu m of n-butylamine was sampled at 0.8 liter per minute, no breakthrough was observed after 240 minutes (190 liters); the capacity of the acid-treated silica gel is at least 6.5 mg under the conditions of these breakthrough studies.
- 2.2 This method is capable of measuring much smaller amounts of n-butylamine if the desorption efficiency is adequate. Desorption efficiency must be determined over the concentration range of interest.
- 2.3 The upper limit of the range of the method is dependent on the adsorptive capacity of the treated silica gel tube. This capacity can vary with the concentrations of analyte and other substances in the air.

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, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_r$) for the total analytical and sampling method in the range of 8.09-35.5 mg/cu m was 0.0923. This value corresponds to a 1.4 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 concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.6% lower than the "true" concentrations 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, no recovery correction should be applied to the final result.
- 4.3 The data are based on validation experiments using the internal standard method.

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 sorbent tubes 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 effect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated with one tube only.
- 5.3 This method is limited to sampling atmospheres where the relative humidity is less than 60%.

6. Apparatus

6.1 Sampling Equipment

- 6.1.1 Sampling Pump. A calibrated personal sampling pump whose flow can be determined to within $\pm 5\%$ at the recommended flow rate of 1.0 liter per minute.

6.1.2 Sampling Tubes. The sampling tube consists of a glass tube with both ends flame-sealed, 7 cm long with a 6-mm O.D. and 4-mm I.D., containing two sections of 20/40 mesh sulfuric acid-treated silica gel. The front adsorbing section contains 150 mg of treated silica gel, the backup section, 75 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm Hg at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

The sulfuric acid-treated silica gel may be prepared as follows: A known amount of 20/40 mesh silica gel is placed in a drying oven at 125°C for one hour to activate the silica gel. The gel is then cooled to a constant weight, W. Reagent grade concentrated sulfuric acid is added dropwise by means of a disposable pipet to 1.25 W, or 25% by weight acid. A glass stirring rod is used to more evenly distribute the sulfuric acid. The treated silica gel is then returned to the drying oven for one hour with intermittent mixing. The treated silica gel should be stored in an airtight container.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.1.6 Hygrometer or other suitable device for measuring relative humidity.

6.2 Gas chromatograph with a flame ionization detector.

6.3 Column (6 ft x 1/4-in O.D. x 2-mm I.D. glass), packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B.

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

6.5 Sample containers, 2-mL with Teflon-lined caps.

6.6 Microliter syringes, 10- and 500-microliter and other convenient sizes for making standards and for taking sample aliquots for dilution.

6.7 Pipets, 1-mL, delivery type.

6.8 Volumetric flasks, 1- and 10-mL, or convenient sizes for making standard solutions.

7. Reagents

- 7.1 50% methanol (50 parts methanol + 50 parts water).
- 7.2 1.0 N potassium hydroxide.
- 7.3 n-Butylamine, reagent grade.
- 7.4 n-Butyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in 1.0 N potassium hydroxide.
- 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 Pumps. Each personal pump must be calibrated with a representative sampling tube in the line; the tube is described in Section 6.1.2. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples

Note: This method is limited to sampling atmospheres where relative humidity is less than 60%.

- 8.3.1 Immediately before sampling, break the two ends of the treated silica gel tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The section containing 75 mg of treated silica gel is used as a backup and should be positioned nearest the sampling pump.
- 8.3.3 The treated silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the treated silica gel.
- 8.3.5 A sample size of 15 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 15 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.

- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The treated silica gel tube 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 one treated silica gel tube which has been handled in the same manner as the sample tubes (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped, treated silica gel 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 in front of the first section of treated silica gel and broken open. The glass wool is removed and discarded. The treated silica gel in the front 150-mg section is transferred to a 2-mL screw-capped sample container. The separating section of glass wool is removed and discarded. The second 75-mg section is transferred to another container. These two sections are analyzed separately.
- 8.4.2 Desorption of Sample. Prior to analysis, 1 mL of 50% methanol is pipetted into each sample container. Desorption should be done for 2 hours. 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 Neutralization of Sample. Withdraw a 500-microliter aliquot of the supernatant liquid and transfer to another 2-mL vial. Add 500 microliters of 1.0 N potassium hydroxide solution.

Note: If the internal standard method is used, add the internal standard solution made up in 1.0 N potassium hydroxide.

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

- 1. 20 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. 175°C injector temperature
5. 195°C manifold temperature (detector)
6. 90°C column temperature

A retention time of approximately ten 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 22 minutes.

8.4.5 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.

8.4.6 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 described 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 sulfuric acid-treated silica gel 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 treated silica gel used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at the OSHA standard level.

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 n-butylamine found in the samples.

The analytical samples are prepared as follows: 150 mg of acid-treated silica gel is measured into a 2-mL screw-capped vial. This treated silica gel must be from the same batch as that used in obtaining the samples. A known amount of a solution of n-butylamine in water (spiking solution) is injected directly into the treated silica gel by means of a microliter syringe. Adjust the

concentration of the spiking solution such that no more than a 10- μ L 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 n-butylamine equivalent to that present in a 15-liter sample at the selected level. A stock solution containing 55.5 milligrams of n-butylamine per milliliter of water was prepared. Two, four and eight microliter aliquots of the solution were added to the treated silica gel tubes to produce 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 treated silica gel. A parallel blank tube was treated in the same manner except that no sample was added to it.

- 8.5.3 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 mL of 50% methanol. A 500-microliter aliquot is transferred and treated with 500 microliters 1.0 N potassium hydroxide. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare all sample solutions using 500 microliters of 1.0 N potassium hydroxide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in μ g recovered from the tube divided by the weight in μ g added to the tube, or

$$D.E. = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependent on the amount of n-butylamine collected on the treated silica gel. Plot the desorption efficiency versus weight of n-butylamine found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

- 9.1 Solutions of n-butylamine should be prepared over the appropriate concentration range. The spiking solution described in Section 8.5.2 should be used with the same syringe used in the preparation

of the samples. Two, four and eight microliter aliquots are added to 1 mL of 50% methanol in 2-mL vials. A 500-microliter aliquot of each standard solution is transferred to a second 2-mL vial and treated with 500 microliters 1.0 N potassium hydroxide.

- 9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area against sample concentration in $\mu\text{g/mL}$.

For the internal standard method, use 1.0 N potassium hydroxide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 65% of the concentration at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in $\mu\text{g/mL}$.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

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 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:

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front (150 mg) sample section}$$

$$\mu\text{g blank} = \mu\text{g found in front (150 mg) blank section}$$

A similar procedure is followed for the backup (75 mg) section.

- 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 total weight by this desorption efficiency to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight (Front Section)}}{\text{DE}}$$

- 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 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.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.3)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{73.14} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature ($^{\circ}\text{C}$) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

73.14 = molecular weight of n-butylamine

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 Back Data Report for n-Butylamine, No. S138, prepared under NIOSH Contract No. 210-76-0123.

Diisopropylamine

Analyte:	Diisopropylamine	Method No.: S141
Matrix:	Air	Range: 8.5-37.4 mg/cu m
OSHA Standard:	5 ppm (20 mg/cu m)	Precision ($\overline{CV}_T$): 0.075
Procedure:	Collection in 0.1N sulfuric acid impingers, GC/FID	Validation Date: 10/28/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through impingers containing 0.1N sulfuric acid to trap the amine vapors present.
- 1.2 An aliquot of the sample solution is neutralized with 0.3N potassium hydroxide and 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 8.5-37.4 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 766 mm Hg using a 120-liter sample volume.
- 2.2 The upper limit of the range of the method is dependent on the collection efficiency. The method is capable of measuring concentrations higher than that noted in Section 2.1 provided the collection efficiency is adequate. Theoretically, if the efficiency of the impinger remains adequate until 90% of the acid is neutralized, 270 mg of diisopropylamine may be collected. This means that an atmosphere containing as much as 2000 mg/cu m can be reliably measured by this method.

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, temperature, 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 method in the range of 8-37.4 mg/cu was 0.075. This value corresponds to a 1.5 mg/cu 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 A collection efficiency of at least 98% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the impingers was 100.4%. In addition, the samples were found to be stable when stored in the dilute sulfuric acid solution for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 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 A disadvantage of the method is the awkwardness in using midget impingers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 The impingers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the impingers during shipping.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:
 - 6.1.1 A glass standard midget impinger.
 - 6.1.2 A calibrated personal sampling pump suitable for sampling at 1 liter per minute for 120 minutes. The pump must be accurate to within $\pm 5\%$ at the recommended flow rate. The sampling pump is

protected from splashover or water condensation by a second impinger or bubbler positioned between the exit arm of the impinger and the pump.

- 6.1.3 Sulfuric acid, 0.1N. Prepare a sufficient amount for collection and transfer of samples.
 - 6.1.4 Pipet, 15-ml or other suitable device for adding 0.1N sulfuric acid to the impingers.
 - 6.1.5 Thermometer.
 - 6.1.6 Barometer.
 - 6.1.7 Stopwatch.
 - 6.2 Gas chromatograph with a flame ionization detector.
 - 6.3 Column, (6-ft x 1/4-in O.D. x 2-mm I.D. glass) packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B.
 - 6.4 An electronic integrator or some other suitable method for measuring peak areas.
 - 6.5 Sample containers with Teflon-lined caps, 2-ml.
 - 6.6 Microliter syringes, 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots for dilution.
 - 6.7 Volumetric flasks, 25-ml or other convenient sizes for making standard solutions and sample dilutions.
7. Reagents
- 7.1 Diisopropylamine, 99%.
 - 7.2 Distilled water.
 - 7.3 Sulfuric acid, 0.1N in distilled water.
 - 7.4 Potassium hydroxide, 0.3N in distilled water.
 - 7.5 Isoamyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in 0.3N potassium hydroxide.
 - 7.6 Nitrogen, purified.
 - 7.7 Hydrogen, prepurified.
 - 7.8 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 impinger 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 Pipet 15 ml of 0.1N sulfuric acid into the first midget impinger.
 - 8.3.2 Assemble the sampling train. Put the first impinger in a suitable impinger holder. The outlet of this impinger is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable impinger holder which is attached to the pump. Liquid collected in the trap must never be returned to the first impinger.
 - 8.3.3 The air being sampled should not pass through any hose or tubing before entering the first impinger.
 - 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. Set the flow rate as accurately as possible using the manufacturer's directions. Record all the necessary information to determine flow rate or volume 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 After sampling, remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1-2 ml of 0.1N sulfuric acid into the midget impinger flask. Repeat this process for liquid collected in the trap. However, do not combine the two solutions in one impinger bottom. Be sure each impinger bottom is properly labeled. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.

- 8.3.6 Attempt to minimize sample spillage. Do not allow the solution level in the first impinger to fall below 10 ml. Replace spilled solution with fresh 0.1N sulfuric acid. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.
- 8.3.7 With each batch of ten samples submit one midget impinger containing 15 ml of 0.1N sulfuric acid prepared from the same stock as that used for sample collection. This impinger must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this impinger as the blank.
- 8.3.8 The impingers in which the samples are stored should be shipped in a suitable container designed to prevent damage or leakage in transit.

8.4 Analysis of Samples

- 8.4.1 Transfer of Sample. Transfer the contents of the impinger into a 25-ml volumetric flask, using 2-3 ml of 0.1N sulfuric acid to rinse the impinger bottle. Add rinse to the volumetric flask, then dilute to the mark with 0.1N sulfuric acid.
- 8.4.2 Neutralization of Sample. Transfer a 500-microliter aliquot of the acidic sample solution to a 2-ml vial. Add 500 microliters 0.3N potassium hydroxide.

Note: If the internal standard method is used, add the internal standard solution made up in 0.3N potassium hydroxide.

- 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. 200°C injector temperature
 5. 240°C manifold temperature (detector)
 6. 125°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 sixteen 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 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 Analytical Method Sample 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 should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to 25 ml of 0.1N sulfuric acid. The solutions are then neutralized and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm 5\%$.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 120-liter sample at the selected level was used to determine the analytical method recovery. Six volumetrics at each of the three levels (0.5, 1, and 2X the OSHA standard) were spiked with diisopropylamine. A parallel blank was also prepared except that no sample was added to it. All solutions were then neutralized and analyzed as described in Section 8.4.

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

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The average recovery values obtained were at least 97% and as such no recovery correction factor has been used in the determination of the "true" values.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 25 ml 0.1N sulfuric acid because the samples are in this amount of sulfuric acid. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. 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 sample in order to minimize the effect of variations in FID response. A calibration curve is established by plotting concentration in mg per 25 ml versus peak area.

For the internal standard method, use 0.3N potassium hydroxide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg/25 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 25 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:

$$\begin{aligned}\text{mg sample} &= \text{mg found in sample solution} \\ \text{mg blank} &= \text{mg found in blank solution}\end{aligned}$$

10.3 Divide the total weight by the analytical method recovery to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 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

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air samples (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = 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.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Directory, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Diisopropylamine, No. S141, prepared under NIOSH Contract No. 210-76-0123.

2-Aminopyridine

Analyte:	2-Aminopyridine	Method No.: S158
Matrix:	Air	Range: 0.91-3.60 mg/cu m
OSHA Standard:	0.5 ppm (2 mg/cu m)	Precision ($\overline{CV}_T$): 0.061
Procedure:	Adsorption on Tenax GC, thermal desorption, GC	Validation Date: 9/30/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through two glass tubes in series containing Tenax GC to trap 2-aminopyridine vapors.
- 1.2 2-Aminopyridine is thermally desorbed from the Tenax GC, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.913-3.59 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 758 mm Hg, using a 12-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 Tenax GC. This capacity may vary with the concentrations of 2-aminopyridine and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 35 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of 0.184 liter/minute and relative humidity of 84% and temperature of 25°C. The breakthrough test was conducted at a concentration of 4.10 mg/cu m.

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 2-aminopyridine 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 0.913-3.59 mg/cu m was 0.061. This value corresponds to a 0.12 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 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.4% lower than the "true" concentrations for 18 samples. 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 1.56 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 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 2-aminopyridine found on the backup Tenax GC tube exceeds 25% of that found on the front tube, the probability of sample loss exists.
- 5.3 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.

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.
- 6.2 Tenax GC Tubes: Separate front and backup sampling tubes are used in this method. The tubes are constructed of glass tubing with both ends unsealed. The tubes are 13 cm long with a 6-mm O.D. and a 4-mm I.D. The front tube contains 35 mg of 35/60 mesh Tenax GC*, and the

* Tenax GC is a solid adsorbent manufactured by Enka, N.V., The Netherlands. It is available through most gas chromatographic equipment suppliers.

backup tube contains 17 mg. Tenax GC is held in place in the tube with 3-mm plugs of glass wool. The Tenax GC is placed within 4 cm of one end of the tube. The sample tube length may need to be adjusted to accommodate the GC inlet. The pressure drop across the tubes must be less than 10 mm of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Before use, each tube must be thermally desorbed for 3 minutes at 240°C using a nitrogen flow through the tube to rid the Tenax GC of any interfering substances. The front and backup tubes are joined together with a short piece of flexible tubing, and the ends of the sampling train are capped with plastic caps.

- 6.3 Thermal Desorption Apparatus: This apparatus is designed to use the gas chromatograph inlet heater as the source of heat for thermal desorption. The inlet should have an opening of at least 6 mm in diameter and be deep enough to allow the sample tube to be inserted. The apparatus consists of three parts as illustrated in Figures S158-1 and S158-2.

6.3.1 Sample Tube Holder (Figure S158-1A): This assembly is composed of a Swagelok Quick-Connect** stem (stainless steel #QC6-S-600) with a 3/8-in tube fitting on the opposite end. The fitting is drilled out to allow the 6-mm O.D. sample tube to pass through it. A Teflon tube (4 cm long with a 3/8-in O.D. and 5.5 mm I.D.) connects the stem to a 3/8 in to 1/4 in tube fitting reducer. Teflon ferrules are used with the connecting nuts to hold the Teflon tube. The sample tube is inserted through the stem and into the Teflon tube. Tightening the connecting nut to finger tightness secures the sample tube in place. The Teflon tube may have to be replaced after excessive use.

6.3.2 Gas Chromatograph Inlet Fitting (Figure S158-1B): This assembly consists of a Swagelok Quick-Connect** body (stainless steel #QC6-B-4PF) which has been rethreaded to fit onto the gas chromatograph injection port. The ball and spring in the body must be removed to allow the sample tube to pass through. This fitting replaces the septum nut. Other injector parts that interfere with insertion of the sample tube must be removed.

The inlet fitting is sealed to the injection port with a Teflon gasket.

6.3.3 Valves and Carrier Gas Lines (Figure S158-2): The flow of carrier gas is regulated by a system incorporating two needle valves and two 3-way valves. The carrier gas is split into two lines regulated by needle valves. When a sample tube is being thermally desorbed, the majority of carrier gas flows

**Patented by Crawford Fitting Company.

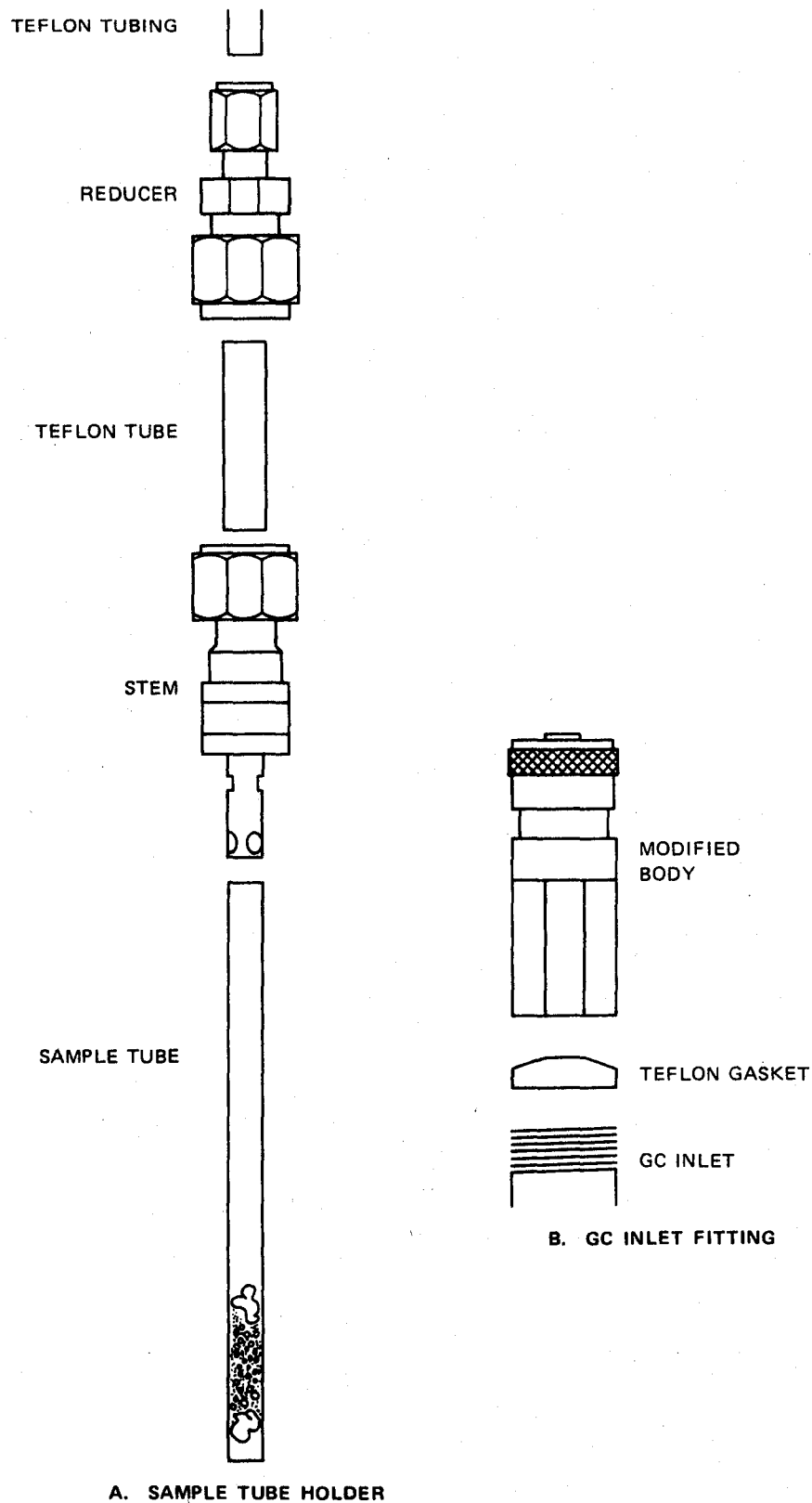


FIGURE S158-1

S158-4

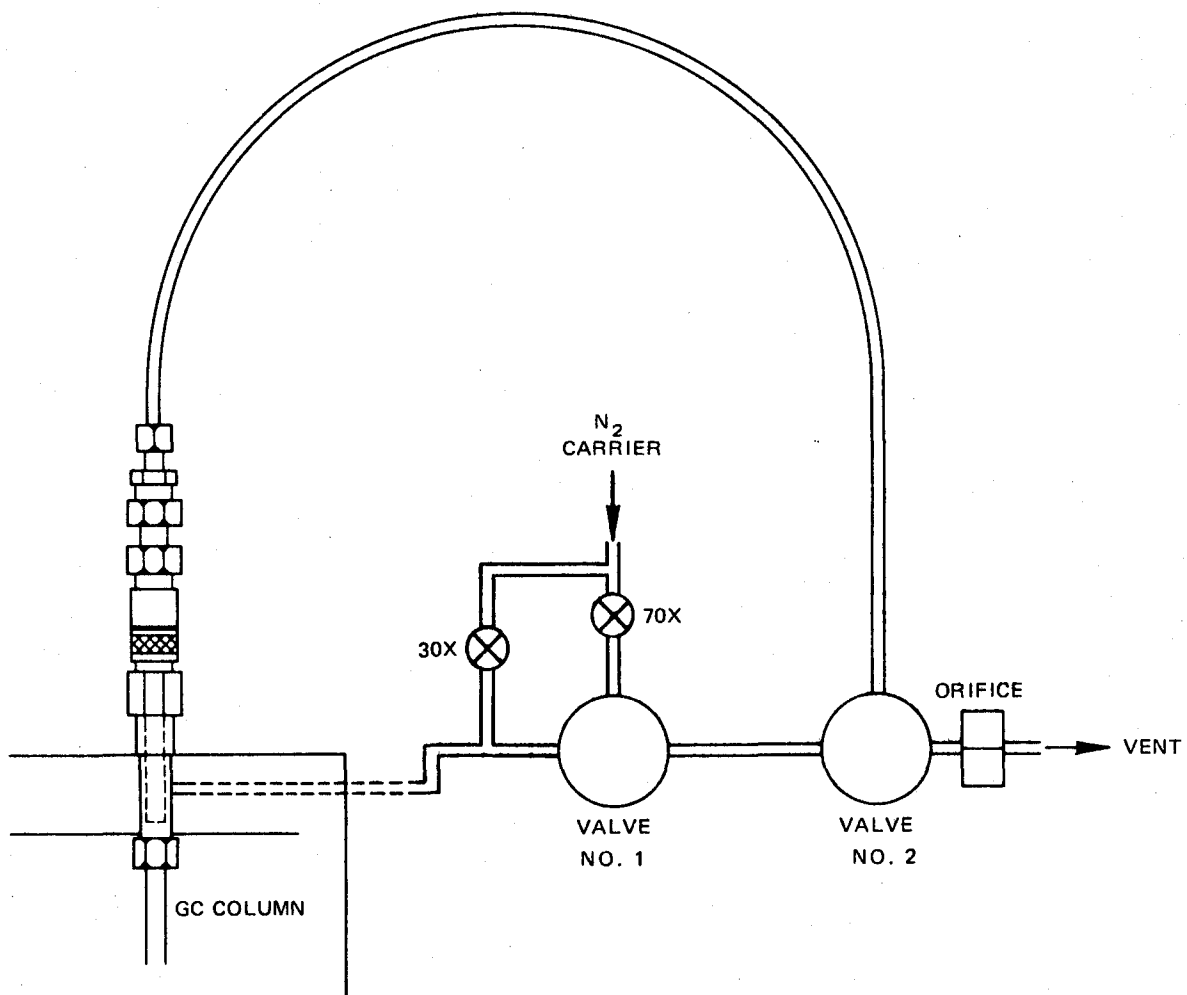


FIGURE S158-2 VALVES AND CARRIER GAS LINES

through the sample tube. A minor flow enters at the normal GC inlet port to allow additional carrier gas to flow over the sample tube. Three-way valve #1 is used to split the carrier flow as described above or route the entire flow to the inlet port for normal use of the GC or injection of standards. Three-way valve #2 is used to vent the carrier flow when the sample tube holder is being loaded with a sample tube. It is also used to relieve pressure before disconnecting the desorber from the inlet after a sample is analyzed. A 0.02-in flow limiting orifice is placed at the valve #2 vent so that pressure is relieved slowly. Sudden changes in pressure may disrupt the gas chromatographic column packing or the sorbent in the sample tube. The thermal desorption assembly is connected to valve #2 with a 1/4-in O.D. Teflon tubing.

- 6.4 Gas Chromatograph equipped with a flame ionization detector.
- 6.5 Column (5-ft long x 1/4-in O.D. glass) packed with Carbowax B coated with 4% Carbowax 20M and 0.8% KOH.
- 6.6 An electronic integrator or some other suitable method of determining peak areas.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

All reagents used must be ACS reagent grade or better.

- 7.1 2-Aminopyridine, reagent grade.
- 7.2 Nitrogen, purified.
- 7.3 Hydrogen, prepurified.
- 7.4 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 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative Tenax GC tubes in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tubes. All tubes must be packed with Tenax GC from the same manufacturer's lot.

8.3.2 The tube containing the smaller amount of Tenax GC is used as a backup tube and should be positioned nearer the sampling pump. Air should flow through the front tube before entering the backup tube.

8.3.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tubes.

8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record sampling time, flow rate, and type of sampling pump used.

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

8.3.7 The Tenax GC tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Tenax GC tube with its corresponding backup tube.

8.3.8 With each batch of 10 samples, submit one set of tubes (a front adsorbing tube containing 35 mg of Tenax GC and a backup tube containing 17 mg of Tenax GC) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

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

8.3.10 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 Tenax GC tubes. A minimum of 18 extra Tenax GC front and backup tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the caps from the ends of the sample tube. Wipe off the outside of the tube with a clean lab wiper.

8.4.2 Thermal Desorption of Samples

1. Place auxillary valves in position so that the carrier gas is split between the sample tube holder and the inlet (valve #1 dividing flow) and so that flow to the sample tube holder is vented (valve #2 open to vent).
2. Load the sample tube holder by inserting the sample tube through the stem and just into the Teflon tube with the connecting nut loose. Tighten the connecting nut to finger tightness to secure the sample tube in place. The sorbent material should be at the end opposite the connecting nut.
3. Insert the sample tube into the gas chromatograph inlet, joining the stem of the sample tube holder to the body of the gas chromatograph inlet fitting.
4. Turn the carrier gas valve #1 to allow the carrier gas to pass through the sample tube.
5. Allow the sample to thermally desorb for 3 minutes at an inlet temperature of 240°C onto the head of the GC column which is set at 125°C.
6. Program the column oven temperature from 125°C to 225°C at a rate of 25°C/minute.

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

1. Thermal desorption mode - 60 ml/min nitrogen carrier gas flow through sample tube holder; 20 ml/min nitrogen carrier gas flow to inlet.
2. Standards injection mode - 80 ml/min nitrogen carrier gas flow to inlet.
3. Both modes - 50 ml/min hydrogen gas flow to detector; 500 ml/min (50 psig) air flow to detector.

- 8.4.4 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.

8.5 Determination of Desorption Efficiency

- 8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC 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 Tenax GC.
- 8.5.2 Tenax GC sample tubes containing 35 mg of Tenax GC from the same batch as that used in obtaining the samples are used to determine the desorption efficiency. A known amount of a water solution of 2-aminopyridine is injected directly onto the Tenax GC with a microliter syringe, and the tube is capped. The amount injected is equivalent to that present in a 12-liter air sample at the selected level. The solutions of 2-aminopyridine in water are prepared so that the amount injected is no more than 2.0 microliters. This is to minimize the effects of excess solvent on the GC column.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared and allowed to stand for at least overnight to assure complete adsorption of the 2-aminopyridine onto the Tenax GC. 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 thermally desorbed and analyzed in exactly the same manner as the sampling tubes described in Section 8.4.

To inject standards into the GC, the normal septum injection port is installed and all of the carrier gas is allowed to flow through the normal inlet position (valve #1 combining flow). The same volume of 2-aminopyridine is injected directly into the GC injection port with the same syringe used in preparation of the samples.

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. One microliter of solvent is 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 2-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 1.9-2.0 microliters in the barrel of the syringe. No more than a 3% difference in area is to be expected between duplicate injections.

Standards are injected into the GC with column oven temperature set at 125°C.

Immediately after injection, the oven temperature is programmed to 225°C at a rate of 25°C/minute. Standards are analyzed before and after a set of samples is analyzed.

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

$$\text{D.E.} = \frac{\text{Average Weight recovered } (\mu\text{g})}{\text{Weight added } (\mu\text{g})}$$

The desorption efficiency is dependent on the amount of 2-aminopyridine collected on the Tenax GC. Plot the desorption efficiency versus weight of 2-aminopyridine found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms versus peak area. 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 FID response.

- 9.1 Prepare a stock standard solution containing 345 mg/ml of 2-aminopyridine in water.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in water. Prepare at least 5 working standards to cover the range of 2.3-70 micrograms/sample. This range is based on a 12-liter sample and 2-microliter injections.
- 9.3 Prepare a standard calibration curve by plotting micrograms 2-aminopyridine versus peak area.

10. Calculations

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

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample} = \mu\text{g found in front sample tube}$

$\mu\text{g blank} = \mu\text{g found in front blank tube}$

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 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total weight}}{\text{DE}}$$

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

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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

10.6 The concentration of 2-aminopyridine in the air sampled can be expressed in mg/cu m .

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10. / 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 (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of 2-aminopyridine = 94.1
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. 017-03-00231-2.
- 11.2 Backup Data Report for 2-Aminopyridine, prepared under NIOSH Contract No. 210-76-0123.

Acetic Acid

Analyte:	Acetic Acid	Method No.: S169
Matrix:	Air	Range: 12.5-50 mg/cu m
OSHA Standard:	10 ppm (25 mg/cu m)	Precision ($\overline{CV}_T$): 0.058
Procedure:	Adsorption on charcoal, desorption with formic acid, GC	Validation Date: 5/13/77

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a tube containing activated coconut charcoal to trap acetic acid vapors.
- 1.2 Acetic acid is desorbed from the charcoal with formic acid, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 12.5-50 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 767 mm Hg, using a 173-liter sample. This sample size is based on the capacity of the charcoal to collect vapors of acetic acid in air. 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 charcoal. This capacity may vary with the concentrations of acetic acid and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test gas mixture. In a breakthrough test, which was discontinued after 4.6 hours, the charcoal tube collected 10.4 mg of acetic acid without breakthrough for a 269-liter air sample with a relative humidity of 90% and a temperature of 23°C. This is equivalent to approximately 2.5 times the OSHA standard for this sample size. It is likely that breakthrough would not occur with even larger amounts of acetic acid.

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 acetic acid 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 12.5-50 mg/cu m was 0.058. This value corresponds to a 1.5 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard were 5.4% higher than the concentrations calculated for the reference method which was based on syringe-drive introduction of the acetic acid into the sample generator. Any difference between the found concentration and the reference concentration (sometimes called the "true" concentration) may not represent a bias in the sampling and analytical method, but rather an uncertainty in the reference concentration. It was therefore assumed that there is no bias in the sampling and analytical method and that no correction for bias is needed. 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 25 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 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 acetic acid found on the backup section of the charcoal tube 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 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 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 two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. 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 must be less than 25 mm of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (1-m long x 4-mm I.D. glass) packed with 60/80 mesh Carbowax B/3% Carbowax 20M/0.5% H₃PO₄.
- 6.5 An electronic integrator or some other suitable method of determining peak areas.
- 6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon caps.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

- 7.1 Formic acid, 88%.
- 7.2 Glacial acetic acid, reagent grade.
- 7.3 Nitrogen, purified.
- 7.4 Hydrogen, prepurified.
- 7.5 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 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative charcoal tube in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.

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

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A sample size of 168 liters is recommended. Sample at a flow rate of 1.0 liter per minute or less. Record the sampling time, flow rate, and type of sampling pump used.

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

8.3.7 The charcoal tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 With each 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 charcoal tubes should be shipped for desorption efficiency determinations.

8.3.9 Capped 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 charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) sec-

tion is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another sample container vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of formic acid is pipetted into each sample container. Desorption should be done for 60 minutes. Tests indicated 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. Care should be taken to avoid contacting formic acid and/or acetic acid with the skin. These reagents may cause severe burns.

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

60 ml/min (60 psig) nitrogen carrier gas flow
50 ml/min (24 psig) hydrogen gas flow to detector
500 ml/min (50 psig) air flow to detector
230°C injector temperature
230°C detector manifold temperature
column temperature, program from 130-180°C as described below.

A retention time of approximately 3-4 minutes is to be expected for acetic acid under these conditions and using the column recommended in Section 6.4.

8.4.4 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. Three 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. Begin temperature programming at a rate of 10°C per minute. The initial temperature should be 130°C and the final temperature should be 180°C. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

- 8.4.5 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.

8.5 Determination of Desorption Efficiency

- 8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal 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 charcoal.
- 8.5.2 Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of acetic acid is injected directly into the activated charcoal with a micro-liter syringe, and the tube is capped with more Parafilm. The density of acetic acid is 1.049 g/ml at 20°C. The amount injected is equivalent to that present in a 168-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the acetic acid onto the charcoal. 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 8.4.

Two or three standards are prepared by injecting the same volume of acetic acid into 1.0 ml of formic acid with the same syringe used in the preparation of the samples. These are analyzed with the samples. These standards are used to confirm the calibration of the gas chromatograph.

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

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of acetic acid collected on the charcoal. Plot the desorption efficiency versus weight of acetic acid found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 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 FID response.

- 9.1 Prepare a stock standard solution containing 42 mg/ml acetic acid in formic acid.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in formic acid. Prepare at least 5 working standards to cover the range of 0.42-12.6 mg/1.0 ml. This range is based on a 168-liter sample.
- 9.3 Prepare a standard calibration curve by plotting concentration of acetic acid in mg/1.0 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 because the standard curve is based on mg/1.0 ml formic acid 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:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

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 weight of the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

- 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
- t = sampling time
- P₁ = pressure during calibration of sampling pump (mm Hg)
- P₂ = pressure of air sampled (mm Hg)
- T₁ = temperature during calibration of sampling pump (°K)
- T₂ = temperature of air sampled (°K)

- 10.6 The concentration of acetic acid in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

11. References

- 11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.3 Backup Data Report for Acetic Acid, prepared under NIOSH Contract No. 210-76-0123.

Quinone

Analyte:	Quinone	Method No:	S181
Matrix	Air	Range:	0.17-0.75 mg/cu m
OSHA Standard:	0.4 mg/cu m	Precision: ($\overline{CV}_T$):	0.085
Procedure:	Adsorption on XAD-2, desorption with ethanol/hexane, analysis by HPLC	Validation Date:	9/30/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a tube containing XAD-2 resin to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.
- 1.2 The XAD-2 in each tube is transferred to a vial and the quinone is desorbed with a solution of 20% ethanol in hexane and analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.17-0.75 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 767 mm Hg using a 24-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at 81% relative humidity when sampling a test atmosphere at 2 times the OSHA standard. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The detection limit of this method is estimated to be at most 0.4 nanograms of quinone based on an injection volume of 20 μ l.

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 solve the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.17-0.75 mg/cu m was 0.0847. This value corresponds to a 0.0339 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 concentrations "found" at the OSHA standard level using the overall sampling and analytical method were 1.1% higher than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.2). Any difference between the two concentrations does not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

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 All samples must be analyzed within one hour of desorption and interspersed among standard solutions prepared within an hour. This limits the number of samples which can be analyzed at once, but is necessary since the solutions are unstable and may not give reliable results after an hour.
- 5.3 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of micrograms that the tube will hold before overloading. When an atmosphere at 81% relative humidity containing 0.794 mg/cu m of quinone was sampled at 0.2 liter per minute, 1.6% breakthrough was observed after 240 minutes (capacity is at least 45 liters or 37 μ g). The sample size recommended is less than the 5% breakthrough capacity at 81% R.H. for a test atmosphere at 2 times the OSHA standard to minimize the probability of overloading the sampling tube.
- 5.4 When the sample value obtained for the backup section of the sorbent tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

- 5.5 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.

6. Apparatus

6.1 Sampling Apparatus

- 6.1.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3).
- 6.1.2 Sampling Tube. Glass tube with both ends flame-sealed, 10-cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.
- 6.1.3 Barometer.
- 6.1.4 Thermometer.
- 6.1.5 Stopwatch.
- 6.2 High pressure liquid chromatograph. The unit must be capable of UV detection at 240 nm.
- 6.3 Column, 25-cm x 4.6-mm I.D. x 1/4" stainless steel Partisiltm PXS 10/25 ODS or equivalent.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Twelve-milliliter screw cap vials with Teflon-lined caps.
- 6.6 Microliter syringes, 10, 25, 50, 100 and 250-microliter and other convenient sizes for preparing standards.
- 6.7 Pipet, 5-ml, delivery type.
- 6.8 Volumetric flasks, 25-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Ethanol, absolute.
- 7.2 Hexane, chromatographic quality, distilled in glass.
- 7.3 Quinone, reagent grade.
- 7.4 Twenty percent ethanol in hexane. Prepare by diluting 200 ml of absolute ethanol to 1000 ml with hexane. This solvent is used for making standard solutions and as a desorption solvent. It is also the mobile phase for the HPLC analysis and is degassed for such use.
- 7.5 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Larger batches may be prepared by using a large size Soxhlet extractor. Overnight (24 hours) extractions are then performed successively with water, methanol, diethylether and n-pentane. Finally, several washings with 20% ethanol in hexane are recommended to reduce possible interferences to a minimum when the sorbent is desorbed with this solvent. Distilled-in-glass solvents are used in all cases. 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 process using nitrogen gas at room temperature from a liquid nitrogen cylinder. The drying process is terminated when no organics are detected experimentally 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 organics should be less than 1000 ppm in concentration.

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 series 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, break the two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (2-mm).
 - 8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump.

- 8.3.3 The resin tube series should be placed in a vertical direction during sampling to minimize channeling through the resin.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the resin tube.
- 8.3.5 A sample size of 24 liters is recommended. Sample at a known flow rate between 0.2 and 0.01 liter per minute for 120 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 Record the ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 The resin tube 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 10 samples, submit one resin tube which has been handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped resin tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 Arrange to have samples analyzed within seven days.
- 8.3.11 Minimize exposure to light and refrigerate samples.
- 8.4 Analysis of Samples
- 8.4.1 Preparation of Samples. In preparation for analysis, each resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the front 100-mg section is transferred to a 12-ml vial. The separating section of glass wool is removed and discarded. The second 50-mg section is transferred to another vial. These two sections are analyzed separately.
- 8.4.2 Desorption of Sample. Prior to analysis 5.0 ml of 20% ethanol in hexane is pipetted into each 12-ml vial. The vial is capped immediately after solvent addition and then agitated. Since all samples must be analyzed within an hour of desorption it is extremely important to desorb only as many samples as can be analyzed within that period of time. The number of standards to be analyzed simultaneously must be taken into account as well. All samples may be analyzed as soon as desorbed. Tests have shown this is

a sufficient time for desorption provided the samples are shaken after solvent addition.

8.4.3 HPLC Conditions. The mobile phase is 20% ethanol in hexane. Typical operating conditions for the chromatograph are:

1. 2 ml/min solvent flow
2. Ambient column temperature
3. 200-300 psi system pressure
4. 240 nm UV detection wavelength

A retention time of approximately 2.2 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3.

8.4.4 A 20-microliter aliquot of the sample solution is injected into the liquid chromatograph. The sample may be injected directly by syringe or fixed volume sample loop provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected. Desorption is done in a 5-ml sample volume to provide an adequate volume for rinsing the syringe between injections of different solutions.

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 the results are read from a standard curve prepared as discussed in Section 9. Peak heights were found to be an unacceptable method of response measurement.

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 XAD-2 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 resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at a sample loading equivalent to the OSHA standard level.

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 quinone found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of quinone found in the samples analyzed.

The analytical samples are prepared as follows: XAD-2, equivalent to the amount in the front section (100 mg), is measured into a 12-ml vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of quinone in 20% ethanol in hexane (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- μ l aliquot is used to prepare the analytical samples.

Note: An ultrasonic cleaner may be needed to break up large particles of quinone.

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 2 times the OSHA standard) were prepared by adding an amount of quinone equivalent to that present in a 24-liter sample at the selected level. A stock solution containing 4.95 milligrams of quinone per milliliter of 20% ethanol in hexane was prepared. One, 2 and 4-microliter aliquots of the solution were added to the XAD-2 resin tubes to produce samples equivalent to 24-liter collections at 0.5, 1 and 2 times the OSHA standard level. The analytical samples were allowed to stand at least overnight to assure complete adsorption of the analyte onto the resin. 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 the desorption efficiency over the concentration range of interest.

- 8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5. Calibration standards are prepared by adding the appropriate volume of spiking solution to 5.0 ml of 20% ethanol in hexane with the same syringe used in the preparation of the samples. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in μ g recovered from the tube divided by the weight in μ g added to the tube or

$$\text{D.E.} = \frac{\text{Average Weight } (\mu\text{g}) \text{ Recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ Added}}$$

The desorption efficiency may be dependent on the amount of quinone collected on the resin. Plot the desorption efficiency versus weight of quinone found. This curve is

used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

- 9.1 Add 5.0 ml of 20% ethanol in hexane to a 12-ml vial. Add aliquots of the same solution as described in Section 8.5.2 to prepare calibration standards or alternatively aliquots of the same solution could be diluted to the appropriate volume. The concentration of standards can be expressed in terms of μg of quinone per 5 ml of 20% ethanol in hexane.
- 9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in $\mu\text{g}/5\text{ ml}$.

It has been determined that solutions of quinone in 20% ethanol in hexane are unstable. To insure reliable results it is imperative that all solutions be analyzed within an hour of desorption or preparation. In addition, to minimize the effect of variation in detector response, standard solutions should be analyzed at the same time as sample solutions.

10. Calculations

- 10.1 Read the weight in units of μg of quinone corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on μg per 5.0 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

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front (100-mg) sample section}$$

$$\mu\text{g blank} = \mu\text{g found in front (100-mg) blank section}$$

A similar procedure is followed for the backup (50-mg) section.

- 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 total weight by this desorption efficiency to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

- 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 = 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 ($^{\circ}\text{K}$)

T_2 = ambient temperature of air sampled ($^{\circ}\text{K}$)

- 10.6 The concentration of quinone in the air sampled can be expressed in mg per cu m which is numerically equal to μg per liter

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.4)}}{\text{Sampling Volume (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{108.1} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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
108.1 = molecular weight of quinone
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Quinone, No. S181, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Mercury

Analyte:	Mercury	Method No.:	S199
Matrix:	Air	Range:	0.046-0.18 mg/cu m
OSHA Standard:	0.1 mg/cu m - Ceiling	Precision ($\overline{CV}_T$):	0.061
Procedure:	Adsorption on silvered Chromosorb P, thermal desorption, flameless AA	Validation Date:	7/8/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass tube containing silvered Chromosorb P (AgCP) to trap mercury vapors. A cellulose ester membrane filter is connected to the front of the sorbent tube to collect particulate mercury interference.
- 1.2 The sample is analyzed by thermally desorbing the mercury and passing it through the absorption cell of a flameless atomic absorption spectrophotometer.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.0456-0.1800 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 760 mm Hg, using a 3-L sample. The method is capable of measuring smaller amounts. A longer AA absorption cell path length may be needed for levels below 0.01 mg/cu m. The range of the absorption cell must be determined by calibration.
- 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. The detector may be saturated at amounts of mercury greater than those in the acceptable range for the absorption cell. 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 AgCP 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 30 mg of AgCP) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of

0.184 liter/minute and relative humidity of 85% and temperature of 25°C. The breakthrough test was conducted at a concentration of 0.244 mg/cu m.

3. Interferences

- 3.1 Loading the prefilter with excess particulate will increase air flow resistance through the sampler. This may overload the battery-operated sampling pumps.
- 3.2 It has been reported that AgCP absorbs methyl mercury chloride. Most other organomercury compounds are not retained.
- 3.3 Strong oxidizing vapors and gases, particularly chlorine, which attack silver, reduce the efficiency of the sampling tube, but do not interfere in the analysis of the sample. These interferences should not be a problem under normal sampling conditions.
- 3.4 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 0.0456-0.1800 mg/cu m was 0.061. This value corresponds to a 0.0006 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 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.7% higher than the "true" concentrations for 17 samples. 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 0.0927 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 A disadvantage of the method is that the range is limited by the path length of the AA absorption cell(s) used in the analytical system.

- 5.3 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.
- 5.4 A disadvantage of the method is the care needed to avoid contamination of the outer surfaces of the sampling tubes.
- 5.5 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 AA 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.
- 6.2 Silvered Chromosorb P (AgCP) Tubes: These tubes are available on special order from SKC, Inc.* If sampling tubes are to be prepared, the preparation of AgCP is described in Section 8.2. 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 30 mg of AgCP. A plug of glass wool, preferably quartz glass wool, is placed at the ends 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.
- 6.3 Prefilter unit: The sample tube is preceded by a 0.8-micrometer/37-mm cellulose ester membrane filter to collect particulate mercury. The filter is placed in a cassette filter holder, and the filter is supported by a cellulose backup pad.
- 6.4 Thermal Desorption Unit and Analysis System: A detailed description of the apparatus and instructions for installation and operation are given in Appendix A.
- 6.5 Flameless atomic absorption mercury analyzer with recorder set at 253.7 nm; Coleman Mercury Analysis System (MAS-50) or equivalent atomic absorption spectrophotometer.
- 6.6 Absorption Cell: 4.0 cm length (3.7 cm inside diameter), made of Pyrex glass with quartz windows. Satisfactory results may be obtained with different path length cells. The system used must be calibrated over the expected concentration range.
- 6.7 Microliter Syringes: 10-microliter for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-mL and other convenient sizes.

* SKC, Inc., Rd. 1 #395 Valley View Rd., Eighty Four, PA 15330

6.9 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.

6.10 Thermometer.

6.11 Manometer.

6.12 Stopwatch.

7. Reagents

All reagents 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 The following reagents are used in the preparation of AgCP:

7.4.1 Chromosorb P, non-acid washed, 30/60 mesh. Chromosorb P is a diatomaceous earth material primarily used as a gas chromatographic support. It is manufactured by Johns-Manville and is available from most gas chromatography equipment suppliers.

7.4.2 Silver nitrate.

7.4.3 Ammonium hydroxide.

7.4.4 Potassium hydroxide.

7.4.5 Dextrose.

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 Preparation of Silvered Chromosorb P (AgCP):

Caution: Use face shield and rubber gloves.

8.2.1 Dissolve 20 g silver nitrate in 300 mL of distilled water (Solution A) in a 1000-mL beaker.

8.2.2 Place a magnetic stirring bar in the solution and stir on a magnetic stirrer.

8.2.3 Slowly add concentrated ammonium hydroxide until a dark brown precipitate of silver oxide forms.

8.2.4 While stirring, add concentrated ammonium hydroxide dropwise until the solution just clears. Disregard any small specks which may form.

- 8.2.5 Take another 2 g of silver nitrate and dissolve in 30 mL distilled water in a separatory funnel (Solution B). Add this solution dropwise to the mixture in the 1000 mL beaker (Section 8.2.4) until the solution turns straw yellow.
- 8.2.6 Slowly add 100 mL of potassium hydroxide solution (14 g KOH in 100 mL of water) while constantly stirring.
- 8.2.7 Add concentrated ammonium hydroxide dropwise until the solution in the 1000-mL beaker just clears.
- 8.2.8 Add more Solution B until a thin straw yellow or light brown precipitate forms. Again disregard any small specks.
- 8.2.9 Remove the 1000-mL beaker from the stirrer and filter the solution (Solution C) through glass wool.
- 8.2.10 Dissolve 7.8 g dextrose in 120 mL of distilled water in a 1000-mL Erlenmeyer flask and add 40 g of Chromosorb P to the dextrose solution.
- 8.2.11 Swirl the Chromosorb P in the dextrose solution until the surfaces are wet and then carefully decant any excess dextrose solution.
- 8.2.12 Slowly add the silver solution (Solution C - Section 8.2.9) to the Chromosorb P, stopper the flask, and shake vigorously until all the surfaces come in contact with the silver solution.
- 8.2.13 Decant and discard the excess silver solution.
- 8.2.14 Rinse and decant the silvered Chromosorb P (AgCP) three times with distilled water.
- 8.2.15 Dry the AgCP in a drying oven at 60°C. Note: Dry in an atmosphere free of sulfides.
- 8.3 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative AgCP tube and prefilter in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.4 Collection and Shipping of Samples
 - 8.4.1 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.
 - 8.4.2 The sample tube is preceded by a 0.8-micrometer/37-mm cellulose ester membrane filter to collect particulate mercury. The filter is placed in a cassette filter holder, and the filter is supported by a cellulose backup pad. The prefilter is

connected to the sample tube with a short piece of flexible tubing.

- 8.4.3 The sample tube should be placed nearer the sampling pump and in a vertical position during sampling to avoid channeling through the the AgCP.
- 8.4.4 Air being sampled should not be passed through any hose or tubing before entering the filter holder. A minimum amount of flexible tubing should be used to connect the filter holder to the sample tube.
- 8.4.5 A sample size of 3 L is recommended. 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. Record sampling time, flow rate, and type of sampling pump used.
- 8.4.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.4.7 After sampling, disconnect the filter cassette from the sampling tube. Return the AgCP tube to the glass vial. Insert cotton into the vial to prevent breakage of the tube during shipping. Gloves or wipers should be used when handling the sample tube. The prefilter should be discarded after sampling, and the filter cassette holder should be cleaned for future use.
- 8.4.8 With each 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.
- 8.4.9 Vials containing the sample tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.4.10 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 AgCP sample tubes.

8.5 Analysis of Samples

- 8.5.1 Preparation of Analysis System. Turn on the atomic absorption spectrophotometer and allow the instrument to stabilize. Turn on the heating tape and the vacuum pump. Observe the rotameter to insure that the flow through the critical orifice has not been interrupted. It should be at approximately 1.0 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 1 minute before analyzing samples.

Note: The thermal desorption system must be optimized so that 100% of the mercury is desorbed from the AgCP tube in one heating (Appendix A).

8.5.2 Preparation of Samples. Remove the clamp between the loading mechanism and desorption unit and insert the AgCP sample tube. Push the sample tube into the first desorption section using the plunger of the loading mechanism and replace the clamp.

8.5.3 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 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.

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 AgCP sample tubes are reusable.

8.5.4 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 Standards

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.

- 9.1 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.
- 9.2 Standard Working Solution A: 0.1 mg/mL, prepared by diluting 1.00 mL of stock solution to 10 mL with 1% nitric acid.
- 9.3 Standard Working Solution B: 0.03 mg/mL, prepared by diluting 3.00 mL of stock solution to 100 mL with 1% nitric acid.
- 9.4 Aliquots of 1 to 10 microliters are withdrawn from the working standards by microliter syringe and injected directly onto the AgCP in the sample tube. Prepare at least 5 working standards to cover the range of 0.03-0.09 microgram mercury. This range is based on a 3-L sample. No more than 10 microliters of the standard should be injected on the AgCP because of the small volume of sorbent. The standards are immediately desorbed and analyzed.
- 9.5 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.

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

where:

$$\begin{aligned} \text{micrograms sample} &= \text{micrograms found in sample tube} \\ \text{micrograms blank} &= \text{micrograms found in blank tube} \end{aligned}$$

- 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:

$$\begin{aligned} f &= \text{flow rate sampled} \\ t &= \text{sampling time} \\ P_1 &= \text{pressure during calibration of sampling pump (mm Hg)} \end{aligned}$$

- P_2 = pressure of air sampled (mm Hg)
 T_1 = temperature during calibration of sampling pump ($^{\circ}$ K)
 T_2 = temperature of air sampled ($^{\circ}$ K)

10.4 The concentration of mercury in the air sampled 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 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

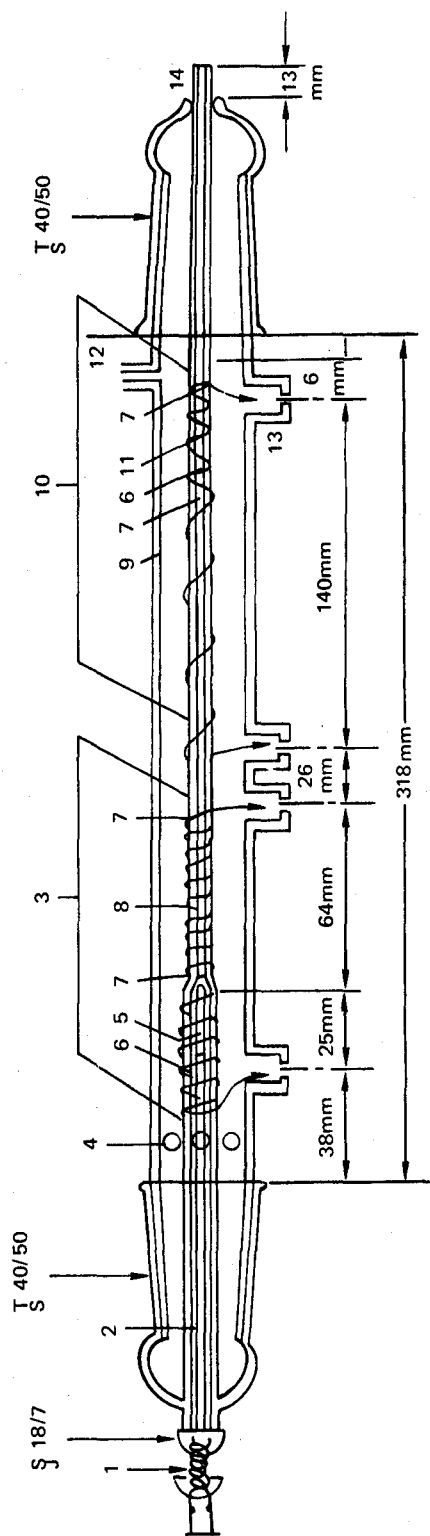
Introduction

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). Sampling tubes are inserted into the first section of the desorption unit where the mercury is thermally desorbed and transferred to a second section. 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 S199-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 S199-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.
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.



1. LOADING MECHANISM	8. CUPRIC OXIDE (CuO)
2. QUARTZ GLASS PLUNGER TUBE	9. COOLING JACKET
3. SAMPLE DESORPTION SECTION	10. SECOND DESORPTION SECTION
4. COOLING AIR VENT HOLES	11. GOLD SECTION
5. SAMPLING TUBE	12. COOLING AIR INTAKE
6. NICHROME WIRE COILS	13. WIRE HOLES AND SOLDERLESS CONNECTORS
7. QUARTZ GLASS WOOL PLUGS	14. OUTLET

Figure S199-A1 THERMAL DESORPTION UNIT

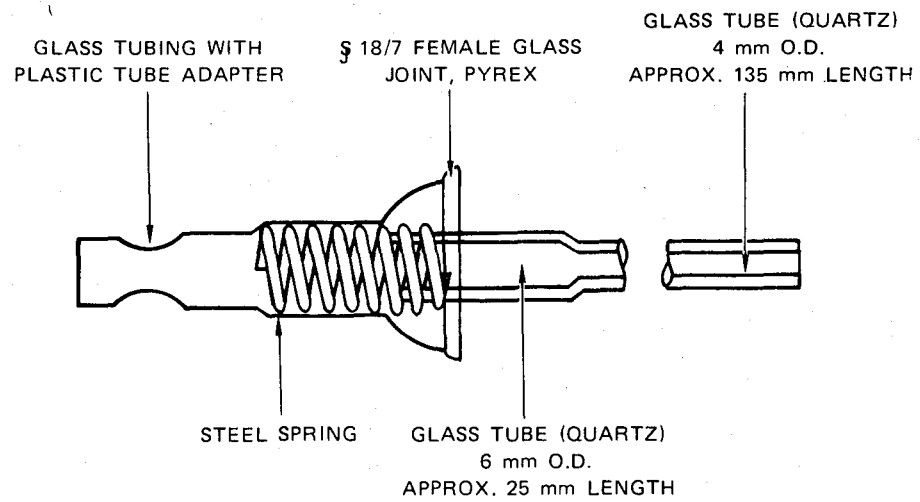


Figure S199-A2 LOADING MECHANISM

S199-A3

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 S199-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 sample tube reaches a maximum of 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. Air supply - The air which passes through the heated sections of the thermal desorption unit is drawn from the room by a vacuum pump. The pump is attached to a ballast tank to prevent fluctuations in air flow.

Before entering the desorption unit, room air passes through a drying tube containing anhydrous $\text{Mg}(\text{ClO}_4)_2$ or any other suitable drying agent. The dimensions of the drying tube and all subsequent filters may vary but should not interfere with the air flow through the system. The drying agent should be changed periodically depending on the humidity of the work area. The dried air passes through a filter containing activated charcoal and 30/60 mesh silvered Chromosorb P or Mersorb charcoal to remove organic vapors and metallic mercury.

The dry, filtered air then 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 flowmeter and into the ballast tank of the vacuum pump. The flowmeter covers a 0 to 5 liter/min range and a critical orifice controls the flow of air through the system.

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 from a plastic tube into the air intake 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.

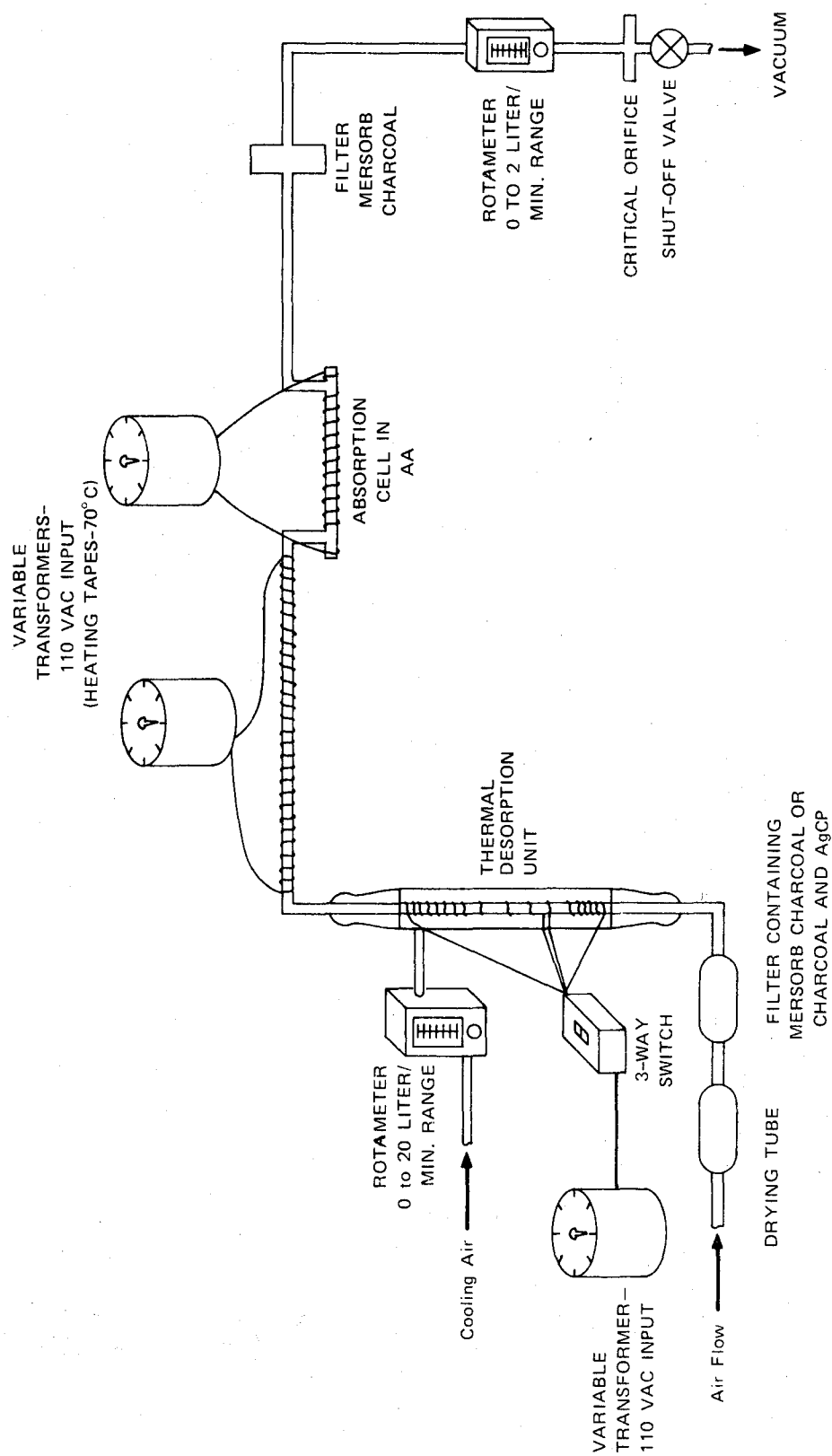


Figure S199-A3 MERCURY ANALYSIS SYSTEM

S199-A6

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.

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 vacuum pump.
4. Observe the rotameter to insure flow through the critical orifice 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 one minute 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. Reload the desorption unit with another sampling tube.
17. Repeat steps 11 through 16 for each analysis.

Cobalt Metal Dust and Fume

Analyte:	Cobalt	Method No.:	S203
Matrix:	Air	Range:	0.031-0.22 mg/cu m* 0.040-0.26 mg/cu m**
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.0687* 0.0713**
Procedure:	Filter collection, Acid Dissolution/ Digestion, Atomic Absorption Spectrophotometry	Validation Date:	2/18/77

1. Principle of the Method

- 1.1 Cobalt metal dust and fume, collected on a mixed cellulose ester membrane filter, is dissolved from the sample-containing filter by treating with aqua regia at room temperature for 30 minutes followed by wet-ashing using aqua regia and nitric acid to destroy the organic matrix. The cobalt is then solubilized in 5% nitric acid.
- 1.2 The solutions of samples and standards are aspirated into an oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for cobalt is used to provide a characteristic cobalt line at 240.7 nm. The absorbance is proportional to the cobalt concentration.

2. Range and Sensitivity

- 2.1 This method was independently validated for cobalt fume over the range of 0.031-0.221 mg/cu m, and for cobalt dust over the range of 0.040-0.262 mg/cu m at an atmospheric temperature and pressure of 18-26°C and 740-765 mm Hg, using a 270-liter and 300-liter sample, respectively.
- 2.2 For a sample size of 300 liters, the working range of the method is estimated to be 0.01-0.30 mg/cu m. The method may be

* This value is for cobalt fume.

**This value is for cobalt dust.

extended to higher values by further dilution of the sample solution; the absolute sensitivity of the method has not been established.

3. Interferences

- 3.1 There are no known spectral line interferences for the cobalt AA assay.
- 3.2 Other particulate cobalt compounds would interfere with the analysis.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.031-0.26 mg/cu m was 0.070. This value corresponds to a 0.007 mg/cu m standard deviation at the OSHA standard concentration. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was also no bias in the analytical method; the average recovery from the filters was 102%. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

This conclusion is supported by data on a separate set of samples in which the generator concentration was determined by an independent method (Reference 11.1).

5. Advantages and Disadvantages

- 5.1 The method is simple and specific for cobalt.
- 5.2 Care must be taken to initially treat the sample at room temperature with aqua regia before hot ashing so as to avoid passivation of cobalt metal.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:
 - 6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm 3-piece filter holder.
 - 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate of 1.5 liters per

minute. The pump must be calibrated with a filter holder and filter in the line.

- 6.1.3 Thermometer.
- 6.1.4 Barometer.
- 6.1.5 Stopwatch.
- 6.2 Mixed cellulose ester membrane filter. 37-mm diameter, 0.8 micrometer pore size.
- 6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for an air-acetylene flame.
 - 6.3.1 Cobalt hollow cathode lamp.
 - 6.3.2 Air.
 - 6.3.3 Fuel: purified acetylene.
 - 6.3.4 Pressure regulators, two-stage, for each compressed gas tank used.
- 6.4 Glassware, borosilicate
 - 6.4.1 50-ml beakers with watchglass covers.
 - 6.4.2 Pipetes, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards.
 - 6.4.3 10-ml volumetric flasks.
- 6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

- 7.1 Water, distilled or deionized.
- 7.2 Nitric acid, concentrated.
- 7.3 Nitric Acid, 5%.
- 7.4 Hydrochloric acid, concentrated.
- 7.5 Aqua Regia, mix 3 parts HCl and 1 part nitric acid.

- 7.6 Aqueous standard stock solutions containing 1000 µg/ml of cobalt (commercially available). This solution can also be prepared by dissolving 1.000 g cobalt metal in a minimum amount of aqua regia and diluting to 1.0 liter with 5% HNO₃.
- 7.7 Cobalt working standard solution, 60 µg/ml. Prepare by appropriate dilution of above solution. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

- 8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.
- 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Collection and Shipping of Samples

- 8.2.1 To collect cobalt metal dust and fume, a personal sampling pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.
- 8.2.2 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 handling as for the samples except that no air is drawn through it. Label this as a blank.
- 8.2.3 Shipping. The filter holders should be shipped in a suitable container, designed to prevent damage in transit.

8.3. Analysis of Samples

- 8.3.1 Open the filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 50-ml beaker.

- 8.3.2 Dissolution/Wet Ashing. To solubilize the cobalt metal, treat the sample with 3 ml of aqua regia at room temperature for 30 minutes. Complete dissolution and destroy the organic filter matrix by heating each beaker with a watchglass on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced nearly to dryness (<0.5 ml). Repeat this process two more times using 3 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to less than 1 ml on the last digestion.
- 8.3.3 Cool solutions and add about 3-4 ml of 5% nitric acid to each one.
- 8.3.4 Quantitatively transfer the clear solution into a 10 ml volumetric flask.
- 8.3.5 Rinse each beaker at least twice with 2-ml portions of 5% nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask.
- 8.3.6 Dilute all samples to 10 ml with 5% nitric acid.
- 8.3.7 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 240.7 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response.
- Note: Follow instrument manufacturer's recommendations for specific operating parameters.
- 8.3.8 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample 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 should be determined in duplicate at each test level chosen so as to cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.
- 8.4.2 Procedure for Determining Recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentra-

tion expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determinations should agree within $\pm 5\%$.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 270-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) were spiked accordingly by adding an aliquot of a solution containing known amounts of dissolved cobalt metal in 5% nitric acid. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 102%.

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

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ Recovered}}{\text{Weight } (\mu\text{g}) \text{ Added}}$$

9. Calibration and Standards

- 9.1 From the cobalt working standard solution, prepare at least six calibration standards to cover the cobalt concentration range from 10 to 60 μg per 10 ml. Prepare these calibration standards fresh daily by dilution of appropriate aliquots of the working standard solution using 5% nitric acid for all dilutions.
- 9.2 Proceed as in Section 8.3.7.
- 9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in $\mu\text{g}/10 \text{ ml}$. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

- 10.1 Read the weight, in μg , corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg per 10 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in blank filter}$$

10.3 Divide the total weight by the recovery to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 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 = sample flow rate

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = 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).

$$\text{mg}/\text{cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

11.1 Cobalt Metal Dust and Fume, S203, Backup Data Report prepared under NIOSH Contract No. 210-76-0123.

11.2 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

Dinitrobenzene
(all isomers)

Analyte:	Dinitrobenzene	Method No.: S214
Matrix:	Air	Range: 0.42-2.4 mg/cu m
OSHA Standard:	1 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.091
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date: 4/15/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 10 ml of ethylene glycol to collect dinitrobenzene.
- 1.2 The filter and bubbler are disconnected. The filter is removed from the cassette holder and added to the bubbler flask. Five milliliters of methanol is added to the flask before analysis.
- 1.3 The resulting sample is analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.418-2.386 mg/cu m at an atmospheric temperature of 23°C and pressure of 758 mm Hg, using 90-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the capacity of the mixed cellulose ester membrane filter connected in series to the midget bubbler and the capacity of the midget bubbler.

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 compound that has the same retention time as dinitrobenzene 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 0.418-2.386 mg/cu m was 0.091. This value corresponds to a standard deviation of 0.09 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 2.4% lower than the "true" concentrations for 18 samples. 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. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, storage stability, and collection efficiency were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.191 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 5.1 Collected samples are analyzed by means of a quick, instrumental method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 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.
- 6.2 A glass midget bubbler containing 10 ml of ethylene glycol.

- 6.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a trap consisting of a second bubbler or impinger downstream from the midget bubbler.
- 6.4 Manometer.
- 6.5 Thermometer.
- 6.6 High pressure liquid chromatograph equipped with a 254-nm fixed wavelength uv detector and a sample injection valve with a 50-microliter external sample loop. The injection valve is fitted with a syringe filter to remove filter fibers which would eventually block the flow to the LC column.
- 6.7 Column (250 mm x 3-mm I.D. stainless steel) packed with Spherisorb ODS. The superficially porous packing material consists of spherical silica particles with a 5% bonded coating of octadecyl groups. This packing can be obtained from Spectra-Physics in Santa Clara, California.
- 6.8 An electronic integrator or some other suitable method for measuring peak areas.
- 6.9 Tweezers.
- 6.10 Microliter Syringes: 50 and 100-microliter.
- 6.11 Volumetric Flasks: Convenient sizes for preparing standard solutions.
- 6.12 Pipets: Convenient sizes for preparing standard solutions and 5- and 10-ml pipets for measuring the extraction medium.
- 6.13 Teflon tubing (15 cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.
7. Reagents
 - 7.1 o-Dinitrobenzene, m-dinitrobenzene, and p-dinitrobenzene, reagent grade.
 - 7.2 Ethylene glycol, reagent grade.
 - 7.3 Methanol, distilled in glass.
 - 7.4 2-Propanol, reagent grade.
 - 7.5 Water, deionized and distilled.
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, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

- 8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a stainless steel screen. Secure the cassette holder together with tape or shrinkable band.
- 8.3.2 Pour 10 ml of ethylene glycol into each midget bubbler. Be sure that the bubbler frit is completely immersed in the ethylene glycol. If necessary adjust liquid level to cover the frit.
- 8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet of the midget bubbler to either the pump's inlet or the trap's inlet. When a trap is used, it is attached to the pump by tape or a holder. The outlet of the trap is connected by tubing to the pump's inlet. Material collected in the trap must never be returned to the midget bubbler. After sampling, discard the material collected in the trap. The bubbler must be maintained in a vertical position during sampling.
- 8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
- 8.3.5 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.
- 8.3.6 Turn the pump on and begin sample collection. 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.
- 8.3.7 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.
- 8.3.8 After sampling, disconnect the filter and bubbler. Remove the bubbler stem, and remove the filter from the filter cassette with clean tweezers and add it to the bubbler. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the

bubbler should be taped securely to prevent leakage during shipping. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of dinitrobenzene from the filter by vaporization may occur.

8.3.9 With each batch of ten samples submit one bubbler containing ethylene glycol and a blank filter from the same lot of filters and bubblers used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

8.3.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.4 Analysis of Samples

8.4.1 If the sample volume is less than 10 ml, add ethylene glycol until the volume reaches the 10-ml mark.

8.4.2 Add 5 ml of methanol to each sample and mix the solution by swirling. If the volume is not exactly 15.0 ml, make an appropriate correction in the calculation in Section 10.1. Allow the samples to stand for 2 hours before analysis.

8.4.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 2500 psi
Flow Rate: 1.9 ml/min
Mobile Phase: 20% methanol/80% water (V/V)
Detector: uv photometer at 254 nm
Capacity Ratio: 8.6

There are three isomers of dinitrobenzene. This method was validated using only the meta isomer, which is the predominant isomer in a mixture of isomers of dinitrobenzene (approximately 93% of the total as given in Reference 3).

Using the HPLC operating conditions above, the isomers can be eluted separately from the column. If more than one isomer is present in the sample, it is important that the HPLC conditions allow adequate separation of the isomers, since they must be quantitated independently. The response for each isomer should be determined.

8.4.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 50-microliter sample loop. Flush this loop thoroughly with the sample (300 microliters), and inject the sample.

- 8.4.5 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.

9. Calibration and Standards

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 LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.

- 9.1 Prepare a 2.25 mg/ml dinitrobenzene stock standard solution (for the isomer of interest) by dissolving 56.25 mg dinitrobenzene in 2-propanol and diluting to 25 ml in a volumetric flask.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and added to 10 ml ethylene glycol and 5 ml methanol. Prepare at least 5 working standards to cover the range of 0.013-0.40 mg/15 ml. This range is based on a 90-liter sample. Analyze samples as per Section 8.4.
- 9.3 Prepare a standard calibration curve by plotting concentration of dinitrobenzene in mg/15 ml versus peak area. A calibration curve should be prepared for each isomer of interest.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of ethylene glycol/methanol and the volume of sample injected is identical to the volume of the standards injected. If more than one isomer is present, combine the mg found for each isomer to give the total weight of dinitrobenzene in the sample.

- 10.2 A correction for the blank must be made for each sample.

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

where:

$$\text{mg sample} = \text{mg found in sample filter}$$

$$\text{mg blank} = \text{mg found in blank filter}$$

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
- t = sampling time
- P₁ = pressure during calibration of sampling pump (mm Hg)
- P₂ = pressure of air sampled (mm Hg)
- T₁ = temperature during calibration of sampling pump (°K)
- T₂ = temperature of air sampled (°K)

10.4 The concentration of dinitrobenzene in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.
- 11.2 Backup Data Report for Dinitrobenzene, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 March, J. Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, McGraw-Hill, New York (1968), 382.

Dinitrotoluene

Analyte:	Dinitrotoluene	Method No.: S215
Matrix:	Air	Range: 0.90-5.0 mg/cu m
OSHA Standard:	1.5 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.063
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date: 5/13/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 10 ml of ethylene glycol to collect dinitrotoluene.
- 1.2 The filter and bubbler are disconnected. Five milliliters of methanol are added to the bubbler flask, and the filter is removed from the cassette holder and added to the bubbler flask.
- 1.3 The resulting sample is analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.900-5.02 mg/cu m at an atmospheric temperature of 20°C and pressure of 764 mm Hg, using 90-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the capacity of the mixed cellulose ester membrane filter connected in series to the midget bubbler and the capacity of the midget bubbler.

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 compound that has the same retention time as dinitrotoluene 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 ($\overline{CVT}$) for the total analytical and sampling method in the range of 0.900-5.02 mg/cu m was 0.063. This value corresponds to a standard deviation of 0.09 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 4% lower than the "true" concentrations for 17 samples. 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. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, storage stability, and collection efficiency were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.800 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 5.1 Collected samples are analyzed by means of a quick, instrumental method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 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, and a 37-mm two-piece cassette filter holder supported by a stainless steel screen. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.
- 6.2 A glass midget bubbler containing 10 ml of ethylene glycol.

- 6.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of 5%. The sampling pump is protected from splasher or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.
- 6.4 Manometer.
- 6.5 Thermometer.
- 6.6 High pressure liquid chromatograph equipped with a 254-nm fixed wavelength uv detector and a sample injection valve with a 10-microliter external sample loop. The injection valve is fitted with a syringe filter to remove filter fibers which would eventually block the flow to the LC column.
- 6.7 Column (250 mm x 3-mm I.D. stainless steel) packed with Spherisorb ODS. The superficially porous packing material consists of spherical silica particles with a 5% bonded coating of octadecyl groups. This packing can be obtained from Spectra-Physics in Santa Clara, California.
- 6.8 An electronic integrator or some other suitable method for measuring peak areas.
- 6.9 Tweezers.
- 6.10 Microliter Syringes: 10 and 100-microliter.
- 6.11 Volumetric Flasks: Convenient sizes for preparing standard solutions.
- 6.12 Pipets: Convenient sizes for preparing standard solutions and 5- and 10-ml pipets for measuring the extraction medium.
- 6.13 Teflon tubing (15 cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

- 7.1 2,4-Dinitrotoluene, reagent grade.
- 7.2 Ethylene glycol, reagent grade.
- 7.3 Methanol, distilled in glass.
- 7.4 2-Propanol, reagent grade.
- 7.5 Water, deionized and distilled.

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, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

- 8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a stainless steel screen. Secure the cassette holder together with tape or shrinkable band.
- 8.3.2 Pipet 10 ml of ethylene glycol into each midget bubbler, and mark the liquid level. Be sure that the bubbler frit is completely immersed in the ethylene glycol.
- 8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.
- 8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
- 8.3.5 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.
- 8.3.6 Turn the pump on and begin sample collection. 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.
- 8.3.7 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.
- 8.3.8 After sampling, disconnect the filter and bubbler. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping.
- 8.3.9 The filters are shipped in the cassette filter holder. Each filter should be marked to identify it with its corresponding backup bubbler.

8.3.10 With each batch of ten samples submit one filter and bubbler containing 10 ml of ethylene glycol from the same lot of filters and bubblers used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.

8.3.11 The cassette filter holders and bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.4 Analysis of Samples

8.4.1 Mix the contents in the bubbler by swirling. If the sample volume is less than 10 ml, add ethylene glycol until the volume reaches the 10-ml mark. If the sample volume is more than 10 ml, determine the volume and make an appropriate volume correction in the calculations indicated in Section 10.1.

8.4.2 Add 5 ml of methanol to each sample and mix the solution by swirling.

8.4.3 Remove the filter from the filter cassette with clean tweezers, and add the filter to the bubbler.

8.4.4 Stopper the bubbler and shake.

8.4.5 Allow the samples to stand for two hours before analysis.

8.4.6 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 1290 psi
Flow Rate: 1.0 ml/min
Mobile Phase: 50% methanol/50% water (V/V)
Detector: uv photometer at 254 nm
Capacity Ratio: 4.9

8.4.7 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 10-microliter sample loop. Flush this loop thoroughly with the sample (100 microliters), and inject the sample.

8.4.8 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.

8.5 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 dinitrotoluene from the cellulose ester membrane filter. The analytical method recovery should be determined over the concentration range of interest.
- 8.5.2 Procedure for Determining Analytical Method Recovery. An appropriate aliquot of a 3.375 mg/ml solution of dinitrotoluene in 2-propanol is added to a 37-mm MCE filter. The amount added is equal to the amount of dinitrotoluene collected in a 90-liter sample at 2X, 1X, and 0.5X the OSHA standard level. Six spiked samples are prepared at each level along with six blanks. The filters are allowed to stand for 2-3 minutes to allow evaporation of 2-propanol. The filter is transferred to a container containing 10 ml of ethylene glycol and 5 ml methanol. The resulting sample is mixed well and allowed to stand for 1 hour before analysis.

Analytical Method Recovery (A.M.R.) equals the weight in mg found on the filter divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg taken}}$$

9. Calibration and Standards

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 LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.

- 9.1 Prepare a 3.375 mg/ml dinitrotoluene stock standard solution by dissolving 33.75 mg dinitrotoluene in 2-propanol and diluting to 10 ml in a volumetric flask.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and added to 10 ml ethylene glycol and 5 ml methanol. Prepare at least 5 working standards to cover the range of 0.013-0.40 mg/15 ml. This range is based on a 90-liter sample. Analyze samples as per Section 8.4.
- 9.3 Prepare a standard calibration curve by plotting concentration of dinitrotoluene in mg/15 ml versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of ethylene glycol/methanol 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 sample.

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

where:

$$\text{mg sample} = \text{mg found in sample filter}$$

$$\text{mg blank} = \text{mg found in blank filter}$$

10.3 Corrections for analytical method recovery (A.M.R.) must be made.

$$\text{Corrected mg/sample} = \frac{\text{mg (Section 10.2)}}{\text{A.M.R.}}$$

10.4 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:

$$f = \text{flow rate sampled}$$

$$t = \text{sampling time}$$

$$P_1 = \text{pressure during calibration of sampling pump (mm Hg)}$$

$$P_2 = \text{pressure of air sampled (mm Hg)}$$

$$T_1 = \text{temperature during calibration of sampling pump (°K)}$$

$$T_2 = \text{temperature of air sampled (°K)}$$

10.5 The concentration of dinitrotoluene in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.2 Backup Data Report for Dinitrotoluene, 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

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.
- 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 (see Section 5.2).

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.

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 which can be taken is limited by the number of milligrams that the tube will hold before overloading. 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 two-thirds the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X the OSHA standard to minimize the probability of overloading the sampling tube.
- 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 $\pm 5\%$ 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 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 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 back-up 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. 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 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- μ l 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 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 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 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 μ g recovered from the vial divided by the weight in μ g added to the vial, or

$$\text{D.E.} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

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

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. The density of the analyte is used to convert milligrams into microliters for easy measurement with a microliter syringe. 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. A calibration curve is established by plotting peak area versus concentration in μg per 2.0 ml.

For the internal standard method, use ethyl acetate containing a pre-determined 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 blank must be made for each sample:

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample vial}$$

$$\mu\text{g blank} = \mu\text{g found in blank vial}$$

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 $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

A similar procedure is followed for the backup (300 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.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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.

Picric acid

Analyte:	Picric acid	Method No:	S228
Matrix:	Air	Range:	0.036 - 0.189 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.082
Procedure:	Filter collection, extraction with 70% aqueous methanol, HPLC	Validation Date:	11/25/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the picric acid aerosol present. This method is not applicable for sampling environments where significant picric acid vapor may be present.
- 1.2 The filter is transferred to a jar and extracted with 70% aqueous methanol.
- 1.3 An aliquot of the sample is injected into a high performance liquid chromatograph (HPLC) equipped with a variable wavelength UV detector set at 360 nm.
- 1.4 The area of the resulting sample peak is used as a measure of analyte concentration by comparison with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.036 - 0.189 mg/cu m at an atmospheric temperature and pressure of 22°C and 772 mm Hg, using a 180-liter sample.
- 2.2 The method may be extended to higher values by further dilution of the sample solution. The detection limit of the analytical method is estimated to be at least 10 ng per 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 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 0.036 - 0.189 mg/cu m was 0.082. This value corresponds to a 0.008 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 A collection efficiency of at least 99% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the filters was 99.3%. In addition, the samples were found to be stable when stored for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 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 This sampling method is applicable for particulate picric acid only; in operations where significant vapor may also be present, this method will not apply.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:
 - 6.1.1 Filter. The filter unit consists of a mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37-mm diameter, supported by a cellulose backup pad, and a 37-mm, three-piece filter holder held together by tape or a shrinkable band.
 - 6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate is needed. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Barometer.

6.1.5 Stopwatch.

6.2 High pressure liquid chromatograph equipped with a detector capable of UV detection at 360 nm.

6.3 Column (30-cm x 3.9-mm I.D. stainless steel) packed with μ Bondapak C₁₈ or equivalent.

6.4 Syringe. Twenty- μ l, for HPLC injection.

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

6.6 Microliter syringes. One hundred-microliter and other convenient sizes for making standard solutions.

6.7 Ointment jars. Use squat form with Teflon film gaskets and screw cap.

6.8 Volumetric flasks. Twenty-five milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Picric acid, reagent grade.

7.2 Distilled water.

7.3 Methanol in distilled water, 70%. Prepare by diluting 700 ml of methanol to 1000 ml with distilled water. This solution is used for sample extraction and also as the mobile phase for the HPLC analysis, but should be degassed prior to such use.

7.4 Picric acid stock solution, 1.8 mg/ml. Dissolve 0.18g of picric acid in 100 ml of 70% 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 Pumps. Each personal pump must be calibrated with a representative filter holder 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 holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane 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.
- 8.3.2 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 180 liters is recommended. Sample at a flow rate of 1.5 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 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, 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 With each batch of samples, submit one filter 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 filter holders 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 lined with a Teflon cap. Label of the bulk sample should match air samples for identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the filter holder. Carefully remove the cellulose membrane filter from the holder with the aid of appropriate tweezers and transfer filter to the 2-oz. ointment jar.
2. Add 5 ml of 70% 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 chromatography. The mobile phase is 70% aqueous methanol. The typical operating conditions for the liquid chromatograph are:

1. 1.0 ml/min solvent flow rate
2. Ambient column temperature
3. 2250 psi system pressure
4. 360 nm UV detection wavelength
5. Capacity ratio: 2.2

8.4.3 Injection. The first step in the analysis is the injection of the sample into the liquid chromatograph. A 20 μ l-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 should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

- 8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter with 5 ml of 70% methanol and analyzed as described in Section 8.4.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 180-liter sample at the selected level was used to determine the analytical method recovery. A stock solution containing 0.975 milligrams of picric acid per milliliter of 70% aqueous methanol was prepared. Ten, 20 and 40-microliter aliquots of the solution were added to the cellulose membrane filters and air-dried to produce samples equivalent to 180-liter collections at 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand overnight. A parallel blank filter was also prepared except that no sample was added to it. All filters were 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

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

- 9.1 From the stock standard solution, prepare at least 6 working standards to cover the concentration range of 9-36 $\mu\text{g}/5 \text{ ml}$. Transfer 25 to 100 μl -aliquots of the stock standard into 25-ml volumetric flasks and dilute to volume with 70% methanol.
- 9.2 This 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 $\mu\text{g}/5 \text{ ml}$ 70% methanol, because samples are extracted in this amount of 70% methanol. Curves are established by plotting concentrations in micrograms per 5.0 ml versus peak area.

NOTE: To minimize effect of variations in LC conditions and detector response due to sample cell conditions, frequent standardization should be practiced.

10. Calculations

10.1 Read the concentration, in $\mu\text{g}/5\text{ ml}$, corresponding to the peak area from the standard curve. No volume corrections for sample aliquots analyzed are needed, because the standard curve is based on μg per 5.0 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.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in blank filter}$$

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 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 = 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

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).

$$\text{mg}/\text{cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

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. 017-033-00231-2.
- 11.2 S228 Backup Data Report for Picric acid, prepared under NIOSH Contract No. 210-76-0123, November 25, 1977.

Stibine

Analyte:	Stibine	Method No.:	S243
Matrix:	Air	Range:	0.119-1.008 mg/cu m
OSHA Standard:	0.1 ppm (0.5 mg/cu m)	Precision (CV_T):	0.087
Procedure:	Collection on mercuric chloride-coated silica gel, acid extraction, colorimetry/Rhodamine B.	Validation Date:	3/18/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a mercuric chloride impregnated silica gel tube to trap the stibine.
- 1.2 The antimony is extracted from the treated silica gel using concentrated hydrochloric acid.
- 1.3 An aliquot of the extracted sample is analyzed for antimony by oxidation of all of the antimony to Sb(V), extraction into isopropyl ether and formation of the Rhodamine B complex. The absorbance of the complex is measured at 552 nm. The absorbance is proportional to the antimony concentration.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.119-1.008 mg/cu m at an atmospheric temperature and pressure of 21°C and 769 mm Hg, respectively, using a 20-liter sample.
- 2.2 Sampling at 0.2 liters per minute for 90 minutes will yield an 18-liter sample. The working range for a sample of this size is estimated to be 0.1-1.5 mg/cu m.
- 2.3 The method may be extended to higher concentrations by further dilution of the extracted sample; however, the maximum capacity of the collection tube has not been established. Based on the breakthrough data, a level as high as 3.89 mg/cu m may be determined.

3. Interferences

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

- 3.2 The colorimetric determination of antimony is subject to interference by any element which also forms a Rhodamine B complex which is extractable into isopropyl ether. Species such as Am(III) (>250 μg), Au (>1000 μg), Fe(III) (>30,000 μg), Tl(I) (> 1000 μg), and Sn(II) (>1000 μg) have been reported (Reference 11.1) to give interference. If the presence of these elements is suspected, their concentration in the extracted solution should be determined to evaluate their effects on the antimony data.
- 3.3 If the possibility of interferences do exist, modification of the analytical procedure must be made to circumvent the problems or an alternative procedure should be used.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $\overline{CV}_T$ for the total sampling method in the range 0.119-1.008 mg/cu m was 0.087. This value corresponds to a standard deviation of 0.0435 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3. Since no analytical set or desorption efficiency data were obtained, the $\overline{CV}_T$ value is based only on the generated set data and pump error.
- 4.2 On the average, the concentration obtained at the OSHA standard level using the overall sampling and analytical procedure was 0.7% higher than the average taken concentration for a limited number of laboratory experiments. Any difference between the found and taken concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined taken ("true") concentration. Thus no recovery corrections should be applied to the final result.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable and involves no liquids.
- 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 cause the volume to be imprecise, because the pump is usually calibrated for only one tube.
- 5.3 The analytical method requires that once the analysis of an extracted sample is started, it be carried out to completion on each individual sample. This may present an inconvenience. However, the complete analysis can and should be completed within 15 minutes.

6. Apparatus

- 6.1 A calibrated personal pump whose flow can be determined within $\pm 5\%$ of the recommended flow rate. The pump must be calibrated with a representative tube in the line.
- 6.2 Treated silica gel tube. Glass tube with both ends flame sealed, 2.5 in. long with 8-mm O.D. and 6-mm. I.D., containing 2 sections of treated silica gel (grade 43, 14/20 mesh, Indicator type, Davison-Grace Co.) The adsorbing section contains 1.0g of treated silica gel and the backup 0.5g. A small wad of silylated glass wool is also placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm. of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool. The silica gel is coated according to the following procedure:
 - 6.2.1 Dry one hundred grams of silica gel at 100°C for 2 hours.
 - 6.2.2 Prepare a 10% w/v mercuric chloride solution in methyl alcohol.
 - 6.2.3 Add the dried silica gel to the mercuric chloride solution and let sit for 15 minutes with occasional stirring.
 - 6.2.4 Drain the excess mercuric chloride solution and dry the remaining silica gel at 80°C for 3 hours.
 - 6.2.5 Cool the silica gel to room temperature in a covered beaker.
 - 6.2.6 Expose the tube to a humid atmosphere until the indicator turns pink.
- 6.3 A spectrophotometer capable of measuring absorbance or transmittance at 552 nm.
- 6.4 Two matched 1-cm silica cells with tight fitting Teflon caps.
- 6.5 Separatory funnel, 125 ml.
- 6.6 Beakers, 50 ml.
- 6.7 Volumetric flasks, 25, 50, 250, and 500 ml.

- 6.8 Pipets. 15 and 20-ml and other convenient sizes to make standard dilutions.
- 6.9 Graduated cylinders, 10 and 25 ml.
- 6.10 Laboratory centrifuge with two 15-ml centrifuge tubes with tight-fitting caps. (Do not use rubber stoppers).
- 6.11 Balance.
- 6.12 Barometer.
- 6.13 Thermometer.
- 6.14 Stopwatch.

7. Reagents

All reagents should be ACS reagent grade or better.

- 7.1 Hydrochloric acid, concentrated.
- 7.2 Antimony standard solution, 1000 ppm. (Commercially available)
- 7.3 Ceric sulfate, $\text{Ce}(\text{SO}_4)_2$, solid.
- 7.4 Isopropyl ether, low in alcohol and water.
- 7.5 Water, distilled or deionized.
- 7.6 Rhodamine B.
- 7.7 Stock Rhodamine B solution, 0.2% in water. Prepare by dissolving 0.5 g in 250-ml volume.
- 7.8 Working Rhodamine B Solution, 0.01% in 0.5 M HCl. Prepare by mixing 25 ml of the stock Rhodamine B solution and 24 ml of concentrated HCl in 500 ml volume. Prepare fresh daily.

8. Procedure

8.1 Cleaning of Equipment

- 8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.

- 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6M nitric acid, tap water, distilled water in that order and then dried. Important: if acetone is used to dry the glassware, it is imperative that no residual acetone be present. The glassware should be perfectly dry.
- 8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. 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, break the two ends of the silica gel tubes to provide an opening of at least one half of the internal diameter of the tube (3 mm).
- 8.3.2 The treated silica gel tubes should be placed in a vertical direction during sampling to minimize channeling through the gel.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the tube.
- 8.3.4 A sample size of 18 liters is recommended. Sample at a known flow rate of 0.2 liters per minute or less for 90 minutes. The flow rate should be known with accuracy of at least $\pm 5\%$.
- 8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.3.6 The treated silica gel tubes should be labeled appropriately and capped with supplied plastic caps. Under no circumstances should rubber caps be used.
- 8.3.7 With each batch of 5 samples, submit one treated silica gel tube which had been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.
- 8.3.8 Capped treated silica gel 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 silica gel tube is scored with a file and broken open. The glass wool is removed with care and discarded making sure that no silica gel is lost in the process. The silica gel in front is transferred to a 50 ml beaker. The separating section of glass wool is removed and discarded. The backup section of silica gel is transferred to another container. These two sections are analyzed separately.
- 8.4.2 Extraction of the sample. Prior to analysis, 15 ml of concentrated HCl is pipetted into each beaker containing the silica gel. The extraction is carried out for 30 minutes at room temperature with occasional swirling during this period. After extraction the hydrochloric acid solution is drained into a 25 ml volumetric flask leaving the silica gel. The remaining gel is washed twice with 4 ml portions of concentrated HCl and the washings are drained and added to the volumetric flask containing the initial extract solution. The extract and washings are made up to volume with concentrated HCl and thoroughly mixed.
- 8.4.3 Spectrophotometer operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 552 nm and set the zero and 100% transmittance scale using a 1 cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.
- 8.4.4 Analytical Procedure
- Note: Steps 8.4.4.1 through 8.4.4.10 should be performed within a 15 minute period.
- 8.4.4.1 Pipet 15 ml of the extracted sample into a 125 ml separatory funnel.
- 8.4.4.2 Add 10-20 mg (spatula tip) ceric sulfate. Swirl to dissolve the solid and let stand for 60 seconds unstoppered.

8.4.4.3 Pipet 15 ml of isopropyl ether into the funnel, stopper and shake for 30 seconds, releasing the pressure only at the beginning and end of that period.

8.4.4.4 Add 7 ml of water, shake for 60 seconds. Allow 60 seconds for the aqueous and non-aqueous layers to separate and discard the lower (aqueous) layer.

Note: It is important to remove all of the aqueous layer and that none remains in the stopcock.

8.4.4.5 Pipet 20 ml of the working Rhodamine B solution. Shake for 60 seconds, releasing the pressure only at the beginning and end of that period.

8.4.4.6 Allow 60 seconds for the two phases to separate. Discard the lower (aqueous) layer.

8.4.4.7 Drain 10 ml of the isopropyl ether solution into a 15 ml centrifuge tube and cap tightly to prevent any evaporation of the ether.

8.4.4.8 Centrifuge for 120 seconds at 2000 RPM.

8.4.4.9 Transfer the sample into a 1 cm absorption cell and stopper immediately.

8.4.4.10 Measure the absorbance or transmittance at 552 nm using isopropyl ether as a blank.

9. Calibration and Standards

9.1 Using the standard antimony solution, prepare at least six calibration standards in concentrated HCl to cover the antimony concentration 2 to 20 μg Sb per 15 ml.

9.2 Prepare these standards fresh daily by appropriate dilution of the stock using concentrated HCl for all dilutions. A blank containing no antimony should also be analyzed.

9.3 Proceed as in Sections 8.4.4.1 to 8.4.4.10.

9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the blank versus the concentration of each standard in μg Sb per 15 ml on linear graph paper.

10. Calculations

- 10.1 Correction for the blank (obtained by extraction and analysis of the silica gel tube marked "blank") must be made for each sample.

$$\text{Abs}_{\text{corr}} = \text{Abs}_{\text{sample}} - \text{Abs}_{\text{blank}}$$

- 10.2 Read the amount of antimony, in $\mu\text{g Sb}$ per 15 ml, corresponding to the Abs_{corr} from the standard curve.

- 10.3 Multiply the total weight of antimony by 1.708 to obtain the corrected $\mu\text{g SbH}_3$ per 25 ml sample.

$$\mu\text{g SbH}_3 \text{ in sample} = \mu\text{g Sb} \times 1.708$$

- 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 appropriate information, such as the 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 (liters per minute)

t = sampling time (minutes)

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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.6 The concentration of analyte in the air sampled can be expressed in mg per cu m (μg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{corrected } \mu\text{g SbH}_3 \text{ (Section 10.4)}}{\text{volume of air sampled in liters}}$$

11. References

- 11.1 F. N. Ward and H. W. Lakin, Analytical Chem., 26, 1168 (1954).
- 11.2 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/76, 11/8/74, subject: Statistical Protocol for Analysis of Data from Contract CDC-99-74-45.
- 11.3 S243 Backup Data Report for Stibine, prepared under NIOSH Contract No. 210-76-0123, 3/18/77.

Benzoyl Peroxide

Analyte:	Benzoyl Peroxide	Method No.: S253
Matrix:	Air	Range: 3.12-19.10 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$): 0.060
Procedure:	Filter collection, ethyl ether extraction, HPLC	Validation Date: 1/21/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to collect benzoyl peroxide.
- 1.2 Benzoyl peroxide is extracted from the filter with ethyl ether, and the sample is analyzed by high pressure liquid chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 3.12-19.10 mg/cu m at an atmospheric temperature of 26°C and pressure of 764 mm Hg, using a 90-liter sample.
- 2.2 The upper limit of the range of the method depends on the capacity of the cellulose ester membrane filter. If higher concentrations than those tested are to be sampled, smaller volumes should be used. Higher volumes can also be used as long as particulate filter loading remains less than 2 mg.

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 compound that has the same retention time as benzoyl peroxide 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 3.12-19.10 mg/cu m was 0.060. This value corresponds to a standard deviation of 0.30 mg/cu m at the OSHA standard level. Statistical information can be found in

Reference 11.1. Details of the test procedures can be found in Reference 11.2.

- 4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. Storage stability studies on samples collected from a test atmosphere at a concentration of 7.30 mg/cu m indicate that after one week there is a 9.3% decrease in the amount of benzoyl peroxide recovered from the filter. In this study the filter samples were held in the filter cassettes at room temperature. Other tests show that benzoyl peroxide is stable in ethyl ether at room temperature for at least one week. Thus, there may be up to 9.3% loss of the analyte if the samples are not extracted immediately or refrigerated. Otherwise, the Coefficient of Variation is a good measure of the accuracy of the method, and no recovery correction should be applied to the final result in Section 10.5.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick instrumental method.
- 5.2 If samples are not returned to the laboratory promptly, there may be loss of material on the filter.

6. Apparatus

- 6.1 Filter unit: The filter unit consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type MF or equivalent) with a pore size of 0.80 micrometer, and a 37-mm two-piece cassette filter holder supported by a cellulose pad.
- 6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined within 5% at the recommended flow rate.
- 6.3 Manometer.
- 6.4 Thermometer.
- 6.5 Scintillation Vials: 20 ml. The vial caps should be lined with Teflon for proper seal.
- 6.6 High performance liquid chromatograph equipped with a 254-nm fixed wavelength uv detector and a sample injection valve with a 20-microliter external sample loop. The injection valve is fitted with a syringe filter to remove filter fibers which eventually block the flow to the LC column.
- 6.7 Column (250 mm x 3-mm I.D. stainless steel) packed with Spherisorb ODS. The superficially porous packing material consists of spherical silica particles with a 5% bonded coating of octadecyl groups. This packing can be obtained from Spectra-Physics in Santa Clara, CA.

- 6.8 An electronic integrator or some other suitable method for measuring peak areas.
- 6.9 Tweezers.
- 6.10 Microliter Syringes: 10 and 100-microliter.
- 6.11 Volumetric Flasks: Convenient sizes for preparing standard solutions.
- 6.12 Pipets: Convenient sizes for preparing standard solutions and 10-ml pipets for measuring the extraction medium.

7. Reagents

- 7.1 Benzoyl peroxide, 99% pure.
- 7.2 Ethyl ether, purified, and containing no stabilizer.
- 7.3 Methanol, distilled in glass.
- 7.4 Water, deionized and distilled.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.
- 8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a cellulose support pad. Secure the cassette holder together with tape or shrinkable band.
 - 8.3.2 Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.
 - 8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
 - 8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liter per minute. The flow rate should be known with an accuracy of 5%.
 - 8.3.5 Turn the pump on and begin sample collection. 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 rotameter should be observed frequently, and sampling should be terminated at any evidence of a problem.

- 8.3.6 Terminate sampling at the predetermined time and record ambient temperature and pressure, sample flow rate, and collection time. If pressure reading is not available, record the elevation.
- 8.3.7 Record the sample identity and all relevant sampling data.
- 8.3.8 With each batch of ten samples, submit one 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 a blank.
- 8.3.9 The cassette filter holders in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.

8.4 Analysis of Samples

Upon receipt in the laboratory, the filters should be transferred to clean scintillation vials with clean tweezers and extracted with ether and the solutions stored in the refrigerator until they are analyzed. If it is not feasible to extract the filters immediately, the filters should be refrigerated as soon as possible. However, extractions should be done as soon as possible.

- 8.4.1 Each sample is analyzed separately.
- 8.4.2 Pipet 10 ml of ethyl ether into each scintillation vial.
- 8.4.3 Swirl the contents in each bottle.
- 8.4.4 Appropriate filter blanks must be analyzed at the same time as the samples.
- 8.4.5 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 1300 psi
Flow Rate: 1.6 ml/min
Mobile Phase: 70% methanol/30% water (V/V)
Detector: uv photometer at 254 nm
Range: 0.08 O.D.

8.4.6 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 20-microliter sample loop. Flush this loop thoroughly with the sample (100 microliters), and inject the sample.

8.4.7 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.

8.5 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 benzoyl peroxide from the cellulose ester membrane filter. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for Determining Analytical Method Recovery. An appropriate aliquot of a 11.25 mg/ml solution of benzoyl peroxide in ethyl ether is added to a 37-mm MCEF filter. The amount added is equal to the amount of benzoyl peroxide collected in a 90-liter sample at 2X, 1X and 0.5X the OSHA standard level. Six spiked samples are prepared at each level along with six blanks. The samples are then analyzed according to the method in Section 8.4.

Analytical Method Recovery (A.M.R.) equals the weight in mg found on the filter divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg taken}}$$

9. Calibration and Standards

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 LC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/10 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the uv detector response.

9.1 Prepare a 11.25 mg/ml benzoyl peroxide stock standard solution by dissolving 281.25 mg benzoyl peroxide in ethyl ether and diluting to 25 ml in a volumetric flask. This solution should be stored in the refrigerator when not in use.

9.2 From the above stock solution, appropriate aliquots are withdrawn

and dilutions are made in ethyl ether. Prepare at least 5 working standards to cover the range of 0.045 mg-1.35 mg/10 ml. This range is based on a 90-liter sample. Analyze samples as per Section 8.4.

- 9.3 Prepare a standard calibration curve by plotting concentration of benzoyl peroxide in mg/10 ml versus peak area.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/10 ml of ethyl ether 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 sample.

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

where:

$$\begin{aligned}\text{mg sample} &= \text{mg found in sample filter} \\ \text{mg blank} &= \text{mg found in blank filter}\end{aligned}$$

- 10.3 Corrections for analytical method recovery (A.M.R.) must be made.

$$\text{Corrected mg/sample} = \frac{\text{mg (Section 10.2)}}{\text{A.M.R.}}$$

- 10.4 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:

$$\begin{aligned}f &= \text{flow rate sampled} \\ t &= \text{sampling time} \\ P_1 &= \text{pressure during calibration of sampling pump (mm Hg)} \\ P_2 &= \text{pressure of air sampled (mm Hg)} \\ T_1 &= \text{temperature during calibration of sampling pump (°K)} \\ T_2 &= \text{temperature of air sampled (°K)}\end{aligned}$$

- 10.5 The concentration of benzoyl peroxide in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.2 Backup Data Report for Benzoyl Peroxide, prepared under NIOSH Contract No. 210-76-0123.

Hydrogen cyanide

Analyte:	Cyanide ion, CN^-	Method No. S288
Matrix:		Range: 5.2-21.0 mg/cu m
OSHA Standard:	10 ppm (11 mg/cu m)	Precision ($\overline{\text{CV}}_T$): 0.081
Procedure:	Filter/bubbler collection, Validation Date: 9/2/77 analysis by cyanide ion selective electrode	

1. Principle of the Method

- 1.1 A known volume of air is drawn through a filter and midget bubbler containing 0.1N potassium hydroxide. Hydrogen cyanide vapor is collected in its ionized form.
- 1.2 The filter is used to remove particulate cyanide interference and is discarded. 0.1N potassium hydroxide is used to rinse the bubbler and dilute the sample to a final volume of 25 ml.
- 1.3 The resulting solution is analyzed by direct potentiometry using a cyanide ion-selective electrode.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 5.18-20.98 mg/cu m at an atmospheric temperature and pressure of 23°C and 753 mm Hg, using a 12-liter sample.
- 2.2 The upper limit of the range of the method is dependent on the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, it is recommended that the sample be diluted to avoid concentrations above 10^{-2} M CN^- .

3. Interferences

- 3.1 Particulate cyanides will be removed by using a 0.8-micron cellulose ester membrane filter connected in front of the midget bubbler. In humid atmospheres, however, it has been observed that during the collection of particulate cyanide, hydrogen cyanide is liberated (Reference 11.1), therefore, particulate interference is not completely removed. The use of a filter would also eliminate a major proportion of the interferences discussed below.
- 3.2 Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if found to be present in the sample.

If sulfide is suspected to be present, check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

- 3.3 Sulfide can be removed by addition of 1 ml of 1 M H_2O_2 and 1 ml of 1 M Na_2SO_3 to sample solutions prior to diluting to volume (Reference 11.2).
- 3.4 When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool contained in an eye dropper and proceed with the analysis.
- 3.5 It should also be noted that the cyanide electrode will malfunction if other ions like chloride, iodide and bromide, which form insoluble silver salts, are present in sufficient quantity. Several metal ions are also known to complex with cyanide, such as cadmium, zinc, silver, nickel, cuprous, iron, and mercury. Consult the instruction manual for a list of these ions and also the proper procedure to use when such ions are believed to be present.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{\text{CV}}_T$) for the total sampling and analytical method in the range of 5.18-20.98 mg/cu m was 0.0813. This value corresponds to a standard deviation of 0.89 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.3. Details of the test procedures can be found in Reference 11.4.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5, 1, and 2X the OSHA standard level were 3.3% lower than the "true" concentrations for 18 samples. 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 Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, storage stability, and collection efficiency were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 10.01 mg/cu m indicate that collected samples are stable for at least one week.

5. Advantages and Disadvantages of the Method

- 5.1 Collected samples are analyzed by means of a quick and simple method.
- 5.2 Hydrogen cyanide collected in its ionized form is stable and non-volatile, making this manner of collection of hydrogen cyanide desirable.

- 5.3 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.
- 5.5 The precision of the method may be limited by the reproducibility of the pressure drop across the prefilter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal samples for the determination of cyanide consists of the following components:
 - 6.1.1 Prefilter Unit. The prefilter unit, which is used to remove particulate interferences, consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer contained in a 37-mm two-piece filter holder. The filter is supported by a cellulose backup pad.
 - 6.1.2 A glass midget bubbler containing the collecting medium, 0.1N potassium hydroxide.
 - 6.1.3 Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or water condensation by a second empty bubbler positioned between the exit arm of the first bubbler and the pump.
 - 6.1.4 Potassium Hydroxide, 0.1N. Prepare a sufficient amount for collection of samples.
 - 6.1.5 Double distilled water.
 - 6.1.6 Pipet, 15-ml or other suitable device for adding 0.1N potassium hydroxide to the bubblers.
 - 6.1.7 Thermometer.
 - 6.1.8 Barometer.
 - 6.1.9 Stopwatch.

- 6.2 Orion 94-06 cyanide ion specific electrode or equivalent.
- 6.3 Orion 90-20-00 double junction reference electrode or equivalent.
- 6.4 Orion Model 801 digital pH/mV meter or equivalent.
- 6.5 Magnetic stirrer and stirring bars.
- 6.6 Pipets, 1-ml and other convenient sizes.
- 6.7 Volumetric flasks, 25-ml and other assorted sizes.
- 6.8 Beakers, 50-ml or other suitable container for potentiometric measurements.

7. Reagents

All reagents used must be ACS reagent grade or better.

- 7.1 Double distilled water.
- 7.2 Potassium cyanide.
- 7.3 Potassium hydroxide, 0.1N. Dissolve 5.6 g potassium hydroxide in distilled water and dilute to 1000 ml.
- 7.4 Cyanide Standards
 - 7.4.1 Cyanide Standard Stock Solution, 10^{-2} M CN^- . Dissolve 65 mg potassium cyanide in 0.1N potassium hydroxide and dilute to 100 ml with additional 0.1N potassium hydroxide.
 - 7.4.2 Working Standards. Prepare at least 6 working standards to cover the concentration range of interest by proper dilution of the stock standard. Use 0.1N KOH for all dilutions. Prepare these calibration standards fresh daily.
- 7.5 Lead acetate paper.
- 7.6 Cadmium carbonate.

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, and dried.
- 8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter holder, bubbler, and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

- 8.3.1 Assemble the filter in the two-piece filter holder and close firmly. The filter is supported by a cellulose backup pad. Secure the filter holder together with tape or shrinkable band.
- 8.3.2 Pipet 15 ml of 0.1N potassium hydroxide into the first midget bubbler.
- 8.3.3 Remove the filter holder plugs and attach the outlet of the holder to the inlet arm of the first midget bubbler using a short piece of flexible tubing. The outlet of this bubbler is connected by tubing to the inlet of the trap. The outlet of the trap is connected by a short piece of tubing to the pump's inlet. The trap is in a suitable holder attached to the pump. Liquid which is collected in the trap must never be returned to the first bubbler. The bubblers must be maintained in a vertical position during sampling.
- 8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.
- 8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate of 0.2 liter per minute. The flow rate should be known with an accuracy of 5%.
- 8.3.6 Turn the pump on and begin sample collection. 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.
- 8.3.7 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.
- 8.3.8 Remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1-2 ml of unused 0.1N potassium hydroxide, and add the wash to the bubbler bottle. Seal the bubbler with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping. Repeat this process for the liquid collected in the trap. Do not combine the two solutions in one bubbler bottom. Be sure each bubbler bottom is properly labeled.

- 8.3.9 Attempt to minimize sample spillage. Do not allow the solution level in the first bubbler to fall below 10 ml. Replace spilled solution with fresh 0.1N potassium hydroxide. If spillage is not evidenced by liquid in the trap or in the tubing, evaporation has probably occurred. Use distilled water to bring the solution volume back up to 15 ml.
- 8.3.10 The filter should be removed from the filter holder and discarded. The holders should be cleaned and saved for future use.
- 8.3.11 With each batch of ten samples submit one bubbler containing 15 ml of 0.1N potassium hydroxide prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.
- 8.3.12 Samples should be stored or shipped in containers which prevent exposure to light so that maximum stability is maintained.

8.4 Analysis of Samples

- 8.4.1 Empty the contents of the bubbler into a 25-ml volumetric flask, using 2 ml of 0.1N potassium hydroxide to rinse the bubbler bottle. Add rinse to the volumetric flask, dilute to 25 ml with 0.1N potassium hydroxide.
- 8.4.2 Potentiometric Measurements
1. The samples are analyzed by immersing the cyanide ion electrode and reference electrode in the sample solutions and recording the millivolt reading. Both the samples and standards should be stirred while the readings are being taken. The reading should be taken after the meter has stabilized. Follow instrument manufacturer's instruction manual for proper operation and measurement procedures.
 2. To obtain the most reliable results, a set of standards should be run both before and after analysis of samples. The standard solutions should be bracket samples of similar responses. A calibration curve is then constructed as given in Section 9.3.
- 8.4.3 Appropriate bubbler blanks must be analyzed by the same procedure used for the samples.

8.5 Determination of Sample Recovery

- 8.5.1 Need for Determination. To eliminate any bias in the analytical method for hydrogen cyanide, it is necessary to determine the recovery of the analyte. The analyte recovery should be determined in duplicate over the concentration range of interest. If the recovery of the analyte is less than 95%, the appropriate correction factor should be used to calculate the "true" value.
- 8.5.2 Procedure for Determining Recovery. A weighed amount of the analyte, preferably equivalent to the concentration found in the sample, is added to 25 ml of 0.1N potassium hydroxide. The solutions are then analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm 5\%$.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of cyanide equivalent to that present in a 12-liter sample at the selected level was used to determine analytical method recovery. Twenty-five milliliters of 0.1N potassium hydroxide was added by pipet to 18 beakers used for potentiometric measurements. Six beakers were spiked with an amount of cyanide equivalent to 0.5, 1 and 2X the OSHA standard. This was accomplished by taking 20, 40 and 80 μ l aliquots of a solution containing 8.21 mg of potassium cyanide per milliliter of 0.1N potassium hydroxide. A parallel blank was also prepared except no sample was added to it. All solutions were then analyzed as in Section 8.4.

The recovery equals the average weight in μ g recovered divided by the weight in μ g added, or

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

The analytical recovery is used to calculate the corrected μ g/sample (Section 10.4). If the recovery is greater than 95% no correction should be applied.

9. Calibration and Standards

- 9.1 Prepare a series of standards equivalent to one-hour collections over the range of 0.1-3 times the OSHA standard (see Section 7.4.2). These standards should be freshly prepared on a daily basis. It is most convenient to express concentration in terms of cyanide molarity. In this way no molecular-weight conversions are needed in calculating hydrogen cyanide concentration.
- 9.2 The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice

will minimize the effect of observed fluctuations or variations in millivolt readings during any given day.

- 9.3 On semilog paper, plot the millivolt readings vs. cyanide ion concentrations of the standards. The cyanide ion concentration in moles per liter is plotted on the log axis.

10. Calculations

- 10.1 Determine the cyanide ion concentration in terms of moles per liter by using the calibration curve constructed in Section 9.3.
- 10.2 To calculate the micrograms of hydrogen cyanide collected, the following formula is used:

$$\mu\text{g Hydrogen Cyanide} = \text{Molarity cyanide ion (Section 10.1)} \\ \times 27.03 \times 10^6 \times 0.025$$

where:

27.03 = molecular weight in grams per mole

0.025 = sample solution volume in liters

- 10.3 Corrections for the blank must be made for each sample bubbler.

$$\text{Total } \mu\text{g HCN} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample}$ = $\mu\text{g HCN}$ found in sample bubbler

$\mu\text{g blank}$ = $\mu\text{g HCN}$ found in blank bubbler.

- 10.4 Divide the total μg of HCN by the recovery to obtain the corrected $\mu\text{g HCN/sample}$.

$$\text{Corrected } \mu\text{g HCN/sample} = \frac{\text{Total } \mu\text{g HCN}}{\text{Recovery (Section 8.5.2)}}$$

- 10.5 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 = sampling 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 ($^{\circ}$ K)

T_2 = temperature of air sampled ($^{\circ}$ K)

- 10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m (μ g per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g HCN (Section 10.4)}}{\text{Sampling Volume (liters)}}$$

- 10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{27.03} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature ($^{\circ}$ C) of air sampled

24.45 = molar volume (liter/mole) at 25° C and 760 mm Hg

27.03 = molecular weight (g/mole) of hydrogen cyanide

760 = standard pressure (mm Hg)

298 = standard temperature ($^{\circ}$ K)

11. References

- 11.1 Cyanide (as CN), NIOSH Method No. S250, prepared under NIOSH Contract No. CDC-99-74-45, 1974-1976.
- 11.2 Technical Services Dept., Orion Research, Cambridge, Mass., personal communication, 1978.
- 11.3 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.
- 11.4 Backup Data Report for Hydrogen Cyanide, No. S288, prepared under NIOSH Contract No. 210-76-0123.

Pentachlorophenol

Analyte:	Pentachlorophenol	Method No.: S297
Matrix:	Air	Range: 0.265-1.130 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.072
Procedure:	Filter and bubbler collection, ethylene glycol extraction, HPLC	Validation Date: 12/23/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter connected in series to a midget bubbler containing 15 ml of ethylene glycol to collect pentachlorophenol.
- 1.2 The filter and bubbler are disconnected. The filter is removed from the filter holder and added to the bubbler flask.
- 1.3 Just before analysis, ten milliliters of methanol is added to the bubbler flask. The resulting sample is analyzed by high performance liquid chromatography using a UV detector set at 254 nm.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.2654-1.131 mg/cu m at an atmospheric temperature of 24°C and pressure of 761 mm Hg, using 180-liter samples.
- 2.2 The upper limit of the range of the method is dependent on the capacity and collection efficiency of the sampling system. The method may be extended to higher values than those tested by dilution of the sample solution.

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 compound that has the same retention time as pentachlorophenol 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 0.2654-1.131 mg/cu m was 0.0721. This value corresponds to a standard deviation of 0.036 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 A collection efficiency of at least 99% was determined for the collection media (filter and bubbler in series), thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method. The average recovery from the filters was 100.9%. The average recovery from samples that were stored eight days was 95.3%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 Collected samples are analyzed by means of a quick, instrumental method.
- 5.2 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 Filter Units. 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 three-piece filter holder. It is important that a stainless steel screen be used since other filter supports may retain part of the vapor.
- 6.2 Flexible Teflon or polyethylene tubing to connect the holder to the bubbler.
- 6.3 A glass midget bubbler containing 15 ml of ethylene glycol.

- 6.4 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ is used. The sampling pump is protected from splashover or solvent condensation by a second empty bubbler positioned between the exit arm of the first bubbler and the pump.
- 6.5 Barometer.
- 6.6 Thermometer.
- 6.7 High performance liquid chromatograph capable of UV detection at a wavelength of 254 nm and a sample injection valve with a 20-microliter external sample loop.
- 6.8 Column (30-cm x 3.9-mm I.D. stainless steel) packed with μ Bondapak C₁₈. The porous packing material consists of silica particles with a bonded coating of C₁₈ organo-silane. This packing can be obtained from Waters Associates, Milford, Massachusetts.
- 6.9 An electronic integrator or some other suitable method for measuring peak areas.
- 6.10 Tweezers.
- 6.11 Microliter syringes, 50 and 100-microliter.
- 6.12 Volumetric flasks, convenient sizes for preparing standard solutions.
- 6.13 Pipets, convenient sizes for preparing standard solutions and 10 and 15-ml pipets for measuring the extraction medium.
- 6.14 Teflon tubing (15-cm long x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

All reagents used must be ACS reagent grade or better.

- 7.1 Pentachlorophenol.
- 7.2 Dowicide EC-7 (purified pentachlorophenol).
- 7.3 Ethylene glycol.
- 7.4 Methanol, distilled in glass.
- 7.5 Isopropanol.
- 7.6 Water, deionized and distilled.

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, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter holder, bubbler and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three-piece filter holder and close firmly. The filter is backed up by a stainless steel screen. Secure the filter holder together with tape or shrinkable band.

8.3.2 Pipet 15 ml of ethylene glycol into each midget bubbler, and mark the liquid level. Be sure that the bubbler frit is completely immersed in the ethylene glycol.

8.3.3 Remove the filter holder plugs and attach the outlet of the filter holder to the inlet arm of the midget bubbler using a short piece of flexible polyethylene or Teflon tubing. Connect the outlet arm of the midget bubbler to a second empty bubbler and then to the personal sampling pump, using short pieces of flexible tubing. The bubblers must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter holder.

8.3.5 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known to within $\pm 5\%$.

8.3.6 Turn the pump on and begin sample collection. 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 checked frequently and readjusted as needed. Sampling should be terminated when the rotameter cannot be readjusted.

8.3.7 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.

- 8.3.8 After sampling, disconnect the filter and bubblers. Remove first the bubbler stem, and remove the filter from the filter holder with clean tweezers and add it to the bubbler. It is necessary to place the filter in the bubbler solution at this time, otherwise loss of pentachlorophenol from the filter by vaporization might occur. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The splashover trap should have the inlet and outlet of the bubbler stem sealed in a similar manner. The standard taper joint of the bubblers should be taped securely to prevent leakage during shipping.
- 8.3.9 With each batch or partial batch of ten samples submit one bubbler containing ethylene glycol and a blank filter from the same lot of filters used for sample collection. This filter and bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label this filter and bubbler as the blank.
- 8.3.10 The bubblers should be shipped in a suitable container, designed to prevent damage in transit. The samples should be shipped to the laboratory as soon as possible.
- 8.3.11 Bulk Sample. A bulk sample of the suspected material should be submitted to the laboratory in a glass container closed by a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

8.4 Analysis of Samples

- 8.4.1 If the sample volume is less than 15 ml, add ethylene glycol until the volume reaches the 15-ml mark. If the sample volume is more than 15 ml, determine the volume and make an appropriate volume correction in the calculations indicated in Section 10.1.
- 8.4.2 Add 10 ml of methanol to each sample just before analysis and mix the solution gently but thoroughly.
- 8.4.3 HPLC Conditions. The typical operating conditions for the high pressure liquid chromatograph are:

Column Temperature: Ambient
Column Pressure: 2300 psi
Flow Rate: 1.6 ml/min
Mobile Phase: 60% methanol/40% water (V/V)
Detector: UV photometer at 254 nm
Capacity Ratio: 1.8

- 8.4.4 Injection. The first step in the analysis is to inject the sample into the high pressure liquid chromatograph. The chromatograph is fitted with a sample injection valve and a 20-microliter sample loop. Flush this loop thoroughly with solvent (300 microliters), then fill the loop with sample solution and inject.
- 8.4.5 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.

8.5 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 should be determined in duplicate and should cover the concentration range of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.
- 8.5.2 Procedure for Determining Recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The filter is then immediately placed into 15 ml of ethylene glycol. Prior to analysis, as described in Section 8.4, 10 ml of methanol is added.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 180-liter sample at the selected level was used to determine the analytical method recovery. A stock solution containing 10.00 milligrams of pentachlorophenol per milliliter of isopropanol was prepared. Aliquots of 4.5, 9 and 18 microliters were added to the cellulose membrane filters and air-dried to produce samples equivalent to 180-liter collections at 0.5, 1 and 2X the OSHA standard level. The analytical samples were then placed in 15 ml of ethylene glycol and allowed to stand overnight. A parallel blank filter was also prepared except that no sample was added to it. Just prior to analysis, as described in Section 8.4, 10 ml of methanol was added.

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

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.25 to 3 times the OSHA standard for the sample under study, is 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 $\mu\text{g}/25\text{ ml}$ versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time as the samples. This will minimize the effect of known day-to-day variations and variations during the same day of the UV detector response.

9.1 Prepare a 10 mg/ml pentachlorophenol stock standard solution by dissolving 100 mg pentachlorophenol in isopropanol and diluting to 10 ml in a volumetric flask.

9.2 From the above stock solution, appropriate aliquots are withdrawn and added to a mixture of 15 ml ethylene glycol and 10 ml methanol. Prepare at least five working standards to cover the range of 22.5-270 $\mu\text{g}/25\text{ ml}$. This range is based on a 180-liter sample. Analyze samples as per Section 8.4.

9.3 Prepare a standard calibration curve by plotting concentration of pentachlorophenol in $\mu\text{g}/25\text{ ml}$ versus peak area.

10. Calculations

10.1 Read the weight, in $\mu\text{g}/25\text{ ml}$, corresponding to each peak area from the appropriate standard curve. No volume correction is needed, because the standard curve is based on $\mu\text{g}/25\text{ ml}$ of ethylene glycol/methanol 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 sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample solution}$$

$$\mu\text{g blank} = \mu\text{g found in blank solution}$$

10.3 Divide the total weight by the recovery (Section 8.5.2) to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

- 10.4 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 = sampling flow rate
- t = sampling time
- P₁ = pressure during calibration of sampling pump (mm Hg)
- P₂ = pressure of air sampled (mm Hg)
- T₁ = temperature during calibration of sampling pump (°K)
- T₂ = temperature of air sampled (°K)

- 10.5 The concentration of pentachlorophenol in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.4)}}$$

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication 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 Pentachlorophenol, prepared under NIOSH Contract No. 210-76-0123.

Sulfur Dioxide

Analyte:	Sulfur Dioxide	Method No.: S308
Matrix:	Air	Range: 6.6-26.8 mg/cu m
OSHA Standard:	5 ppm (13 mg/cu m)	Precision ($\overline{CV}_T$): 0.054
Procedure:	Bubbler collection, titration with barium perchlorate	Validation Date: 7/8/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a midjet bubbler containing hydrogen peroxide. Sulfur dioxide vapor is collected and oxidized to sulfuric acid.
- 1.2 Isopropyl alcohol is added to the contents in the bubbler, and the pH of the sample is adjusted with dilute perchloric acid.
- 1.3 The resulting solution is titrated with 0.005 M barium perchlorate using Thorin as the indicator. There is a sharp color change from yellow or yellow-orange to pink when the end point is reached.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 6.55-26.8 mg/cu m at an atmospheric temperature and pressure of 21°C and 757 mm Hg, using a 90-liter sample.
- 2.2 The upper limit of the range of the method is dependent on the capacity of the midjet bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

3. Interferences

- 3.1 The presence and suspected identities of other air contaminants must be recorded and reported to the laboratory. Volatile phosphates will be a significant interference. Volatile metals can be converted to metallic ions in the bubbler. The presence of these and other air contaminants must be noted so that the analyst can pretreat the sample.
- 3.2 Particulate contaminants such as sulfate, sulfuric acid, and metals are removed by the prefilter.

- 3.3 Metal particulates will also be removed using the 0.8 micrometer cellulose ester membrane filter. Volatile metal interferences that are converted to metallic ions in the midget bubbler can be removed by passing the sample through a cation exchange resin.
- 3.4 Concentrations of phosphate ions greater than the sulfate ion concentration will cause appreciable interference. Particulate phosphates will be removed using the 0.8 micrometer cellulose ester membrane filter connected in front of the midget bubbler. Phosphates can also be removed by precipitation with magnesium carbonate.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 6.55-26.8 mg/cu m was 0.054. This value corresponds to a standard deviation of 0.70 mg/cu m at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.5% lower than the "true" concentrations for 18 samples. 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 Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, storage stability, and collection efficiency were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 12.90 mg/cu m indicate that collected samples are stable for at least one week.

5. Advantages and Disadvantages of the Method

- 5.1 Collected samples are analyzed by means of a quick and simple method.
- 5.2 The sulfuric acid formed is stable and nonvolatile, making this manner of collection of sulfur dioxide desirable.
- 5.3 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.
- 5.5 The precision of the method is limited by the reproducibility of the pressure drop across the prefilter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

6. Apparatus

- 6.1 Prefilter unit: The prefilter unit, which is used to remove particulate interferences, consists of a 37-mm diameter cellulose ester membrane filter (Millipore Type AA or equivalent) with a pore size of 0.80 micrometer contained in a 37-mm two-piece cassette filter holder. The filter is supported by a stainless steel screen.
- 6.2 A glass midget bubbler containing the collecting medium.
- 6.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a trap. The trap is a midget bubbler or impinger with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.
- 6.4 Thermometer.
- 6.5 Manometer.
- 6.6 Volumetric Flasks: Convenient sizes for preparing standard solutions.
- 6.7 Beakers: 250-ml.
- 6.8 Pipets: Convenient sizes for preparing standard solutions and for measuring the collection medium.
- 6.9 Burette: A burette of 10-ml capacity, graduated in 0.05 ml.
- 6.10 Daylight fluorescent lamp to aid in identifying the end point.

7. Reagents

- 7.1 Isopropanol, reagent grade.
- 7.2 Barium Perchlorate, 0.005 M. Dissolve 2.0 g barium perchlorate trihydrate in 150 ml of distilled water and add 850 ml of isopropanol. Adjust the pH to about 3.5 with perchloric acid. Standardize against 0.005 M sulfuric acid.
- 7.3 Thorin. Prepare a 0.1% to 0.2% solution in distilled water.
- 7.4 Standard Sulfate Solution. Prepare a 0.005 M solution of sulfuric acid and standardize by titration with 0.02 M sodium hydroxide.
- 7.5 Perchloric Acid, 1.8%. Dilute 25 ml of reagent grade perchloric acid (70-72%) to one liter with distilled water.
- 7.6 Hydrogen Peroxide, 0.3 N. Dilute 17 ml of 30% hydrogen peroxide solution to one liter with distilled water.
- 7.7 pH paper, Hydrion.

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, and dried.
- 8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette, bubbler, and splashover tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The filter is backed up by a stainless steel screen rather than a filter pad. Secure the cassette holder together with tape or shrinkable band.
 - 8.3.2 Pipet 15 ml of 0.3 N hydrogen peroxide into each midget bubbler.
 - 8.3.3 Remove the filter holder's plugs and attach the outlet of the filter holder to the inlet arm of the midget bubbler with a short piece of flexible tubing. The outlet of the midget bubbler is attached to the pump's inlet or a trap which may be used to protect the pump during personal sampling. The trap is a midget impinger or bubbler with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.
 - 8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
 - 8.3.5 At levels corresponding to the standard, a sample size of 90 liters is recommended. Sample at a known flow rate between 1.5 and 1.0 liter per minute.

At levels outside of range over which the method was validated, adjust the sample volume to collect between 0.6 and 2.3 milligrams of sulfur dioxide.
 - 8.3.6 Turn the pump on and begin sample collection. 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.
 - 8.3.7 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.

- 8.3.8 Remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1-2 ml of unused 0.3 N hydrogen peroxide, and add the wash to the bubbler bottle. Replace the bubbler stem. The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping.
- 8.3.9 The filter should be removed from the cassette filter holder and discarded. The cassette holders and stainless steel screens should be cleaned and saved for future use. Care should be taken to minimize spillage or loss of sample by evaporation at all times.
- 8.3.10 With each batch of ten samples submit one bubbler containing 15 ml of 0.3 N hydrogen peroxide prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.

8.4 Analysis of Samples (Reference 11.3)

- 8.4.1 Empty the contents of the bubbler into a 250-ml beaker, using 2 ml of 0.3 N hydrogen peroxide to rinse the bubbler flask. Add rinse to the beaker.
- 8.4.2 Add 100 ml of isopropanol to the beaker.
- 8.4.3 Adjust the pH of the sample to 3.5 with 1.8% perchloric acid. Add 8-10 drops of Thorin indicator, and titrate the sample with barium perchlorate to a pink colored end point.
- 8.4.4 Analyze the standard and absorbing solution blank in the same manner.

9. Calibration and Standards

- 9.1 The barium perchlorate solution is standardized by titrating a 5-ml aliquot of the standardized 0.005 M sulfuric acid to the end point with Thorin as the indicator.
- 9.2 The molarity of barium perchlorate is calculated as follows:

$$M_{\text{Ba}(\text{ClO}_4)_2} = \frac{\text{ml}_{\text{H}_2\text{SO}_4} \times M_{\text{H}_2\text{SO}_4}}{\text{ml}_{\text{Ba}(\text{ClO}_4)_2}}$$

where:

$\text{ml}_{\text{H}_2\text{SO}_4}$ = ml H_2SO_4 solution needed to titrate $\text{Ba}(\text{ClO}_4)_2$

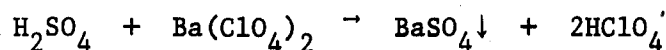
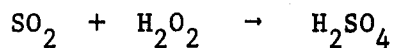
$M_{\text{H}_2\text{SO}_4}$ = molarity of H_2SO_4

$\text{ml}_{\text{Ba}(\text{ClO}_4)_2}$ = ml $\text{Ba}(\text{ClO}_4)_2$ used

The molarity of $\text{Ba}(\text{ClO}_4)_2$ should be checked periodically.

10. Calculations

10.1 The following reactions are the basis for this analytical method.



10.2 The mg of SO_2 can be calculated as follows:

$$\text{mg SO}_2 = M_{\text{Ba}(\text{ClO}_4)_2} \times \text{ml}_{\text{Ba}(\text{ClO}_4)_2} \times 64$$

where:

$M_{\text{Ba}(\text{ClO}_4)_2}$ = molarity of $\text{Ba}(\text{ClO}_4)_2$ solution

$\text{ml}_{\text{Ba}(\text{ClO}_4)_2}$ = ml of $\text{Ba}(\text{ClO}_4)_2$ solution needed to titrate the sample.

64 = molecular weight of SO_2

10.3 Corrections for the blank must be made for each sample.

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

where:

mg sample = mg SO_2 found in sample bubbler

mg blank = mg SO_2 found in blank bubbler

10.4 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
t = sampling time
P₁ = pressure during calibration of sampling pump (mm Hg)
P₂ = pressure of air sampled (mm Hg)
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K)

10.5 The concentration of sulfur dioxide in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.3)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters)} \text{ (Section 10.4)}}$$

10.6 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 (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of sulfur dioxide
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.
- 11.2 Backup Data Report for Sulfur Dioxide, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Fritz, J. S. and S. S. Yamamura, Anal. Chem., 27, 1461, (1955).

Zinc Oxide Fume

Analyte:	Zinc Oxide Fume	Method No.:	S316
Matrix:	Air	Range:	2.4 - 9.9 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.1039
Procedure:	Collection on filter, X-ray diffraction analysis	Validation Date:	6/10/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a membrane filter (copolymer of polyvinylchloride and acrylonitrile) to collect zinc oxide fume.
- 1.2 The filter samples are scanned by X-ray diffraction to determine the presence of zinc oxide fume and other phases that cause matrix interference.
- 1.3 The mass of zinc oxide fume present is determined by measuring the diffraction peak intensity of zinc oxide at 31.75° . The mass is calculated from calibration data obtained from external standards prepared by filtration of a suspension of zinc oxide in isopropanol.

2. Range and Sensitivity

- 2.1 This method was validated for zinc oxide fume over the range of 2.4-9.9 mg/cu m for a 180-liter sample at atmospheric temperature and pressure in the range of $20-22^\circ\text{C}$ and 760-767 mm of Hg.
- 2.2 For a sample size of 180 liters, the working range of the method is estimated to be 1-10 mg/cu m. For concentrations greater than 10 mg/cu m, a 180-liter sample size would yield zinc oxide levels beyond the linear range of the calibration curve.
- 2.3 The method may be extended to higher sample concentrations by collecting a smaller sample volume in order to prevent collection of too much sample particulate. Collection of too much sample is undesirable not only because it can bring about loss of collected sample through flaking off the filter but also because of the probability of sample X-ray absorption which would prevent accurate intensity measurement.

- 2.4 For screening an unknown sample, the presence of 50 μg or more of zinc oxide can be determined by an X-ray diffraction scan. Once the zinc oxide has been established to be present in the sample, it is estimated that the method can be used to determine as little as 15 μg , although the working range is as noted in Section 2.2. The absolute detection limit has not been rigorously established.

3. Interferences

- 3.1 Several minerals have diffraction peaks that interfere with the diffraction peaks for zinc oxide; these include the following at the primary and secondary peaks:

<u>Primary Peak</u>	<u>Secondary Peak</u>
0.2476 nm ($36.26=2\theta$, Cu K α)	0.2816 nm ($31.75=2\theta$, Cu K α)
α - Fe_2O_3	$\text{Zn}(\text{NH}_3)_2 \text{Cl}_2$
$(\text{NH}_4)_3 \text{Zn Cl}_5$	$(\text{NH}_4)_2 \text{Zn Cl}_4$
$(\text{NH}_4)_2 \text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2 \text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Zn	$(\text{NH}_4)_3 \text{Zn Cl}_5$

Many other compounds may interfere and their presence must be determined for each sample. The presence of matrix phase interference can be verified by X-ray diffraction analysis. Analytical measurements are made using the secondary peak of zinc oxide to avoid interference by Zn or Fe_2O_3 although it has a poorer detection limit and precision than the primary peak.

- 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.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analysis method for zinc oxide fume in the range of 2.4-9.9 mg/cu m was 0.1039. This value corresponds to a 0.52 mg/cu m standard deviation at the OSHA standard level for zinc oxide fume. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.
- 4.2 A collection efficiency of 100% was determined for the collection medium at the 2S level; thus, no bias was introduced in the sample collection step. Likewise, no significant bias in the analytical method is expected beyond the errors associated with the X-ray measurement. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical

method. This is supported by the results of the independent verification of generator concentration described in Reference 11.1

5. Advantages and Disadvantages

- 5.1 The X-ray diffraction method is specific for zinc oxide fume with sensitivity equivalent to or greater than other methods (infrared and colorimetric). The method is non-destructive, rapidly performed, reduces sample manipulation to a minimum and may be automated.
- 5.2 The method does not distinguish zinc oxide fume from zinc oxide dust.
- 5.3 The method has several disadvantages that may affect its accuracy. As it is an external standard method, the mass absorption coefficient of the sample is not easily measured and is necessarily ignored. This should present no difficulty if sample loadings are kept below $225 \mu\text{g}/\text{cm}^2$ for copper K α radiation. The problem is less critical for more penetrating radiation. Absorption may also be a problem with regard to particle size. If the zinc oxide fume collected in the field has a very different particle size range from that of the zinc oxide standard used, some problems could arise due to differences in particle penetration into the filter matrix before being trapped. The filter material absorbs the radiation causing an error that cannot be corrected for.
- 5.4 Application of the method requires an experienced analyst.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of zinc oxide fume content has the following components:
 - 6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm, 3-piece filter holder.
 - 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.
 - 6.1.3 Thermometer
 - 6.1.4 Barometer
 - 6.1.5 Stopwatch

- 6.2 Filter Media: membrane filter (copolymer of polyvinylchloride and acrylonitrile), 37-mm diameter, 0.8 micrometer pore size.
- 6.3 X-ray diffraction equipment with a copper target X-ray tube.
- 6.4 Microbalance.
- 6.5 Aluminum filter holder for XRD.
- 6.6 Chip of mica (~ 0.5 sq mm by 0.02 mm thick) glued to an aluminum plate or equivalent, for use as an instrument calibration standard. Other standard materials may be substituted.
- 6.7 Storage chamber with desiccant.
- 6.8 Non-serrated, non-magnetic forceps.
- 6.9 Volumetric flask, 1-liter capacity.
- 6.10 Ultrasonic agitator.
- 6.11 Graduated cylinder, 50 ml or convenient size
- 6.12 Filtration Unit - Pyrex filter funnel (with 34-mm frit support) and clamp. This filtration assembly will hold a 47-mm filter.
- 6.13 Filter flask, 500 ml or convenient size.
- 6.14 PetriSlide (Millipore) or a plastic Petri dish to hold the filter samples.
- 6.15 Flow Meter.

7. Reagents

All reagents used should be ACS reagent grade or better.

- 7.1 Zinc oxide powder. Average particle size should be less than $1.0 \mu\text{m}$ (available from N.J. Zinc Company, 160 Front Street, New York, N.Y., Photox 801, particle size $0.37 \mu\text{m}$).
- 7.2 Isopropanol
- 7.3 Desiccant such as Drierite or equivalent.
- 7.4 Standard suspensions of zinc oxide in isopropanol, prepared fresh daily as described in Section 9.1.

8. Procedure

- 8.1 **Cleaning of Equipment.** All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water. Then the glassware should be washed with nitric acid, tap water and distilled water and then dried.
- 8.2 **Calibration of Personal Pumps.** Each personal pump must be calibrated with a representative filter holder 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 To collect zinc oxide fume, a personal sampling pump is used to pull air through a membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.
- 8.3.2 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 handling as for the samples except that no air is drawn through it. Label this as a blank.
- 8.3.3 **Shipping.** The filter holders should be shipped in a suitable container, designed to prevent damage in transit.
- 8.4 **Analysis of Samples**
- 8.4.1 Open the filter holder, carefully remove the membrane filter from the backup pad with the aid of forceps and secure (with double-sided tape, for example) to an aluminum (or magnesium) sample holder for the diffractometer.
- 8.4.2 Insert into the diffractometer and scan over the range of 10 to 70° in 2θ for CuK_α radiation. The presence of crystalline zinc oxide is determined by the presence of diffraction peaks as follows:

<u>Phase</u>	<u>Primary Peak</u>	<u>Secondary Peak</u>	<u>Tertiary Peak</u>
Zinc Oxide	36.25°	31.75°	34.44°

The presence of interfering compounds can be determined by identifying other X-ray diffraction peaks.

- 8.4.3 The most intense diffraction peak (primary or secondary only) of zinc oxide that is free from matrix interference is analyzed by hand peaking (or scanning) to the maximum intensity and measuring intensity by the fixed time scaler mode. (This method was validated using the secondary peak and a 60 second scan time.) A comparable measurement is made for background intensity at a nearby position selected by reference to the diffraction scan (Section 8.4.2). The measured peak intensity is then corrected for background. Use a similar method for determining instrument stability using mica standards.
- 8.4.4 If there is matrix interference with all usable diffraction peaks for the zinc oxide (Section 8.4.3), the level of interference must be determined from the relative intensity of other diffraction peaks associated with the interfering phase for correcting the measured zinc oxide intensity.
- 8.4.5 At periodic intervals (every four to six samples), peak ($2\theta=26.9$ for $\text{CuK}\alpha$ radiation) and background intensities are collected for the mica calibration standard by the procedure described in Section 8.4.3. This procedure allows a rapid check of instrument stability.
- 8.4.6 All intensity values are recorded on a suitable analysis data sheet.

9. Calibration and Standards

- 9.1 Zinc oxide fume standards are prepared by the suspension/filtration method. A set of at least six standards should be prepared within the range of 250-3000 micrograms per filter. These standards are prepared as described below.
 - 9.1.1 Preparation of alcohol suspension.
 - 1. Quantatively transfer a weighed sample (5-60 mg) of pure zinc oxide powder into a 1-liter volumetric flask. It is preferable to prepare independent standard solutions such that a 50-ml aliquot of the solutions would give the desired amount of zinc oxide on the filter (250-3000 micrograms). Treat this sample with approximately 50-100 ml of isopropyl alcohol. Do not dilute to volume at this point.
 - 2. Put the flask in an ultrasonic agitator for 10 minutes. Cool flask to room temperature before dilution to volume.

3. Dilute to the 1-liter mark with more isopropyl alcohol and leave in the ultrasonic agitator for another 30 minutes. Cool to room temperature and add more isopropyl alcohol, if necessary. Note: Manually shake this suspension, which will be used to prepare the standard filters, before removing any aliquot.

9.1.2 Preparation and analysis of calibration standards.

1. A 47-mm membrane filter (copolymer of polyvinyl-chloride and acrylonitrile) is placed in position between the funnel section and frit support of the filtration unit assembly (Section 6.12) and the unit is secured together with a clamp.
2. Attach the filtration unit assembly to a filter flask. Do not apply vacuum at this point.
3. Manually shake or agitate the appropriate stock standard suspension and measure 50 ml (or desired volume but not less than 50 ml) of the suspension in a graduated cylinder.
4. Transfer the aliquot to the filter funnel. Rinse the graduate with a small volume (ca. 3 times) of isopropanol and add rinsings to the aliquot in the filter funnel.
5. Apply a vacuum with a water aspirator. Immediately wash down the walls of the filter funnel with a gentle flow of isopropanol before all of the suspension has been filtered. Dry the filter by continuous filtration under vacuum for a few minutes (2-5).
6. Carefully remove the filter from the filtration unit and transfer to the PetriSlide holder with the aid of the forceps. Store container over a desiccant.
7. For each standard filter, measure the zinc oxide peak and background intensities by the procedure described in Section 8.4.3.
8. Prepare a calibration curve by plotting on linear graph paper, the peak intensity (corrected for background intensity) vs the mass of zinc oxide on the filter per effective unit area in sq cm. This area can be determined by measuring the internal diameter of the filter funnel which determines the exposed area of the filter. Express concentration

in micrograms zinc oxide per sq cm. This procedure will normalize the probable differences between the area of calibration standards prepared by the liquid suspension/filtration method and the area of the sample filters. The effective collection area of the air sample filter is 8.92 sq cm.

10. Calculations

10.1 Read the mass loading, in $\mu\text{g}/\text{sq cm}$, corresponding to the sample peak intensity minus background intensity from the standard curve.

10.2 Multiply this mass loading by the effective filter area.

$$W = LA$$

where:

W = mass of zinc oxide in the sample in μg

L = mass loading in $\mu\text{g}/\text{sq cm}$ determined from the calibration curve

A = effective area of sample (8.92 sq cm)

10.3 Corrections for the blank must be made for each sample.

$$\text{Correlated } \mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample}$ = W found in sample filter

$\mu\text{g blank}$ = W found in blank filter

10.4 For personal sampling pumps with rotameters only, the following correction for air volumes sampled 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 = sample flow rate

t = sampling time

P_2 = pressure during calibration of sampling pump (mm Hg)

P_1 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 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).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

- 11.1 Zinc Oxide Fume, S316, Backup Data Report prepared under NIOSH Contract No. 210-76-0123.
- 11.2 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/75, 11/8/74, Subject: "Statistical Protocol for Analysis of Data from Contract No. CDC-99-74-75".
- 11.3 P&CAM No.222, Zinc Oxide, published by National Institute of of Occupational Safety and Health, Dept. of HEW, Cincinnati, Ohio.
- 11.4 Haartz, J.C., Bolyard, M. B. and Abell, M. T., "Quantitation of Zinc Chloride and Zinc Oxide in Airborne Samples," presented at the American Industrial Hygiene Conference, Minneapolis, Minnesota, June 1975.

Nitric Acid

Analyte:	Nitrate Ion	Method No:	S319
Matrix:	Air	Range:	2.60 - 10.8 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.082
Procedure:	Impinger collection, ion specific elec- trode	Validation Date:	8/5/77

1. Principle of the Method

- 1.1 Samples are collected by drawing a known volume of air through a midget impinger containing distilled water.
- 1.2 The contents of the impinger are analyzed by direct potentiometry using an ion specific electrode.
- 1.3 The concentration of nitric acid in the sample is determined by comparison of the potential obtained for the sample solution to a calibration curve obtained by measurement of standard solutions.
- 1.4 A calibration standard is run before and after each sample to assure that reliable results are obtained.

2. Range and Sensitivity

- 2.1 This method was validated over the range 2.60 - 10.8 mg/cu m using a 180-liter air sample.
- 2.2 The lower limit of detection for nitrate using the nitrate ion specific electrode is 6×10^{-6} M or 0.4 $\mu\text{g/ml}$ according to the electrode manufacturer.

3. Interference

Constituents of the buffer solution complex, precipitate, decompose or otherwise remove the common interfering anions including Br^- , Cl^- , F^- , I^- , PO_4^{3-} , and NO_2^- (Reference 11.1). However, high concentrations of any of these species should be avoided.

4. Precision and Accuracy

- 4.1 The coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 2.60 - 10.8 mg/cu m was 0.0824. This value corresponds to a 0.4 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 11.2 and 11.3.

- 4.2 A collection efficiency of 97% was determined for HNO_3 in water; thus, no bias was introduced in the sample collection step from this source.
- 4.3 The average concentrations "found" at the OSHA standard levels using the overall sampling and analytical method were 4.3% lower than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.3). In addition, samples were found to be stable when stored for seven days. Thus, CV_T is a satisfactory measure of the precision of the sampling method.

5. Advantages and Disadvantages

- 5.1 Advantages of the method include simplicity, specificity, and speed.
- 5.2 Disadvantages of the method are associated with the collection device, the midget impinger. Not only is it inconvenient, but there is the possible loss of sample if the impinger is not maintained in an upright position during sampling.

6. Apparatus

6.1 Sampling Apparatus

- 6.1.1 Personal Sampling Pump. A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow rate (Reference 11.3). The pump is protected from splashover or water condensation by a piece of glass wool loosely packed within the tubing used to connect the pump and midget impinger.
- 6.1.2 Midget impinger.
- 6.1.3 Distilled water.
- 6.1.4 Pipet, 20-ml or other suitable device for filling the impinger.
- 6.1.5 Barometer.
- 6.1.6 Thermometer.
- 6.1.7 Stopwatch.

- 6.2 Orion 92-07 Nitrate Liquid Ion Exchange Membrane Electrode or equivalent.
- 6.3 Orion 90-02 Double Junction Reference Electrode or equivalent.
- 6.4 Orion Model 801 Digital pH/mV Meter or equivalent.
- 6.5 Volumetric flasks, 25-ml.
- 6.6 Pipets, 20-ml, 5-ml.
- 6.7 Beakers, 50-ml.
- 6.8 Magnetic stirrer and Teflon-coated stirring bars.

7. Reagents

All reagents must be ACS reagent grade or better.

- 7.1 Buffer Solution. Dissolve 4.3g aluminum sulfate, 1.6g boric acid, 3.9g silver sulfate, and 2.4g sulfamic acid in distilled water and dilute to 500 ml. The purpose of this buffer is explained in Reference 11.1.

7.2 Nitric Acid Standards

- 7.2.1 Nitric Acid Stock Solution. Pipet 5 ml of concentrated nitric acid into a 500-ml volumetric flask and dilute to the mark with distilled water. The concentration of the stock solution should be determined accurately by titration of 15-ml aliquots with 0.1N Sodium hydroxide using phenolphthalein as an indicator. Duplicate titrations should agree within 0.1 ml. Calculate the molarity of the stock solution using the equation

$$\text{Molarity} = \frac{(\text{Molarity of NaOH}) \times (\text{ml of NaOH})}{15 \text{ ml}}$$

- 7.2.2 Nitric Acid Working Solution. Pipet 5 ml of the nitric acid stock solution into a 500-ml volumetric flask and dilute to the mark with distilled water.
- 7.2.3 Working Standards. Working standards corresponding to the amounts of nitric acid collected at the 0.5, 1, and 2X the OSHA standard can be prepared by pipeting 5, 10, and 20 ml respectively of the nitric acid working solution into three 25-ml volumetric flasks, each of which contains 5 ml of the buffer solution, and diluting to the mark with distilled water. The concentrations of the working standards are calculated by multiplying the concentration of the nitric acid stock solution by the appropriate dilution factors.

- 7.3 Saturated Sodium Sulfate Solution. Add sufficient sodium sulfate to distilled water to form a saturated solution. The supernatant is used for the outer chamber filling solution in the double junction reference electrode.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware should be washed with detergent and rinsed thoroughly with distilled water.
- 8.2 Calibration of Personal Pump. Each personal pump must be calibrated with a representative midget impinger in the line.
- 8.3 Collection and Shipping of Samples
- 8.3.1 Connect a midget impinger containing 20 ml of distilled water to a sampling pump using a piece of flexible tubing. The tubing should be loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation.
- 8.3.2 The impinger must be maintained in a vertical position during sampling.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the impinger.
- 8.3.4 A sample size of 180 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 180 minutes. The flow rate should be known with an accuracy of at least +5%.
- 8.3.5 Record the ambient temperature and barometric pressure.
- 8.3.6 Remove the impinger stem and tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Rinse the impinger stem with 1 ml of distilled water and add the wash to the impinger bottle. Seal the impinger with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping.
- 8.3.7 With each batch of 10 samples submit one impinger containing 20 ml of distilled water. This impinger should be handled in the same manner as the samples except that no air is drawn through it. Label this impinger as the blank.

8.4 Analysis of Samples

8.4.1 Pipet 5 ml of the buffer solution into a 25-ml volumetric flask.

8.4.2 Transfer the contents of the impinger to the volumetric flask and dilute to the mark with distilled water.

8.4.3 Empty the contents of the volumetric flask into a 50-ml beaker. Add a magnetic stirring bar.

8.4.4 Potentiometric Measurements

8.4.4.1 Immerse the nitrate ion electrode and reference electrode in the sample solution and record the millivolt reading. Both samples and standards should be stirred while readings are taken. The reading should be taken after the meter has stabilized to ± 0.1 mV/10 sec. Follow the instrument manufacturer's instruction manual for proper operation and measurement procedures.

8.4.4.2 Samples should be interspersed between standards as described in Section 9.2.

8.4.5 Appropriate blanks must be analyzed by the same procedure used for the samples.

9. Calibration and Standards

9.1 Nitric acid standards should be prepared as described in Section 7.2. A series of at least three standards should be analyzed prior to the measurement of samples. Plot the potentials in millivolts developed in the standards (on the linear axis) against the molarity of the standards (on the log axis) on semilogarithmic graph paper. The slope of the best straight line fitted to the standards measurements should be equal to 59.2 mV $\pm$ 1 mV/10-fold change in concentration. If the slope of the line does not fall within these limits, consult the troubleshooting section of the electrode manufacturer's instruction manual.

9.2 Samples should be interspersed between standards having concentrations which bracket the concentrations of the samples. At the conclusion of the analysis of a series of samples, calculate the average response in millivolts for each standard. Plot the data as described in Section 9.1. The resulting calibration line is used to calculate the concentrations of the samples.

10. Calculations

- 10.1 Determine the molarity of nitric acid in the sample from the calibration line. Calculate the weight of nitric acid in micrograms corresponding to the molarity of the sample using the equation

$$\text{Molarity} \times (1.575 \times 10^6) = \mu\text{g}$$

- 10.2 Corrections for the blank must be made for each sample impinger.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample impinger}$$

$$\mu\text{g blank} = \mu\text{g found in blank impinger}$$

- 10.3 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

P₁ = atmospheric pressure during calibration of sampling pump (mm Hg)

P₂ = atmospheric pressure of air during sampling (mm Hg)

T₁ = ambient temperature during calibration of sampling pump (°K)

T₂ = ambient temperature of air sampled (°K)

- 10.4 The concentration of nitric acid in the sampled air can be expressed in mg/cu m (= μg/liter) as follows:

$$\text{mg/cu m} = \frac{\mu\text{g (Section 10.2)}}{\text{Air volume sampled (Section 10.3)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg):

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

- P = barometric 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
- MW = molecular weight
- 760 = standard pressure (mm Hg)
- 298 = standard temperature (°K)

11. References

- 11.1 P.J. Milham, A.S. Awad, R.E. Paull, and J.H. Bull, Analyst, 95, 751 (1970).
- 11.2 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.
- 11.3 Backup Data Report for Nitric Acid, No. S319, prepared under NIOSH Contract No. 210-76-0123.
- 11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Nitrogen Dioxide

Analyte:	Nitrite ion, NO_2^-	Method No.: S320
Matrix:	Air	Range: 3.1 - 11.5 ppm
OSHA Standard:	5 ppm (9 mg/cu m)	Precision ($\overline{\text{CV}}_T$): 0.063
Procedure:	Collection on TEA-coated molecular sieve, desorption with TEA, spectrophotometric analysis	Validation Date: 10/28/77

1. Synopsis

A known volume of air is drawn through a sampling tube containing 400 mg triethanolamine-impregnated molecular sieve followed by a backup section of 200 mg triethanolamine-impregnated molecular sieve. Both triethanolamine-impregnated molecular sieve sections in each tube are transferred to flasks, and the nitrogen dioxide is desorbed with an aqueous triethanolamine solution. An aliquot is treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride and the reacted nitrite ion is measured spectrophotometrically.

2. Working Range, Sensitivity and Detection Limit

- 2.1 This method was validated over the range of 3.07-11.49 ppm using a 3.9-liter sample volume. This method is capable of measuring much smaller amounts, since the collection and desorption efficiency has been shown to be adequate at levels of approximately 0.5 ppm NO_2 (Reference 11.1).
- 2.2 The upper limit of the sampling and analytical method is dependent on the adsorptive capacity of the triethanolamine-impregnated molecular sieve section. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. When an atmosphere at 84% relative humidity containing 11.59 ppm NO_2 was sampled at 0.064 liter per minute, 5% breakthrough was not observed after 180 minutes. By comparison with data in reference 11.1, it is expected that breakthrough will occur after three hours (capacity = 90 μL NO_2) at a concentration of 30 ppm NO_2 . The sample size recommended is less than two-thirds the 5% breakthrough capacity to minimize the probability of overloading the sampling tube.

2.3 At levels in excess of 4X the OSHA standard, the treated sample must be diluted so that absorbance is in the linear portion of the standard curve.

2.4 The detection limit under the prescribed sampling and analytical conditions is approximately 0.10 ppm NO₂.

3. Interferences

3.1 Sampling 50 ppm (2X the OSHA standard for NO) nitric oxide interferent on triethanolamine-impregnated molecular sieve is observed to correspond to less than 0.19 ppm NO₂ and can thus be ignored (Reference 11.1).

3.2 Any compound which is collected on triethanolamine-impregnated molecular sieve and which reacts with the colorimetric reagents may act as a positive or negative interference. If such an interference exists, its impact must be determined by independent analysis.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 3.07-11.49 ppm was 0.0630. This value corresponds to a 0.315 ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures may be found in References 11.2 and 11.3.

4.2 In validation experiments, this method was found to be capable of coming within $\pm 25\%$ 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 environmental limit were 2.0% lower than the dynamically generated test concentrations (n=18). The desorption efficiency/analytical method recovery was determined to be 1.047 for a collector loading of 11.82 μ L. In storage stability studies the mean of samples analyzed after seven days were within 9.2% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.3.

A serious bias is possible if the stoichiometric factor for conversion of nitrogen dioxide (gas) to nitrite ion (0.63) is not correct. Several authors have reported values from 0.5-0.9. The value determined by Blacker (Reference 11.4) under similar experimental conditions is 0.63. No recovery correction should be applied to the final result.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal due to the analytical specificity which has been corroborated by years of experimentation by many authors.
- 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 nitrogen dioxide found on the backup TEA tube exceeds 25% of that found on the front tube, the probability of sample loss exists.
- 5.3 The sampling tubes are analyzed by a somewhat tedious spectrophotometric method which utilizes a readily available visible spectrophotometer.
- 5.4 Both adsorbent sections must be analyzed since some breakthrough (<1%) does occur at 2X the OSHA standard level.
- 5.5 A somewhat uncertain stoichiometric factor (0.63) is used in calculation of concentration.
- 5.6 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.

6. Apparatus

6.1 Sampling Equipment

- 6.1.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate of 50 milliliters per minute. The pump must be calibrated with a sampling tube in line.
- 6.1.2 Sampling Tubes. The sampling tube consists of a glass tube, flame-sealed at both ends, with a 7-mm O.D. and a 5-mm I.D., packed with two sections of triethanolamine-impregnated Type 13X, 30-40 mesh molecular sieve. The two sections include a front adsorbing section containing 400 mg and a backup section containing 200 mg. The two sections are separated by a 2-mm portion of silylated glass wool. A 3-mm portion of silylated glass wool 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 triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL

beaker; add 4 g glycerol, 50 mL acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.2 A spectrophotometer capable of measuring absorbance or transmittance at 540 nm.

6.3 Two matched 1-cm silica cells.

6.4 Volumetric flasks, 50-mL and other convenient sizes.

6.5 Beakers, 100-mL.

6.6 Pipets, 1, 5 and 10-mL and other convenient sizes to make standard dilutions.

6.7 Balance.

7. Reagents

Wherever possible, reagents should be ACS reagent grade or better.

7.1 Liquid Absorber. Prepare by dissolving 15.0 g triethanolamine in approximately 500 mL distilled water, adding 0.5 mL n-butanol, and diluting to 1 liter.

7.2 Hydrogen Peroxide Solution 0.02% (v/v). Prepare by diluting 0.2 mL, 30% hydrogen peroxide to 250 mL with distilled water.

7.3 Sulfanilamide Solution. Prepare by dissolving 10 g sulfanilamide in 400 mL distilled water, adding 25 mL concentrated phosphoric acid and diluting to 500 mL.

7.4 NEDA Solution. Prepare by dissolving 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride in distilled water and diluting to 500 mL.

- 7.5 Stock Nitrite Solution, 100 ppm NO_2^- . Prepare by dissolving 0.1500 g sodium nitrite in 1 liter of water.
- 7.6 Working Nitrite Solution, 2 ppm NO_2^- . Prepare by diluting 2 mL of the stock nitrite solution to 100 mL with absorbing solution.

8. Procedure

8.1 Cleaning of Equipment

- 8.1.1 Before use, all glassware should be initially soaked in a mild detergent to remove any residual grease or chemicals.
- 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water, in that order, and then dried.

8.2 Calibration of Personal Sampling Pumps. Each personal pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. 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, break the two ends of the sampling tube to provide an opening of at least one-half of the internal diameter of the tube (5 mm).
- 8.3.2 The tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.
- 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the tube.
- 8.3.4 A sample size of 3.0 liters is recommended. Sample at a known flow rate of 0.05 liter per minute for 60 minutes. The flow rate should be known with accuracy of at least $\pm 5\%$.
- 8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.3.6 The exposed tube should be labeled appropriately and capped with supplied plastic caps.
- 8.3.7 With each batch of five or fewer samples, submit one sampling tube which had been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.

- 8.3.8 Capped sampling 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 order to facilitate removal of the sorbent, the broken ends of each tube are widened with tweezers. The glass wool is removed carefully and discarded, making sure that no sorbent is lost in the process. Both triethanolamine-impregnated molecular sieve sections are transferred to 50-mL volumetric flasks. These two sections are analyzed separately.

8.4.2 Extraction of the Sample. Prior to analysis, liquid absorber is added to the flask to bring the volume to 50 mL. The flask is shaken vigorously for about 30 seconds and the solids allowed to settle.

A blank is prepared similarly with a TEA/molecular sieve section of an unexposed sampling tube.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 540 nm and set the zero and 100% transmittance scale using a 1-cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

1. Pipet 10 mL of the extracted sample into a 50-mL volumetric flask.
2. Add 1.0 mL 0.02% hydrogen peroxide solution, 10.0 mL sulfamilamide solution, and 1.4 mL NEDA solution with thorough mixing after each addition.
3. Allow ten minutes for complete color development.
4. Transfer some of the sample into a 1-cm absorption cell.
5. Measure the absorbance or transmittance at 540 nm using a reagent blank to set zero absorbance.

9. Calibration and Standardization

A series of standards varying in concentration over the range of interest is prepared and analyzed under the same conditions and

during the same time period as the unknown samples. It is convenient to express concentration of standards in terms of μg per 10 mL since 10 mL aliquots of samples are analyzed. A calibration curve is established by plotting absorbance versus concentration in μg per 10 mL.

- 9.1 Using freshly prepared working nitrite solution, prepare at least five calibration standards in absorbing solution to cover a nitrite concentration range of 1 to 18 μg nitrite per 10 mL.
- 9.2 Prepare these standards fresh daily by appropriate dilution of the working nitrite solution using absorbing solution for all dilutions. A reagent blank containing no nitrite should also be prepared.

10. Calculations

- 10.1 Correction for the sample blank (obtained by extraction and analysis of the sampling tube marked "blank") must be made for each sample.

$$\text{Abs}_{\text{corr}} = \text{Abs}_{\text{sample}} - \text{Abs}_{\text{sample blank}}$$

- 10.2 Read the amount of nitrite ion, in $\mu\text{g NO}_2^-$ (ion) per 10 mL, corresponding to the Abs_{corr} from the standard curve.
- 10.3 Multiply the amount of nitrite ion per 10 mL by the factor shown below to obtain the $\mu\text{L NO}_2$ (gas) per 50 mL (total sample) at 25°C and 760 mm Hg.

$$\mu\text{L NO}_2 \text{ (gas) in sample} = \mu\text{g NO}_2^- / 10 \text{ mL} \times \frac{5}{1.88 \times 0.63}$$

where:

$$1 \mu\text{L NO}_2 \text{ (gas)} = 1.88 \mu\text{g NO}_2^- \text{ (gas) at } 25^\circ\text{C and } 760 \text{ mm Hg}$$

$$1 \mu\text{g NO}_2^- \text{ (gas)} = 0.63 \mu\text{g NO}_2^- \equiv \text{"Stoichiometric Factor"}$$

- 10.4 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.5 The concentration of analyte in the air sampled can be expressed in ppm (at standard conditions of 25°C and 760 mm Hg).

$$\text{ppm NO}_2 = \frac{\mu\text{L NO}_2 \text{ (gas) (see Section 10.3)}}{\text{Air volume sampled (liters)} \times \frac{P}{760} \times \frac{298}{T + 273}}$$

Another method of expressing concentration is mg/cu m.

$$\text{mg/cu m} = \text{ppm} \times \frac{46.01}{24.45}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature ($^{\circ}\text{C}$) of air sampled

760 = standard pressure (mm Hg)

298 = standard temperature ($^{\circ}\text{C}$)

24.45 = molar volume (liter/mole) of air at 25°C and 760 mm Hg

46.01 = molecular weight of nitrogen dioxide

11. References

- 11.1 M.A. Willey, C. McCammon, Jr., and L. Doemeny, Am. Ind. Hyg. Assoc. J., 38, 358 (1977).
- 11.2 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.

11.3 Backup Data Report S320 for Nitrogen Dioxide, prepared under NIOSH Contract No. 210-76-0123.

11.4 J. H. Blacker, Am. Ind. Hyg. Assoc. J., 34, 390 (1973).

Nitric Oxide

Analyte:	Nitrite ion, NO_2^-	Method No.: S321
Matrix:	Air	Range: 11.1 - 48 ppm
OSHA Standard:	25 ppm (30 mg/cu m)	Precision ($\overline{\text{CV}}_T$): 0.062
Procedure:	Oxidation to nitrogen dioxide, collection on triethanolamine-coated molecular sieve, desorption with triethanolamine, spectrophotometric analysis	Validation Date: 8/5/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a sampling tube containing in series: 400 mg triethanolamine-impregnated molecular sieve; 1.2 g Draeger oxidizer; 400 mg triethanolamine-impregnated molecular sieve. The first section removes ambient nitrogen dioxide. The Draeger oxidizer transforms nitric oxide to nitrogen dioxide and the last section adsorbs the nitrogen dioxide.
- 1.2 The last triethanolamine-impregnated molecular sieve section in each tube is transferred to a flask, and the nitrogen dioxide is desorbed and hydrolyzed in an aqueous triethanolamine solution to yield nitrite ion. An aliquot is treated with hydrogen peroxide, sulfanilamide and N-(1-naphthyl)-ethylene-diamine dihydrochloride and the reacted nitrite ion is measured spectrophotometrically.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 11.14-47.7 ppm at an atmospheric temperature of 19°C and atmospheric pressure of 764 mm Hg using a 1.5-liter sample volume. This sample volume is based on the adsorptive capacity of the triethanolamine-impregnated molecular sieve to collect nitric oxide vapors at high relative humidity. This method is capable of measuring much smaller amounts, since the collection and desorption efficiency has been shown to be adequate at levels of approximately 0.5 ppm NO_2 and 9 ppm NO (Reference 11.1).
- 2.2 The upper limit of the sampling and analytical method is dependent on the oxidation efficiency of the Draeger oxidizer

and adsorptive capacity of the triethanolamine-impregnated molecular sieve section. Breakthrough is defined as the time that the effluent concentration from the collection tube reaches 5% of the concentration in the test gas mixture. After sampling 108 minutes at 20.94 mL/minute from an atmosphere containing 46.1 ppm NO at 84% relative humidity, 3.8% breakthrough occurred. The recommended sampling volume is thus less than two-thirds the 5% breakthrough capacity. It is expected that the sampling tube will not be suitable at concentrations much in excess of 2X the OSHA standard. Of course, other oxidizable compounds in the air may also reduce the collection efficiency of the sampling tubes.

- 2.3 The detection limit under the prescribed sampling conditions is approximately 0.19 ppm NO.

3. Interferences

- 3.1 Nitrogen dioxide is an interference in this method at some undetermined concentration in excess of 50 ppm. This is due to the unknown capacity of nitrogen dioxide on the first triethanolamine-impregnated molecular sieve section of the sampling tube. Since this is far in excess of the recommended OSHA standard of 1 ppm, such an occurrence is probably not common in the workplace.
- 3.2 Interference due to collection of nitric oxide on the first section of triethanolamine-impregnated molecular sieve is observed to correspond to less than 1% of the NO at 2X the OSHA standard.
- 3.3 Any compound which is collected on the second triethanolamine-impregnated molecular sieve section and which reacts with the colorimetric reagents may act as a positive or negative interference. If such an interference exists, its impact must be determined by independent analysis.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling and analytical method in the range of 11.14-47.7 ppm was 0.0621. This value corresponds to a 1.552 ppm standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3.
- 4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.4% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the

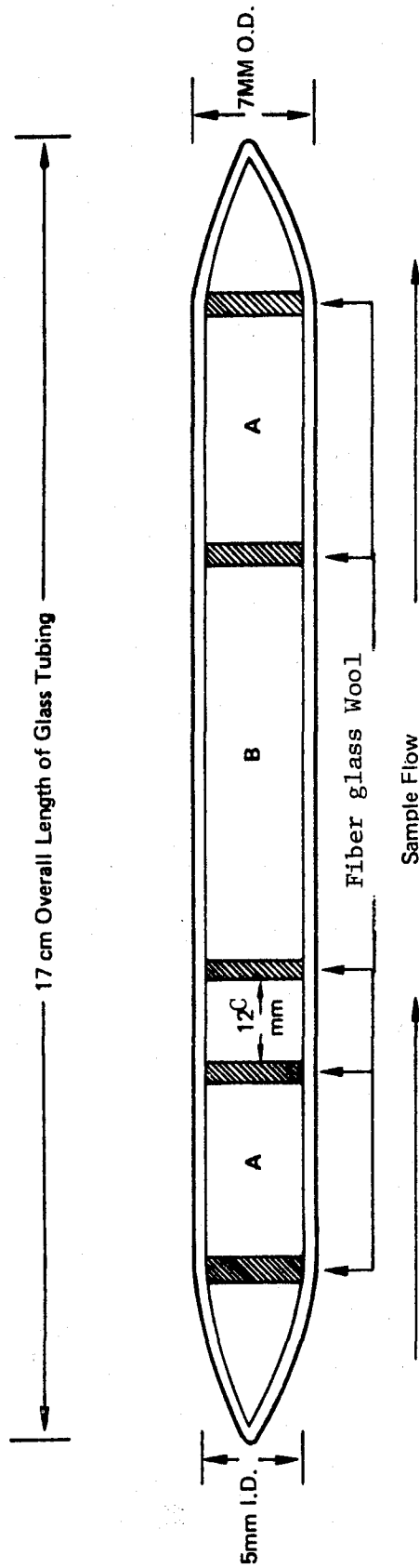
"found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Another possibility is that the stoichiometric factor for conversion of nitrogen dioxide (gas) to nitrite ion (0.63) is not correct. Several authors have reported values from 0.5-0.9. The value determined by Blacker (Reference 11.4) under similar experimental conditions is 0.63. The analytical data described in Reference 11.3 corroborates this value and, therefore, it has been used for method validation. Storage stability studies conducted on samples collected from an atmosphere containing 19.9 ppm NO indicate that collected samples are stable at least 7 days. For these reasons, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal due to the analytical specificity.
- 5.2 The method utilizes a readily available visible spectrophotometer.
- 5.3 If the concentration of nitrogen dioxide present in the environment sampled exceeds the proposed OSHA standard (1 ppm), its concentration may be determined with the same sampling tube as used for nitric oxide analysis.
- 5.4 If the nitric oxide concentration exceeds 2X the OSHA standard, the collection device will not quantitatively collect all of the analyte present.
- 5.5 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 with one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate of 25 milliliters per minute. The pump must be calibrated with a sampling tube in line.
- 6.2 Sampling Tubes. Glass tube with both ends flame-sealed, 17 cm long with 7 mm O.D. and 5 mm I.D., containing the sections listed below and shown schematically in Figure S321-1. The pressure drop across the tube is about 3 cm of H₂O at a flow rate of 25 milliliters per minute.



A. 400 mg Triethanolamine — Impregnated Type 13 X, 30-40 Mesh Molecular Sieve

B. 1.2 g of Oxidation Material No. 1900277 from Draeger Company of Germany, supplied by National Mine Service Co.

C. 12 mm glass spacer tube, 4.0 mm O.D., 2.6 mm I.D.

NITRIC OXIDE SAMPLING TUBE

FIGURE S321-1

S321-4

- 6.2.1 Small plugs of glass wool as shown in Figure S321-1.
- 6.2.2 400-mg triethanolamine-impregnated Type 13X, 30-40 mesh molecular sieve.
- 6.2.3 12-mm glass spacer tube with 4.0 mm O.D., and 2.6 mm I.D.
- 6.2.4 1.2 g, oxidizer, No. 1900277, oxidation material produced by Draeger Company. Available from National Mine Service Company, 3001 Koppers Bldg., Pittsburgh, PA 15219.

The triethanolamine-impregnated molecular sieve can be prepared as follows: Add 25 g triethanolamine to a 250-mL beaker; add 4 g glycerol, 50 mL acetone and sufficient distilled water to bring up to 100 mL. To the mixture add about 50 mL Type 13X, 30-40 mesh molecular sieve. Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for one hour. The sorbent should be free flowing. Store in a closed glass container.

- 6.3 A spectrophotometer capable of measuring absorbance or transmittance at 540 nm.
- 6.4 Two matched 1-cm silica cells.
- 6.5 Volumetric flasks, 50-mL and other convenient sizes.
- 6.6 Beakers, 100-mL.
- 6.7 Pipets, 1, 5 and 10-mL and other convenient sizes to make standard dilutions.
- 6.8 Balance.
- 6.9 Barometer.
- 6.10 Thermometer.
- 6.11 Stopwatch.

7. Reagents

All reagents should be ACS reagent grade or better. They are the same as described in Reference 11.1.

- 7.1 Liquid Absorber. Prepare by dissolving 15.0 g triethanolamine in approximately 500 mL distilled water, adding 0.5 mL n-butanol, and diluting to 1 liter.
- 7.2 Hydrogen Peroxide Solution 0.02% (V/V). Prepare by diluting 0.2 mL, 30% hydrogen peroxide to 250 mL with distilled water.
- 7.3 Sulfanilamide Solution. Prepare by dissolving 10 g sulfanilamide in 400 mL distilled water, adding 25 mL concentrated phosphoric acid and diluting to 500 mL.
- 7.4 NEDA Solution. Prepare by dissolving 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride in distilled water and diluting to 500 mL.
- 7.5 Stock Nitrite Solution, 100 ppm NO_2^- . Prepare by dissolving 0.1500 g sodium nitrite in 1 liter of water.
- 7.6 Working Nitrite Solution, 2 ppm NO_2^- . Prepare by diluting 2 mL of the stock nitrite solution to 100 mL with absorbing solution.

8. Procedure

8.1 Cleaning of Equipment

- 8.1.1 Before use, all glassware should be initially soaked in a mild detergent to remove any residual grease or chemicals.
- 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6 M nitric acid, tap water, distilled water, in that order, and then dried.

8.2 Calibration of Personal Sampling Pumps. Each personal pump must be calibrated with a representative sampling tube in the line. The tube is described in Section 6.2. 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, break the two ends of the sampling tube to provide an opening of at least one half of the internal diameter of the tube (5 mm).

- 8.3.2 The tube should be oriented so that the inner glass tube (12 mm) is farthest from the pump.
- 8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the tube.
- 8.3.5 A sample size of 1.5 liters is recommended. Sample at a flow rate of exactly 0.025 liter per minute for 60 minutes. The flow rate should be known with accuracy of at least $\pm 5\%$. No other flow rate is suitable.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.3.7 The exposed tube should be labeled appropriately and capped with supplied plastic caps.
- 8.3.8 With each batch of five or fewer samples, submit one sampling tube which has been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.
- 8.3.9 Capped sampling 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, the broken ends of each tube are widened to facilitate removal of the sorbent. The glass wool is removed carefully and discarded, making sure that no sorbent is lost in the process. The triethanolamine-impregnated molecular sieve in back (farthest from the 12-mm inner glass tube) is transferred to a 50-mL volumetric flask. If it is desired to quantify the NO_2 concentration (see restriction noted in Section 5.3) as well as the NO concentration, the triethanolamine-impregnated molecular sieve in front may be transferred to a separate 50-mL volumetric flask. These two sections may be analyzed separately.
- 8.4.2 Extraction of the Sample. Prior to analysis, liquid absorber is added to the flask to bring the volume to 50 mL. The flask is shaken vigorously for about 30 seconds and the solids allowed to settle.

A blank is prepared similarly with a TEA/molecular sieve section from an unexposed sampling tube.

8.4.3 Spectrophotometer Operation. Turn on the spectrophotometer and allow sufficient time for warmup. Follow the instrument manufacturer's recommendations for specific operating parameters. Adjust the wavelength to 540 nm and set the zero and 100% transmittance scale using a 1-cm cell filled with distilled water. Check these settings prior to making any measurement to check on instrument drift.

8.4.4 Analytical Procedure

1. Pipet 10 mL of the extracted sample into a 50 mL volumetric flask.
2. Add 1.0 mL hydrogen peroxide solution, 10.0 mL sulfanilamide solution, and 1.4 mL NEDA solution with thorough mixing after each addition.
3. Allow ten minutes for complete color development.
4. Transfer some of the sample to a 1-cm absorption cell.
5. Measure the absorbance or transmittance at 540 nm using a reagent blank to set zero absorbance.

9. Calibration and Standards

- 9.1 Using freshly prepared working nitrite solution, prepare at least five calibration standards in absorbing solution to cover a nitrite concentration range of 1 to 18 μg nitrite per 10 mL.
- 9.2 Prepare these standards fresh daily by appropriate dilution of the working nitrite solution using absorbing solution for all dilutions. A reagent blank containing no nitrite should also be prepared.
- 9.3 Proceed as in Section 8.4.4.
- 9.4 Prepare a calibration curve by plotting the absorbance of the standards after subtraction of the reagent blank versus the concentration of each standard in μg NO_2^- per 10 mL on linear graph paper.

10. Calculations

- 10.1 Correction for the sample blank (obtained by extraction and analysis of the sampling tube marked "blank") must be made for each sample.

$$\text{Abs}_{\text{corr}} = \text{Abs}_{\text{sample}} - \text{Abs}_{\text{sample blank}}$$

- 10.2 Read the amount of nitrite ion, in $\mu\text{g NO}_2^-$ per 10 mL, corresponding to the Abs_{corr} from the standard curve (Section 9.4).
- 10.3 Multiply the amount of nitrite ion per 10 mL by the factor shown below to obtain the $\mu\text{L NO}_2$ (gas) per 50 mL (total sample) at 25°C and 760 mm Hg.

$$\mu\text{L NO}_2(\text{gas}) \text{ in sample} = \mu\text{g NO}_2^-/10 \text{ mL} \times \frac{5}{1.88 \times 0.63}$$

where:

1 $\mu\text{L NO}_2(\text{gas}) = 1.88 \mu\text{g NO}_2(\text{gas})$ at 25°C and 760 mm Hg, and

1 $\mu\text{g NO}_2(\text{gas}) = 0.63 \mu\text{g NO}_2^- \equiv$ "stoichiometric factor"

- 10.4 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)

- 10.5 The concentration of analyte in the air sampled can be expressed in ppm (at standard conditions of 25°C and 760 mm Hg).

$$\text{ppm NO} = \frac{\mu\text{L NO (gas) (see Section 10.3)}}{\text{Air volume sampled (liters)} \times \frac{P}{760} \times \frac{298}{T}}$$

Another method of expressing concentration is mg/cu m

$$\text{mg/cu m} = \text{ppm} \times \frac{30.01}{24.45}$$

where:

P = Pressure (mm Hg) of air sampled

T = Temperature (°C) of air sampled

760 = Standard Pressure (mm Hg)

298 = Standard Temperature (°C)

24.45 = Molar volume (liter/mole) of air at 25°C and 760 mm Hg

30.01 = Molecular weight of nitric oxide

11. References

- 11.1 M.A. Willey, C. McCammon, Jr., and L. Doemeny, Am. Ind. Hyg. Assoc. J. (38), 358 (1977).
- 11.2 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.
- 11.3 S321 Backup Data Report for Nitric Oxide, prepared under NIOSH Contract No. 210-76-0123.
- 11.4 J.H. Blacker, Am. Ind. Hyg. Assoc. J. (34), 390 (1973).

Formaldehyde

Analyte:	Formaldehyde derivative	Method No.: S327
Matrix:	Air	Range: 1.4-6.2 ppm (8-hr T.W.A.) 4.6-19.8 ppm (Peak)
OSHA Standard:	3 ppm (8-hr T.W.A.) 10 ppm (Peak) 5 ppm (Ceiling)	Precision ($\overline{CV}_T$): 0.052 (8-hr T.W.A.) 0.058 (Peak)
Procedure:	Bubbler collection, derivatization with Girard T reagent, polarography	Validation Date: 9/2/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a midjet bubbler containing a buffered solution of Girard T reagent. Formaldehyde is derivatized with the Girard T reagent.
- 1.2 The formaldehyde-Girard T reagent derivative is measured by polarography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 1.4-6.2 ppm at an atmospheric temperature and pressure of 21°C and 759 mm Hg, using an 18-L sample, representing an 8-hour time-weighted average (T.W.A.) collection. This method was also validated over the range of 4.62-19.84 ppm for 30-minute peak samples at an atmospheric temperature and pressure of 21°C and 757 mm Hg.
- 2.2 The upper limit of the method is dependent on the concentration of Girard T reagent. While collection efficiency has not been tested outside of the method range, a 80-fold molar excess of Girard T reagent should be maintained over the total amount of formaldehyde sampled.

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 The use of polyvinyl chloride tubing preceding the midget bubbler should be kept to a minimum. Products from the tubing may interfere in the method.
- 3.3 Other volatile aldehydes such as acrolein, crotonaldehyde, and benzaldehyde may cause significant 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 1.4-6.2 ppm (8-hr T.W.A.) was 0.052. This corresponds to a 0.16 ppm standard deviation at 1X the 8-hr T.W.A. OSHA standard. The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 4.62-19.84 ppm (peak) was 0.058. This corresponds to a 0.58 ppm standard deviation at 1X the ceiling OSHA standard. Statistical information can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the 8-hr T.W.A. OSHA standard were 3.5% higher than the "true" concentrations for 18 samples. The concentrations obtained at 0.5X, 1X, and 2X the peak OSHA standard were 1.1% lower than the "true" concentrations for 18 samples. 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 3.02 ppm indicate that collected samples are stable for at least 7 days. Collection efficiency of the midget bubbler was determined to be 1.00, so no correction for collection efficiency is needed.

5. Advantages and Disadvantages of the Method

- 5.1 The formaldehyde-Girard T reagent derivative has adequate storage stability.
- 5.2 Collected samples are analyzed by a quick instrumental method.
- 5.3 A disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.
- 5.4 The bubblers are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the bubblers during shipping.

6. Apparatus

- 6.1 A glass midget bubbler.

- 6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined to an accuracy of 5%. The sampling pump is protected from splashover or solvent condensation by a trap. The trap is a midget bubbler or impinger with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.
- 6.3 Thermometer.
- 6.4 Manometer.
- 6.5 Volumetric Flasks: 1-L and other convenient sizes for preparing standard solutions.
- 6.6 Pipets: Convenient sizes for preparing stock standard solutions and for measuring the collection medium.
- 6.7 Buret: 0-50 mL capacity with graduations of 0.1 mL.
- 6.8 Erlenmeyer Flask: 250 mL.
- 6.9 Ice Bath.
- 6.10 Magnetic Stirrer.
- 6.11 Syringes: Convenient sizes for preparing spiked standard samples.
- 6.12 Polarograph which is capable of DC or sampled DC polarography with reference to a saturated calomel electrode.
- 6.13 China Marker.
- 6.14 Teflon tubing (15 cm x 7-mm I.D.) or Teflon plugs for sealing the inlet and outlet of the bubbler stem before shipping.

7. Reagents

- 7.1 Citric acid, reagent grade.
- 7.2 Disodium hydrogen phosphate, reagent grade.
- 7.3 Girard T reagent, reagent grade.
- 7.4 Triton X-100, 0.075% solution. Dilute 750 microliters of Triton X-100 to 1 liter with distilled water. Triton X-100 is a commonly used polarographic maximum suppressor.
- 7.5 Buffered Girard T reagent. Dissolve 13.257 g disodium hydrogen phosphate, 10.773 g citric acid, 3.926 g Girard T reagent in a 1-L volumetric flask. Add 6.6 mL of the Triton X-100 solution and dilute to 1 liter with distilled water. The pH of the resulting solution is 4.5.
- 7.6 Formaldehyde, 37% solution, reagent grade.

- 7.7 Formaldehyde Solution A, 1 mg/mL. Dilute 2.7 mL 37% formaldehyde solution to 1 liter with distilled water.
- 7.8 Iodine, 0.1 N (approximate). Dissolve 25 g of potassium iodide in about 25 mL of distilled water, add 12.7 g of iodine and dilute to 1 liter.
- 7.9 Iodine, 0.01 N. Dilute 100 mL of the 0.1 N iodine solution to 1 liter. Standardize against sodium thiosulfate.
- 7.10 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 of boiling water. Cool, add several milliliters of chloroform as a preservative, and store in a stoppered bottle. Discard if a mold growth is noticed.
- 7.11 Sodium Carbonate Buffer Solution. Dissolve 80 g of anhydrous sodium carbonate in about 500 mL of distilled water. Slowly add 20 mL of glacial acetic acid and dilute to 1 liter.
- 7.12 Sodium Bisulfite, 1%. Dissolve 1 g of sodium bisulfite in 100 mL of distilled water.
- 7.13 Sodium Thiosulfate, 0.05 N. Dissolve 12.410 g sodium thiosulfate in 1 liter of distilled 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, and dried.
- 8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette, bubbler, and splashover trap in the line to minimize errors associated with uncertainties in the volume sampled.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Pipet 15 mL of Girard T reagent solution buffered at a pH of 4.5 into each midjet bubbler. Mark the liquid level on the bubbler with a china marker.
 - 8.3.2 The outlet of the midjet bubbler is attached to the pump's inlet or a trap which may be used to protect the pump during personal sampling. The trap is a midjet impinger or bubbler with the stem broken off which is used to collect spillage. The trap is attached to the pump with a metal holder. The outlet of the trap is connected to the pump by flexible tubing.
 - 8.3.3 Air being sampled should not be passed through any hose or tubing before entering the midjet bubbler. (Polyvinyl chloride tubing is known to give interferences in the method).

- 8.3.4 At levels corresponding to the 8-hour time-weighted average standard, a sample size of 18 liters is recommended. Sample at a flow rate of 0.2 liter/minute. Levels corresponding to the peak standard should be collected for 30 minutes at approximately 0.2 liter/minute.
- 8.3.5 Turn the pump on and begin sample collection. 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.
- 8.3.6 The inlet and outlet of the bubbler stem should be sealed by connecting a piece of Teflon tubing between them or inserting Teflon plugs in the inlet and outlet. Do not seal with rubber. The standard taper joint of the bubbler should be taped securely to prevent leakage during shipping. Care should be taken to minimize spillage or loss of sample by evaporation at all times.
- 8.3.7 With each batch of ten samples, submit one bubbler containing 15 mL of the collection medium prepared from the same stock as that used for sample collection. This bubbler must be subjected to exactly the same handling as the samples except that no air is drawn through it. Label this bubbler as the blank.
- 8.3.8 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 bubblers.
- 8.3.9 Do not return the material in the trap.
- 8.4 Analysis of Samples
- 8.4.1 Each sample is analyzed separately. Remove the bubbler stem and tap the stem lightly against the flask to drain the contents into the bubbler flask. If necessary, bring the liquid volume to the 15-mL mark with distilled water. Swirl the bubbler flask to mix the contents well.
- 8.4.2 Transfer the mixed solution to a clean, dry polarographic receptacle which contains a small amount of mercury (approximately 0.3 mL) on the bottom. Place the receptacle on the polarograph and purge the sample for 5 minutes with oxygen-free nitrogen at a flow rate of 200 mL/minute.
- 8.4.3 Analyze the sample by sampled DC polarography using the following conditions:
- Drop Time: 1 second
Scan Rate: 5 mV/second
Scan from -0.7 V to -1.3 V versus a saturated calomel electrode.

8.4.4 Rinse the electrodes with distilled water between samples.

8.4.5 Measure the diffusion current from the reduction of the formaldehyde-Girard T reagent derivative. The half-wave potential, $E_{1/2}$, of the formaldehyde-Girard T reagent derivative is -0.99 V vs. a saturated calomel electrode. The results of the analysis are read from a calibration curve prepared as described below.

9. Calibration and Standards

9.1 The calibration curve is prepared using standardized 37% formaldehyde solution. The following procedure is used to standardize the 37% formaldehyde solution (Reference 11.3).

9.1.1 Pipet 1 mL of formaldehyde solution "A" into a 250-mL erlenmeyer flask. Into another flask, pipet 1 mL of distilled water. The distilled water serves as the blank.

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

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.

9.1.6 The excess inorganic bisulfite is now completely oxidized to sulfate, and the solution is ready for the assay of the formaldehyde bisulfite addition product.

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

9.1.8 One mL of 0.0100 N iodine is equivalent to 0.15 mg of formaldehyde. Therefore, since 1 mL of formaldehyde standard solution was titrated, the volume in mL of 0.01 N iodine used in the final titration multiplied by the factor, 0.15, gives the formaldehyde concentration of the standard solution in mg/mL. The factor, 0.15 must be adjusted or determined accordingly on the basis of the exact normality of the iodine solution.

9.2 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 polarographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in

micrograms/15 mL versus diffusion current. 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.

9.2.1 Prepare a stock standard solution containing 6.63 mg/mL standardized formaldehyde in deionized water.

9.2.2 From the above stock solution, appropriate aliquots are withdrawn and added to 15 mL of the collection medium. Prepare at least 6 working standards to cover the range of 6-220 micrograms/sample. This range is based on a 18-L sample at the 8-hour time weighted average standard and a 30-minute (5-L) sample for the ceiling standard.

9.2.3 Prepare a standard calibration curve by plotting micrograms/15 mL formaldehyde versus diffusion current.

10. Calculations

10.1 Read the weight, in micrograms, corresponding to each diffusion current from the standard curve. No volume correction is needed, because the standard curve is based on micrograms/15 mL of solution.

10.2 Corrections for the blank must be made for each sample.

$$\text{micrograms} = \text{microgram sample} - \text{microgram blank}$$

where:

microgram sample = micrograms found in sample bubbler
microgram blank = micrograms found in blank bubbler

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
t = sampling time
P₁ = pressure during calibration of sampling pump (mm Hg)
P₂ = pressure of air sampled (mm Hg)
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K)

10.4 The concentration of formaldehyde in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \text{micrograms/L} = \frac{\text{Corrected micrograms}}{\text{Corrected air volume sampled (L)}}$$

10.5 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 (L/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of formaldehyde
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 for Formaldehyde, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 NIOSH Method No. P&CAM 125, Formaldehyde in Air.

Phosphorus (Yellow)

Analyte:	Phosphorus (yellow)	Method No.: S334
Matrix:	Air	Range: 0.056-0.244 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision (CV_T): 0.090
Procedure:	Collection on Tenax-GC, extraction with xylene, GC/FPD.	Validation Date: 11/25/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a tube containing Tenax-GC resin to trap the phosphorus vapors present. The tube consists of 100 mg of 35/60 mesh Tenax-GC held in place by two pieces of silylated glass wool followed by a 50-mg backup section.
- 1.2 The phosphorus is extracted from the Tenax-GC resin using a known amount of xylene.
- 1.3 An aliquot of the extracted sample is analyzed by injection into a gas chromatograph equipped with a phosphorus specific flame photometric detector. 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 0.056-0.244 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 763 mm Hg using a 12-liter sample volume. This sample volume is less than two-thirds of the 5% breakthrough capacity determined at >85% relative humidity when sampling a test atmosphere at 3X the OSHA standard. This method is capable of measuring much 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 capacity of the sorbent tube and stability of the analyte. The method is capable of measuring concentrations higher than noted in Section 2.1, provided the capacity is adequate and desorption of the analyte is performed with a larger volume of xylene to bring the concentration of phosphorus in the extract to a level less than 5 µg/ml.

3. Interferences

- 3.1 When two or more phosphorus compounds are known or suspected to be present in the air, such information, including their suspected identifies, should be transmitted with the sample.
- 3.2 It must be emphasized that any phosphorus 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, temperature, 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 method in the range^T 0.056-0.244 was 0.0901. This value corresponds to a 0.009 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 analysis procedure was 2.1% higher than the average taken concentration for a limited number of laboratory experiments. Any difference between the found and taken concentrations may not represent a bias in the sampling and analytical method but rather a random variation from the experimentally determined taken ("true") concentration. In addition, samples collected at a concentration of 0.1028 mg/cu m were found to be stable for at least seven days.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable and involves no liquids.
- 5.2 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.
- 5.3 The precision of the method is affected by the reproducibility of the pressure drop across the tube. This drop will affect the flow rate and cause the volume to be imprecise, since the pump is usually calibrated for only one tube.
- 5.4 The amount of sample which can be taken is limited by the capacity that the tube will hold before overloading. When an

atmosphere containing 0.31 mg/cu m of phosphorus at 85% relative humidity was sampled at 0.2 liter per minute, 0.2% breakthrough was observed after 240 minutes of sampling (capacity is at least 45 liters or 13.9 µg). The sample size recommended is less than 5% breakthrough capacity at 85% relative humidity for a test atmosphere of 3X the OSHA standard to minimize the probability of overloading the sampling tube.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the solid sorbent collection method consists of the following components:
 - 6.1.1 A calibrated personal sampling pump suitable for sampling at 0.2 liter per minute for 60 minutes. The pump must be accurate to within +5% at the recommended flow rate. The pump must be calibrated with a representative sorbent tube in line.
 - 6.1.2 Sampling Tubes. Glass tube with both ends flame sealed (8-cm long with 8-mm O.D. and 6-mm I.D.) containing two sections of Tenax-GC (35/60 mesh, Applied Science Laboratories, Inc.). The absorbing section contains 100 mg of resin, the backup section, 50 mg. Small wads of silylated glass wool are placed in front of the absorbing section, between the two sections, and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of Hg at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.
 - 6.1.3 Thermometer.
 - 6.1.4 Barometer.
 - 6.1.5 Stopwatch.
- 6.2 Gas chromatograph with a phosphorus specific flame photometric detector.
- 6.3 Column (1.82 m x 6.35 mm O.D. x 2 mm I.D. glass) packed with 3% OV-101 on 80/100 mesh Supelcoport.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Sample containers with Teflon-lined caps, 2-ml.
- 6.6 Microliter syringes, 10-microliter and other convenient sizes for making standards and taking sample aliquots for dilution.

- 6.7 Pipets, 1-ml and other convenient sizes.
- 6.8 Volumetric flasks, 10-ml and other convenient sizes for making standard solutions.
- 6.9 Glove box.

7. Reagents

All reagents must be ACS reagent grade or better.

- 7.1 Phosphorus (yellow), stored under distilled water.
- 7.2 Xylene, mixture of ortho-, meta-, and para-isomers.
- 7.3 Acetone.
- 7.4 Hydrogen, prepurified.
- 7.5 Air, filtered, compressed.
- 7.6 Helium, dried.
- 7.7 Nitrogen, dried

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 sorbent tube in 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, break the two ends of the tube to provide an opening of at least one half of the internal diameter of the tube (3-mm).
 - 8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest to the sampling pump.
 - 8.3.3 The sampling tube should be placed in a vertical direction during sampling to minimize channeling through the sorbent.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

- 8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate 0.2 liter per minute for 60 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.
- 8.3.7 The sorbent tube should be labeled appropriately and capped with supplied plastic caps. Under no circumstances should rubber caps be used.
- 8.3.8 With each batch of ten samples, submit one sorbent tube which had been handled in the same manner as the sample tubes (break, seal, transport), except that no air is sampled through this tube. This tube should be labeled as blank.
- 8.3.9 Capped sorbent 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 sorbent tube is scored with a file and broken open. The glass wool is removed with care, making sure that a minimal amount of resin is lost in the process. The resin in the front 100-mg section is then transferred to a 2-ml vial. The second 50-mg section is transferred to another vial. The two sections are analyzed separately.
- 8.4.2 Desorption of the Sample. Prior to analysis, 1 ml of mixed xylene is pipetted into each vial containing the sorbent. The desorption is carried out for 30 minutes at room temperature with occasional swirling during this period.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (40 psig) helium carrier gas flow.
 2. 35 ml/min (40 psig) hydrogen gas flow to detector.
 3. 220 ml/min (60 psig) air flow to detector.
 4. 200°C injector temperature.
 5. 200°C detector temperature.
 6. 80°C column temperature.

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 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 Tenax-GC 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 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 sample concentration range which should be tested, the collected samples are analyzed first and then the analytical samples are prepared based on the relative amount of phosphorus found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of phosphorus found in the samples. Duplicate determination should agree within $\pm 5\%$.

For the validation studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 12-liter sample at the selected level was used to determine the analytical method recovery. Six vials at each of the three levels (0.5 l and 2X the OSHA standard) containing 100 mg of sorbent were spiked with 2, 4 and 8 μ l aliquots of a solution of phosphorus in xylenes (0.296 mg/ml). A parallel blank was also prepared except that no sample was added to it. All samples were then analyzed as described in Section 8.4.

The sample recovery equals the average weight in μ g recovered from the sorbent divided by the weight in μ g added to the sorbent, or

$$D.E. = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered} - \text{Blank } (\mu\text{g})}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependent on the amount of phosphorus collected on the resin. Plot the desorption efficiency versus weight of phosphorus found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of μg per ml of xylene because the samples are prepared in this amount of solvent. The standard solutions are prepared by the appropriate dilution of a stock solution made by dissolving an acetone washed and dried piece of phosphorus (yellow) into a pre-tared 10-ml volumetric flask containing 5 ml of xylene under a nitrogen or other inert gas atmosphere in a glove box. The amount of phosphorus added is determined from the difference in weight, and the flask is then made up to volume. A series of standards varying in concentration over the range of interest is prepared and analyzed using the same GC conditions and during the same time period as the unknown samples in order to minimize the effect of variations in FPD response. A calibration curve is established by plotting concentration in μg per 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 one ml and the volume of sample injected is identical to the volume of the standards injected.

10.2 Correction for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\begin{aligned} \mu\text{g sample} &= \mu\text{g found in sample solution} \\ \mu\text{g blank} &= \mu\text{g found in blank solution} \end{aligned}$$

10.3 Divide the total weight by the desorption efficiency to obtain the corrected μg per sample

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight in } \mu\text{g (Front Section)}}{D.E.}$$

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 = sample flow rate
- t = sampling time
- P_1 = pressure during calibration of sampling pump (mm Hg)
- P_2 = pressure of air samples (mm Hg)
- T_1 = temperature during calibration of sampling pumps ($^{\circ}\text{K}$)
- T_2 = temperature of air sampled ($^{\circ}\text{K}$)

- 10.6 The concentration of the analyte in the air sampled can be expressed in mg/cu m which is numerically equal to $\mu\text{g/liter}$.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{30.97} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

- P = pressure (mm Hg) of air sampled
- T = temperature ($^{\circ}\text{C}$) of air sampled
- 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
- 30.97 = atomic weight of phosphorus
- 760 = standard pressure (mm Hg)
- 298 = standard temperature ($^{\circ}\text{K}$)

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. 757-057/6708.
- 11.2 Backup Data Report for Phosphorus, No. S334, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 NIOSH Contract No. 210-75-0047 Final Report "Development of Methods for the Determination of Elemental Phosphorus and Phosphine in Air," Southern Research Institute, Birmingham, Alabama, January 1977.

Carbon Monoxide

Analyte:	Carbon Monoxide	Method No.:	S340
Matrix:	Air	Range:	24.7 ~ 115.4 ppm
OSHA Standard:	50 ppm (57 mg/cu m)	Precision ($\overline{CV}_T$):	0.0146
Procedure:	Collection in gas sampling bag, electro-chemical analysis	Validation Date:	4/15/77

1. Principle of the Method

- 1.1 A known volume of air is collected in an evacuated five-layer gas sampling bag by means of a low flow rate personal sampling pump capable of filling a bag.
- 1.2 The carbon monoxide content of the samples is determined by electrochemical analysis.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 24.7-115.4 ppm at an atmospheric temperature of 23°C and atmospheric pressure of 750 mm Hg using a 3.5-liter sample volume. The working range of the method is estimated to be 5-120 ppm, under the experimental conditions cited.
- 2.2 The instrument specifications indicate that the response of the analyzer is linear up to 600 ppm. However, no studies have been conducted at this higher concentration range.

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 several gaseous pollutants (e.g., NO, NO₂, SO₂) when in excess of 25 ppm can cause an interference equivalent to 1 ppm CO or greater (see Manufacturer's Specifications).
- 3.3 If the possibility of interference exists, the magnitude must be determined by further experimentation.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 24.7-115.4 ppm was 0.0146. This value corresponds to a 0.7-ppm 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 There was no bias in the analytical method since the average recovery from the bags was 1.015. A collection efficiency of 100% is assumed since the collection medium is an impermeable gas sampling bag whose integrity and storage stability have been confirmed. By independent verification (Reference 11.2), the CO concentration obtained at the OSHA standard level using the overall sampling and analytical method was found to be 1% lower than the "true" concentration for a limited number of laboratory experiments. Any difference between the "found" and "true" concentration may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages

- 5.1 The sampling device is portable, and involves no liquids. Interferences are minimal but may not be easily corrected. The gas samples are analyzed by means of a quick and portable 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.

6. Apparatus

- 6.1 Personal Sampling Pump. A personal sampling pump capable of filling a bag at approximately 0.05 liter per minute is required. This pump should be calibrated to within $\pm 5\%$.
- 6.2 Gas Sampling Bag. 5-liter capacity; only the five-layer sampling bags manufactured by Calibrated Instruments, Inc., (731 Saw Mill Road, Ardsley, New York 10502) were tested for sample collection and storage for at least 7 days. The bag is fitted with a metal valve and hose bib. For the preparation of calibration standards in the laboratory, 5-liter Saran or Tedlar bags could be used.

- 6.3 Ecolyzer - such as an electrochemical analyzer, Series 2000, manufactured by Energetics Science Inc., or equivalent.
- 6.4 Recorder. Any suitable laboratory recorder with a range of 2 V full scale.
- 6.5 Gas-tight syringes. 500 μ l and other convenient sizes for making standards.
- 6.6 Calibrated rotameters of convenient sizes for making standards.

7. Reagents

- 7.1 Carbon monoxide, 99.5% or higher purity.
- 7.2 Air, zero grade (<1 ppm CO).

8. Procedure

- 8.1 Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the closure mechanism 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 carbon monoxide-free air and evacuated. This procedure is repeated at least twice.

Bags may be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Observe for any discernable leaks and any volume changes or slackening of the bag, preferably over at least a one-hour period.

- 8.2 Calibration of Personal Pumps. Each personal pump should be calibrated to minimize errors associated with uncertainties in the sample volume collected. Although sample volume is not actually used in this determination, the pump should be calibrated to avoid over filling the bags; i.e., a maximum sampling time can be determined based on flow rate and sample volume which should be limited to approximately 80% of the volume-capacity of the bag (ca. 4 liters for a 5-liter bag).

8.3 Collection and Shipping of Samples

- 8.3.1 Immediately before sampling, attach a small piece of Tygon or plastic tubing to the hose bib of the five-layer gas sampling bag.
- 8.3.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump.

- 8.3.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required.
- 8.3.4 A sample size of 3-4 liters is recommended. Sample at a flow rate of 0.05 liters per minute or less, but not less than 0.01 liters per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.5 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.6 The gas sampling bag should be labeled appropriately and sealed tightly.
- 8.3.7 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of puncture during shipping.

8.4 Analysis of Samples

- 8.4.1 Electrochemical Analysis. Open the valve and attach the gas sampling bag to the inlet port of the "Ecolyzer" via a short piece of tubing. Turn the instrument "on" and allow the sample to be automatically pumped through the electrochemical cell until an equilibrium is attained. Record the instrument output on a laboratory recorder. While the instrument's meter can be used to read the concentration directly, the recorder allows the measurement of concentrations slightly in excess of 100 ppm CO (full scale meter reading) since the calibration curve is linear up to about 120 ppm.
- 8.4.2 Measurement of Peak Height. The peak height is measured directly from the chart recorder. The peak height reaches its maximum (constant) level after pumping the sampling bag about 1.5 minutes. The results are read from a standard curve as discussed in Section 9.

9. Calibration and Standards

- 9.1 Completely evacuate a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Introduce a known volume (3-4 liters) of zero air via a septum into the bag. This can be done by using an air cylinder equipped with a calibrated rotameter. Then add a known volume of carbon monoxide gas through a septum using a gas tight syringe. Knead the bag to ensure complete mixing. It is necessary to know accurately the volume of carbon monoxide added

and the total volume of zero air to determine concentration in ppm. The concentration in ppm is equal to the volume of carbon monoxide divided by the volume of air (volume of CO is negligible).

- 9.2 The instrument is zeroed as per the manufacturer's instructions and then the instrument is calibrated using a span gas standard with a concentration of about 90-100 ppm CO. The instrument should be rezeroed and recalibrated with the span gas standard several times. Due to a slow, diffusion-limited return to zero, this process may take up to an hour. However, once completed, the instrument is stable within 1% full scale during at least 12 hours.

Note: Calibration standards should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in cell response.

10. Calculations

- 10.1 Read the concentration in ppm, corresponding to each peak area from standard curve.
- 10.2 Another method of expressing concentration is mg/cu m (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{mg/cu m} = \text{ppm} \times \frac{\text{MW}}{24.45} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Carbon Monoxide, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Parker, C.D., and Strong, R.B., "Evaluation of Portable Direct-Reading Carbon Monoxide Meters", prepared by Research Triangle Institute under NIOSH Contract No. HSM-99-73-1 (T.O. No. 1), September, 1974.

Allyl Glycidyl Ether

Analyte:	Allyl Glycidyl Ether	Method No.: S346
Matrix:	Air	Range: 19-87 mg/cu m
OSHA Standard:	10 ppm (45 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on Tenax-GC desorption with ether, GC/FID	Validation Date: 1/21/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a Tenax-GC tube to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.
- 1.2 The Tenax-GC in each tube is transferred to a vial and the allyl glycidyl ether is desorbed with diethyl ether and analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 19-87 mg/cu m at an atmospheric temperature of 17°C and atmospheric pressure of 752 mm Hg using a 3-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 2X OSHA standard. This method is capable of measuring much 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 Tenax-GC resin tube. This capacity can vary with the concentrations of analyte and other substances in the air. (See Section 5.2)

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, temperature, 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 method in the range of 19-87 mg/cu m was 0.057. This value corresponds to a 2.6 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 concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.5% lower than the "true" concentrations 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, no recovery correction should be applied to the final result.

The data are based on validation experiments using the internal standard method.

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 sorbent tubes are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When an atmosphere at 90% relative humidity containing 92 mg/cu m of allyl glycidyl ether was sampled at 0.8 liter per minute, 5% breakthrough was observed after 15 minutes (capacity = 12 liters or 1.1 mg). The sample size recommended is two-thirds the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard to minimize the probability of overloading the sampling tube and allow sampling with the 0.2 lpm sampling pump.
- 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.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate of 0.2 liters per minute (Reference 11.3).

6.2 Resin tubes. Glass tube with both ends flame-sealed, 10-cm long with 8-mm O.D. and 6-mm I.D., containing 2 sections of 35/60 mesh Tenax-GC resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.

6.3 Gas chromatograph with a flame ionization detector.

6.4 Column, (20-ft x 1/8 in. stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Sample containers with Teflon-lined caps, 5-ml.

6.7 Microliter syringes. 10- and 500-microliter, and other convenient sizes for making standards and for taking sample aliquots for dilution.

6.8 Pipettes. 2-ml, delivery type.

6.9 Volumetric flasks. 1- and 10-ml or convenient sizes for making standard solutions and dilution of samples.

7. Reagents

7.1 Diethyl ether, anhydrous.

7.2 Allyl glycidyl ether, 99%.

7.3 Isoamyl alcohol or other suitable internal standard. The appropriate solution of the internal standard is prepared in ether.

7.4 Hexane. This solvent is used to prepare the allyl glycidyl ether solutions for the desorption efficiency determination.

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 Pumps. Each personal pump must be calibrated with a representative sampling tube series in the line; the tube is described in Section 6.2. 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, break the two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (3 mm).
- 8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump.
- 8.3.3 The resin tube series should be placed in a vertical direction during sampling to minimize channeling through the resin.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the resin tube.
- 8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate of 0.2 liter per minute for 15 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The resin tube 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 10 samples, submit one resin tube which has been handled in the same manner as the sample tubes (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped resin 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 resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the front 100-mg section is transferred to a 5-ml screw-capped sample container. The separating section of glass wool is removed and discarded.

The second 50-mg section is transferred to another container. These two sections are analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 ml of ether is pipetted into each sample container. 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 internal standard solution in ether.

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. 200°C injector temperature
5. 280°C manifold temperature (detector)
6. 150°C column temperature

A retention time of approximately 10.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The internal standard elutes between ether and the allyl glycidyl ether.

8.4.4 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 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 Tenax-GC 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 resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at the equivalent 1X OSHA standard level.

- 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 allyl glycidyl ether found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of allyl glycidyl ether found in the sample.

The analytical samples are prepared as follows: Tenax-GC, equivalent to the amount in the front section (100 mg), is measured into a 5-ml screw capped vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of allyl glycidyl ether in hexane (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- μ l 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 (0.5X, 1X and 2X of the OSHA standard) were prepared by adding an amount of allyl glycidyl ether equivalent to that present in a 3-liter sample at the selected level. A stock solution containing 67.34 milligrams of allyl glycidyl ether per milliliter of hexane was prepared. One, 2 and 4 microliter aliquots of the solution were added to the Tenax-GC resin tubes to produce 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 resin. 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 experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 ml of ether with the same syringe used in the preparation of the samples. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of ether containing a known amount of the internal standard.

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

$$\text{D.E.} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependent on the amount of allyl glycidyl ether collected on the resin. Plot the desorption efficiency versus weight of allyl glycidyl ether found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

- 9.1 Solutions of allyl glycidyl ether should be prepared over the appropriate concentration range in diethyl ether. The solutions should be prepared by addition of allyl glycidyl ether to 2.0 ml of diethyl ether in 5-ml vials. The allyl glycidyl ether may either be added neat using a microliter syringe or one may use the hexane solution described in Section 8.5.2. The concentration of standards can be expressed in terms of μg of allyl glycidyl ether per 2 ml of ether.
- 9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in $\mu\text{g}/2.0 \text{ ml}$.

For the internal standard method, use ether containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in $\mu\text{g}/2.0 \text{ ml}$.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

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 ether 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

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front (100-mg) sample section}$$

$$\mu\text{g blank} = \mu\text{g found in front (100-mg) blank section}$$

A similar procedure is followed for the backup (50-mg) section.

10.3 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

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 = flow rate sampled

t = sampling time

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

P_2 = pressure of air samples (mm Hg)

T_1 = temperature during calibration of sampling pump ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

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.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.4)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Allyl Glycidyl Ether, No. S346, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

n-Butyl Mercaptan*

Analyte:	n-Butyl Mercaptan	Method No.:	S350
Matrix:	Air	Range:	16.8-74 mg/cu m
OSHA Standard:	10 ppm (35 mg/cu m)	Precision ($\overline{CV}_T$):	0.062
Procedure:	Adsorption on Chromosorb 104, desorption with acetone, GC	Validation Date:	1/21/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass tube containing Chromosorb 104 to trap n-butyl mercaptan vapors.
- 1.2 n-Butyl mercaptan is desorbed from the Chromosorb 104 with acetone, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 16.8-74.2 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 759 mm Hg, using a 1.5-liter sample. This sample size is based on the capacity of the Chromosorb 104 to collect vapors of n-butyl mercaptan in air at high relative humidity. 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 Chromosorb 104. This capacity may vary with the concentrations of n-butyl mercaptan and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Chromosorb 104) reaches 5% of the concentration in the test gas mixture. Breakthrough occurred after sampling for 2.9 hours at an average sampling rate of 0.023 liter/minute and relative humidity of 94% and temperature of 25°C. The breakthrough test was conducted at a concentration of 74.2 mg/cu m.

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

* 1-Butanethiol

transmitted with the sample.

- 3.2 Any compound that has the same retention time as n-butyl mercaptan 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 16.8-74.2 mg/cu m was 0.062. This value corresponds to a 2.2 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 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 2% lower than the "true" concentrations for 18 samples. 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 35.9 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 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 n-butyl mercaptan found on the backup section of the sorbent tube 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 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.

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.
- 6.2 Chromosorb 104 Tubes: Glass tubes with both ends unsealed, 8.5-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of

60/80 mesh Chromosorb 104* separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Chromosorb 104, and the backup section contains 75 mg. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be less than 10 mm of mercury at a flow rate of 0.025 liter per minute. Immediately prior to packing, the tubes should be acetone rinsed and dried at room temperature to eliminate the problem of Chromosorb 104 adhering to the walls of the glass tubes. The Chromosorb 104 tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to usage, Chromosorb 104 is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch to batch differences in production. A quantity of Chromosorb 104 is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone equal to twice the volume of sorbent is added to the sorbent and mixed, and a vacuum is applied. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C under 25 inches mercury vacuum for four hours.

- 6.3 Gas chromatograph equipped with a flame photometric detector with a sulfur filter. The gas chromatograph should be equipped with a venting valve to vent the solvent to the air before it reaches the detector.
- 6.4 Column (4-foot x 1/4-inch O.D. glass) packed with 60/80 mesh Chromosorb 104.
- 6.5 An electronic integrator or some other suitable method of determining peak areas.
- 6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon lined caps.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

* Chromosorb 104 is a polymeric solid adsorbent which is manufactured by Johns-Manville, and is commonly used as a gas chromatographic column packing material.

7. Reagents

- 7.1 Acetone, reagent grade.
- 7.2 1-Butanethiol, reagent grade.
- 7.3 n-Hexane.
- 7.4 Nitrogen, purified.
- 7.5 Hydrogen, prepurified.
- 7.6 Oxygen, purified.
- 7.7 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 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative Chromosorb 104 tube in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.3)
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, remove the caps from the ends of the Chromosorb 104 tube. All tubes must be packed with Chromosorb 104 from the same manufacturer's lot and that has been prewashed in acetone.
 - 8.3.2 The smaller section of Chromosorb 104 is used as a backup and should be positioned nearer the sampling pump.
 - 8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the Chromosorb 104.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Chromosorb 104 tube.
 - 8.3.5 A sample size of 1.5 liters is recommended. Sample at a flow rate between 0.010 and 0.025 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record sampling time, flow rate, and type of sampling pump used.
 - 8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The Chromosorb 104 tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 With each 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.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the Chromosorb 104 tubes. Because of postal and DOT regulations, the bulk sample should be shipped by surface mail. A minimum of 18 extra Chromosorb 104 tubes should be provided to the analyst for desorption efficiency determinations.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Chromosorb 104 tube. Remove the glass wool plug and transfer the first (larger) section of Chromosorb 104 to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Chromosorb 104 to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to effect complete transfer of the Chromosorb 104.
- 8.4.2 Desorption of Samples. Prior to analysis, pipet 1.0 ml of acetone into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the n-butyl mercaptan is desorbed.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

50 ml/min (60 psig) nitrogen carrier gas flow
150 ml/min (30 psig) hydrogen gas flow to detector
20 ml/min (20 psig) oxygen gas flow to detector
30 ml/min (20 psig) air flow to detector
150°C injector manifold temperature
200°C detector manifold temperature
140°C column temperature

A retention time of approximately 5 minutes is to be expected for n-butyl mercaptan under these conditions and using the column recommended in Section 6.4. The acetone will elute from the column before the n-butyl mercaptan.

8.4.4 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. Three 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. At the GC conditions described in Section 8.4.3, venting the acetone solvent for 60 seconds after injection is required. If the solvent is not vented, the flame may be extinguished and the detector may temporarily malfunction. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Chromosorb 104.

8.4.5 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.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Chromosorb 104 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 104.

8.5.2 Chromosorb 104 equivalent to the amount in the first section of the sampling tube (150 mg) is measured into a 64-mm, 4-mm I.D. glass tube flame sealed at one end. This Chromosorb 104 must be from the same batch as that used in obtaining the samples. The Chromosorb 104 must also be prewashed with acetone as described in Section 6.2. The open end is capped with Parafilm. A known amount of a hexane solution of analyte containing 13.73 mg/ml is injected directly into the Chromosorb 104 with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in

a 1.5-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the Chromosorb 104, because the amounts to be added would be too small to measure accurately.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the n-butyl mercaptan onto the Chromosorb 104. 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 8.4.

Since the response of the flame photometric detector is non-linear, a series of standards are prepared to cover variations over each of the three levels (0.5X, 1X, and 2X the OSHA standard) as in Section 9. These are analyzed with the samples. The standards are used to confirm the calibration of the gas chromatograph.

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

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of n-butyl mercaptan collected on the Chromosorb 104. Plot the desorption efficiency versus weight of n-butyl mercaptan found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area². 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 FPD response.

- 9.1 Prepare a stock standard solution containing 13.73 mg/ml n-butyl mercaptan in acetone.
- 9.2 From the above ~~stock~~ solution, appropriate aliquots are withdrawn and dilutions are made in acetone. Prepare at least 5 working standards to cover the range of 0.0055-0.165 mg/1.0 ml. This range is based on a 1.5-liter sample.

- 9.3 Prepare a standard calibration curve by plotting concentration of n-butyl mercaptan in mg/1.0 ml versus peak area².

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/1.0 ml acetone 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:

$$\begin{aligned}\text{mg sample} &= \text{mg found in front section of sample tube} \\ \text{mg blank} &= \text{mg found in front section of blank tube}\end{aligned}$$

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 8.5.2) for the amount found in the front section. 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 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:

$$\begin{aligned}f &= \text{flow rate sampled} \\ t &= \text{sampling time} \\ P_1 &= \text{pressure during calibration of sampling pump (mm Hg)} \\ P_2 &= \text{pressure of air sampled (mm Hg)} \\ T_1 &= \text{temperature during calibration of sampling pump (°K)} \\ T_2 &= \text{temperature of air sampled (°K)}\end{aligned}$$

- 10.6 The concentration of n-butyl mercaptan in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 n-butyl mercaptan
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.2 Backup Data Report for n-Butyl Mercaptan, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Copper Fume

Analyte:	Copper	Method No.:	S354
Matrix:	Air	Range:	0.05-0.37 mg/cu m in a 480-liter sample
OSHA Standard:	0.1 mg/cu m	Precision ($\overline{CV}_T$):	0.058
Procedure:	Filter collection, acid digestion, AA	Validation Date:	9/30/77

1. Synopsis (Reference 11.1)

- 1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to collect copper fume.
- 1.2 The samples are ashed using concentrated nitric acid to destroy the filter and other organic materials in the sample. The copper is taken up in 1% nitric acid.
- 1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for copper is used.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 0.0548-0.372 mg/cu m using a 480-liter sample at an atmospheric temperature of 22°C and an atmospheric pressure of 761 mm Hg. Under the conditions of sample size (480 liters), the working range of the method is estimated to be 0.01-0.3 mg/cu m. The method may be extended to higher values by dilution of the solution before AA analysis.
- 2.2 The sensitivity of the AA analysis as reported by the manufacturer is 0.04 microgram/ml of aqueous solution. This is the concentration of the solution which produces a signal of 1% absorbance.
- 2.3 The detection limit of the AA analysis as reported by the manufacturer is 0.003 microgram/ml of aqueous standard solution.

3. Interferences

- 3.1 Any particulate material other than copper fume containing copper or copper salts will result in a high value being reported as copper fume.

- 3.2 Incomplete digestion of the filter or a high zinc/copper ratio in the atmosphere may lead to depression of the copper absorbance.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.0548-0.372 mg/cu m was 0.058. This value corresponds to a 0.006 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures can be found in Reference 11.3.
- 4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. The Coefficient of Variation is a good measure of the accuracy of the method. Storage stability studies on samples collected from a test atmosphere at a concentration of 0.1181 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages

The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

- 6.1 Filter unit: The filter unit consists of a 37-mm diameter, 0.8-micrometer pore size mixed cellulose ester membrane filter supported by a glass fiber backup pad, and an appropriate 37-mm two-piece cassette filter holder.
- 6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate.
- 6.3 Atomic absorption spectrophotometer equipped with an air-acetylene burner head.
- 6.3.1 Copper hollow cathode lamp.
- 6.3.2 Oxidant: compressed air.
- 6.3.3 Fuel: acetylene.
- 6.3.4 Pressure-reducing valves: A 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank.
- 6.4 Manometer.
- 6.5 Thermometer.

6.6 Glassware, borosilicate

6.6.1 Phillips beakers: 125 ml.

6.6.2 Watchglass covers.

6.6.3 Pipets of convenient sizes.

6.6.4 Volumetric flasks: 10-ml and other appropriate sizes.

6.7 Polyethylene Bottles

6.7.1 Five 100-ml capacity polyethylene bottles for working atomic absorption standards.

6.7.2 One 1000-ml capacity polyethylene bottle for stock atomic absorption standard.

6.8 Hot Plate: Adjustable thermostatically controlled hot plate capable of reaching 160°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, concentrated.

7.3 1% Nitric acid (V/V).

7.4 Aqueous standard stock solutions containing 1000 micrograms/ml of copper (commercially available).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling 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 two-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a glass fiber backup pad. Secure the cassette holder together with tape or shrinkable band.

8.3.2 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.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 480 liters is recommended. Sample at a flow rate of 2.0 liters per minute. The flow rate should be known with an accuracy of 5%.

8.3.5 Since the filter may become plugged or overloaded as evidenced by caking, the filter and pump's sampling rate should be checked periodically. When the filter becomes overloaded or when the pump's flow rate cannot be adjusted to 2.0 liter/minute, terminate sampling.

8.3.6 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.

8.3.7 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 handling as the samples, except that no air is drawn through it. Label this as a blank.

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

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample with 10 ml of concentrated nitric acid. Cover each beaker with a watchglass and heat on a hot plate (140-160°C) in a fume hood until most of the acid

has evaporated. Add 3 ml more of concentrated nitric acid and repeat the procedure. Evaporate the sample to 0.5 ml. Keep the beakers covered with a watchglass during the entire ashing procedure. When the beakers are cool, rinse the watchglass with 1% nitric acid into the beaker.

8.4.3 Quantitatively transfer the clear solutions to a 10-ml volumetric flask using 1% nitric acid.

8.4.4 Rinse each beaker at least three times with 2-ml portions of 1% nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 10 ml with 1% nitric acid.

8.4.5 Aspirate samples (Section 8.4.4) and standard solutions (Section 9.1) into an oxidizing air-acetylene flame and record the absorbance at 324.7 nm. The sample absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.6 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standardization

9.1 From the 1000 micrograms/ml stock standard (Section 7.4), prepare at least five working standards to cover the range from 0.5 to 15 micrograms/ml. Prepare all standard solutions in 1% nitric acid and remake each day. Store the standard solutions in 100-ml polyethylene bottles.

9.2 Proceed as in Section 8.4.5.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram/ml. Standards should be run both before and after the series of samples are analyzed to ensure that conditions have not changed.

10. Calculations

10.1 Read the concentration in micrograms/ml, corresponding to the total absorbance from the calibration curve. The micrograms in each sample equals:

$$\text{micrograms/ml (from curve)} \times 10 \text{ ml} = \text{micrograms Cu/sample}$$

10.2 Corrections for the blank must be made for each sample.

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

where:

microgram sample = microgram found in sample filter

microgram blank = microgram found in blank filter

10.3 For personal sampling pumps with rotameters only, the following air 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

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.4 The concentration of copper fume in the air sample can be expressed in mg/cu m (microgram/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{microgram (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

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.

11.3 Backup Data Report for Copper Fume, prepared under NIOSH Contract No. 210-76-0123.

Furfuryl Alcohol

Analyte:	Furfuryl Alcohol	Method No.:	S365
Matrix:	Air	Range:	120-470 mg/cu m
OSHA Standard:	50 ppm (200 mg/cu m)	Precision ($\overline{CV}_T$):	0.072
Procedure:	Adsorption on Porapak Q, desorption with acetone, GC	Validation Date:	2/18/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass tube containing Porapak Q to trap furfuryl alcohol vapors.
- 1.2 Furfuryl alcohol is desorbed from the Porapak Q with acetone, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 117-469 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 765 mm Hg, using a 6-liter sample. This sample size is based on the capacity of the Porapak Q to collect vapors of furfuryl alcohol in air at high relative humidity. 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 Porapak Q. This capacity may vary with the concentrations of furfuryl alcohol and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for seven hours at an average sampling rate of 0.044 liter/minute and relative humidity of greater than 80% and temperature of 19°C. The breakthrough test was conducted at a concentration of 418 mg/cu m.

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 furfuryl alcohol 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 117-469 mg/cu m was 0.072. This value corresponds to a 34 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 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.6% lower than the "true" concentrations for 18 samples. 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 224.2 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 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 furfuryl alcohol found on the backup section of the Porapak Q tube 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 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.

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.
- 6.2 Porapak Q Tubes: Glass tube with both ends unsealed, 8.5-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 50/80 mesh Porapak Q* separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Porapak Q, and the backup section contains 75 mg. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be less than 10 mm of mercury at a flow rate of 0.05 liter per minute. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. The Porapak Q tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to useage, Porapak Q is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch to batch differences in production. A quantity of Porapak Q is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Porapak Q, is added to the sorbent and mixed, and a vacuum is applied. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C under 25 inches mercury vacuum for four hours.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (3-ft long x 1/8-inch O.D. stainless steel)packed with 50/80 mesh Porapak Q.
- 6.5 An electronic integrator or some other suitable method of determining peak areas.
- 6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Polyseal** caps or equivalent.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.

* Porapak Q is a solid adsorbent which is manufactured by Waters Associates, Inc., and is commonly used as a gas chromatographic column packing material.

** The Polyseal Corp., Baltimore, Maryland.

6.11 Manometer.

7. Reagents

7.1 Acetone, reagent grade.

7.2 Furfuryl alcohol, "Baker Grade" from J. T. Baker Chemical Company or equivalent. Furfuryl alcohol is a clear viscous liquid. If furfuryl alcohol is received from the manufacturer as a dark colored liquid, it should be distilled before use. The boiling point of furfuryl alcohol is 170°C.

7.3 Benzene, chromatographic quality.

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, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative Porapak Q tube in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.3)

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of Porapak Q is used as a backup and should be positioned nearer the sampling pump.

8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the Porapak Q.

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

8.3.5 A sample size of 4 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record the sampling time, flow rate, and type of sampling pump used.

- 8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The Porapak Q tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 With each 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 Porapak Q tubes should be provided for desorption efficiency determinations.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Polyseal cap. This sample should not be transported in the same container as the Porapak Q tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Porapak Q tube. Remove the glass wool plug and transfer the first (larger) section of Porapak Q to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Porapak Q to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to affect complete transfer of the Porapak Q.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the furfuryl alcohol is desorbed.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

50 ml/min (60 psig) nitrogen carrier gas flow
65 ml/min (24 psig) hydrogen gas flow to detector
500 ml/min (50 psig) air flow to detector
225°C injector manifold temperature
225°C detector manifold temperature
200°C column temperature

A retention time of approximately 11 minutes is to be expected for furfuryl alcohol under these conditions and using the

column recommended in Section 6.4. The acetone will elute from the column before the furfuryl alcohol.

8.4.4 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. Three 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. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Porapak Q.

8.4.5 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.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Porapak Q 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 Porapak Q.

8.5.2 Porapak Q equivalent to the amount in the first section of the sampling tube (150 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This Porapak Q must be from the same batch as that used in obtaining the samples. The open end is capped with Parafilm. A known amount of a benzene solution of furfuryl alcohol containing 300 mg/ml is injected directly into the Porapak Q with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 6-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the Porapak Q, because the amounts to be added would be too small to measure accurately.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the furfuryl alcohol onto the Porapak Q. 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 8.4.

Two or three standards are prepared by injecting the same volume of furfuryl alcohol into 1.0 ml of acetone with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of furfuryl alcohol collected on the Porapak Q. Plot the desorption efficiency versus weight of furfuryl alcohol found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 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 FID response.

- 9.1 Prepare a stock standard solution containing 120 mg/ml of furfuryl alcohol in acetone.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in acetone. Prepare at least 5 working standards to cover the range of 0.12-3.6 mg/1.0 ml. This range is based on a 6-liter sample.
- 9.3 Prepare a standard calibration curve by plotting concentration of furfuryl alcohol in mg/1.0 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 because the standard curve is based on mg/1.0 ml acetone 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 front section of sample tube

mg blank = 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 weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. 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 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

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.6 The concentration of furfuryl alcohol in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 (liter/mole) at 25°C and 760 mm Hg

M.W. = molecular weight (g/mole) of furfuryl alcohol
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.2 Backup Data Report for Furfuryl Alcohol, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Iron Oxide Fume

Analyte:	Iron Oxide Fume	Method No.: S366
Matrix:	Air	Range: 3.9-18.2 mg/cu m
OSHA Standard:	10 mg/cu m	Precision ($\overline{CV}_T$): 0.067
Procedure:	Filter collection, atomic absorption	Validation Date: 11/26/76

1. Principle of the Method (References 11.1 and 11.2)

- 1.1 A known volume of air is drawn through a cellulose ester membrane filter to collect iron oxide fume.
- 1.2 The samples are ashed using hydrochloric and nitric acids to destroy the filter and other organic materials in the sample, and the iron oxide is then solubilized in nitric acid.
- 1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for iron is used.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 3.87-18.19 mg/cu m using a 145-liter sample at an atmospheric temperature of 23°C and an atmospheric pressure of 764 mm Hg. Under the conditions of sample size (145 liters), the working range of the method is estimated to be 1.3-35.7 mg/cu m.
- 2.2 The sensitivity of the sampling and analytical method for a 145-liter air sample using the 250-ml final solution volume is 143 micrograms of iron oxide, corresponding to 0.6 microgram/ml iron oxide. The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling time, or by scale expansion to increase instrumental response.

3. Interferences

- 3.1 Iron and other iron compounds which are collected on the cellulose ester membrane filter will cause a positive interference. The suspected identities of these compounds should be recorded and transmitted with the samples.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 3.87-18.19 mg/cu m is 0.067. This value corresponds to a 0.70 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.3. Details of the test procedures can be found in Reference 11.4.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no apparent bias in the sampling and analytical method. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Filter unit: The filter unit consists of a 37-mm diameter, 0.8-micrometer pore size mixed cellulose ester membrane filter, and an appropriate 37-mm three-piece cassette filter holder.

6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate.

6.3 Atomic absorption spectrophotometer equipped with an air-acetylene burner head.

6.3.1 Iron hollow cathode lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure-reducing valves: A 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank.

6.4 Manometer.

6.5 Thermometer.

6.6 Glassware, borosilicate

6.6.1 Phillips beakers: 100-ml.

6.6.2 Watchglass covers.

6.6.3 Pipets, delivery or graduated: 1, 3, 5, 7, and 10-ml.

6.6.4 Volumetric flasks: 250-ml.

6.7 Polyethylene Bottles

6.7.1 Five 100-ml capacity polyethylene bottles for working atomic absorption standards.

6.7.2 One 1000-ml capacity polyethylene bottle for stock atomic absorption standard.

6.8 Hot Plate: Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, concentrated.

7.3 Nitric acid, dilute: 5 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water.

7.4 Hydrochloric acid, 1:1 solution in distilled water.

7.5 Iron metal for preparation of AA standards.

7.6 Iron oxide powder, Fe_2O_3 , 325 mesh.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling 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 cellulose membrane filter is held in place by a cellulose backup pad. Secure the cassette holder together with tape or shrinkable band.

- 8.3.2 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.
- 8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
- 8.3.4 A sample size of 150 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of 5%.
- 8.3.5 Since the filter may become plugged by oil mist or overloaded as evidenced by caking, the filter and pump's sampling rate should be checked periodically. When the filter becomes overloaded or when the pump's flow rate cannot be adjusted to 1.5 liters per minute, terminate sampling.
- 8.3.6 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.
- 8.3.7 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 handling as the samples, except that no air is drawn through it. Label this as a blank.
- 8.3.8 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

- 8.4.1 Transfer each sample to a clean 100-ml Phillips beaker.
- 8.4.2 Wet Ashing. Treat the sample with 3 ml of 1:1 hydrochloric acid to solubilize any iron oxide which may be present. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Repeat twice. Repeat this procedure again three times except use concentrated nitric acid instead of hydrochloric acid. After the digestion process is complete, cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a fume hood until a white ash appears. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse the sides of the beaker, and allow to evaporate to dryness.

- 8.4.3 Cool each beaker and dissolve residues in 12.5 ml concentrated nitric acid.
- 8.4.4 Quantitatively transfer the clear solutions to a 250-ml volumetric flask.
- 8.4.5 Rinse each beaker at least three times with 2-3 ml portions of distilled or deionized water and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 250 ml with distilled or deionized water.
- 8.4.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 248.3 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume before aspiration. In such a case, use no more acid solution in 8.4.3 than is necessary to effect a quantitative transfer.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

- 8.4.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

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 iron oxide. The analytical method recovery should be determined over the concentration range of interest.
- 8.5.2 Procedure for determining analytical method recovery. Place one 0.8-micron cellulose ester membrane filter into each of 24 clean 100-ml beakers. Amounts of iron oxide powder (Fe_2O_3) (to the nearest 0.01 mg) equal to the amount collected in a 150-liter sample at 2X, 1X, and 0.5X the OSHA standard level are added to the beakers: six at each level and six blanks. Three milligrams is the amount of Fe_2O_3 used at the 2X level; 1.5 mg at the 1X level; and 0.75 mg at the 0.5X level. The filters are then analyzed according to the method in Section 8.4.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or,

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

- 9.1 Prepare a 100 microgram/ml iron stock standard by dissolving 0.100 g iron metal in 50 ml hot concentrated nitric acid and diluting to 1 liter. Transfer to a 1-liter polyethylene bottle.
- 9.2 From the 100 ppm stock standard, prepare at least five working standards to cover the range from 250 to 2500 micrograms/250 ml. Prepare all standard solutions in dilute nitric acid and remake each day. Store the standard solutions in 100-ml polyethylene bottles.
- 9.3 Aspirate each of the standard samples and record the absorptions.
- 9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

- 10.1 Read the weight, in micrograms, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/250 ml.
- 10.2 Corrections for the blank must be made for each sample.

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

where:

$$\text{microgram sample} = \text{microgram found in sample filter}$$

$$\text{microgram blank} = \text{microgram found in blank filter}$$

- 10.3 Corrections for analytical method recovery (A.M.R.) must be made.

$$\text{Corrected microgram/sample} = \frac{\text{microgram (Section 10.2)}}{\text{A.M.R.}}$$

- 10.4 Calculate the micrograms of iron oxide by multiplying the micrograms iron found (Section 10.3) by 1.43, which is a conversion factor to convert micrograms iron to micrograms iron oxide.
- 10.5 For personal sampling pumps with rotameters only, the following air 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
t = sampling time
P = pressure during calibration of sampling pump (mm Hg)
P₁ = pressure of air sampled (mm Hg)
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K)

10.6 The concentration of iron oxide in the air sample can be expressed in mg/cu m (microgram/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{microgram (Section 10.4)}}{\text{Air Volume Sampled (liter)}}$$

11. References

11.1 Analytical Methods for Flame Spectrophotometry, Varian Associates, 1972.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.4 Backup Data Report for Iron Oxide Fume, prepared under NIOSH Contract No. 210-76-0123.

Methoxychlor

Analyte:	Methoxychlor	Method No.: S371
Matrix:	Air	Range: 7.7-31 mg/cu m in a 100-L sample
OSHA Standard:	15 mg/cu m	Precision ($\overline{CV}_T$): 0.054
Procedure:	Filter collection, iso-octane extraction, GC, electrolytic conductivity detection	Validation Date: 12/23/77

1. Synopsis

- 1.1 A known volume of air is drawn through a glass fiber filter to collect particulate matter containing methoxychlor.
- 1.2 Methoxychlor is extracted from the filter with iso-octane, and the sample is analyzed by gas chromatography using ECD.

2. Working Range Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 7.7-31 mg/cu m at an atmospheric temperature of 23°C and atmospheric pressure of 761 mm Hg, using a 100-liter sample.
- 2.2 The upper limit of the range of the method depends on the capacity of the glass fiber filter. If higher concentrations than those tested are to be sampled, smaller volumes should be used.

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 compound that has the same retention time as methoxychlor 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 Technical formulations usually contain 6-12% of the o,p' isomer of methoxychlor. Gas chromatographic conditions should be adjusted so the isomers are separated.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 7.7-31 mg/cu m was 0.054 for 18 samples collected from test atmospheres. This value corresponds to a 0.81 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 On the average, the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.3% higher than the "true" concentrations for 18 samples. 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. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries, collection efficiency of the filter, and storage stability were good and would not contribute to a bias in a determined concentration. Storage stability studies on samples collected from a test atmosphere at a concentration of 15.36 mg/cu m indicate that collected samples are stable for at least 7 days. The mean of samples analyzed immediately versus the mean of samples analyzed after 7 days of collection compare within 5%.

5. Advantages and Disadvantages

- 5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.
- 5.2 The analytical method is selective for halogenated compounds.

6. Apparatus

- 6.1 Filter Unit: The filter unit consists of a 37-mm diameter glass fiber filter (Gelman Type A/E or equivalent) and a polystyrene 37-mm two-piece cassette filter holder. The filter is held in the two-piece filter holder supported by a backup pad. The filter must be free of organic binders. Filter holders made of Tenite should not be used.
- 6.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative filter cassette in the line to minimize errors associated with uncertainties in the volume sampled.
- 6.3 Manometer.
- 6.4 Thermometer.
- 6.5 Scintillation vials: 20-mL, with Teflon-lined caps, or equivalent.

- 6.6 Gas chromatograph equipped with an electrolytic conductivity detector.
- 6.7 Column (5.5-m long x 4-mm I.D. glass) packed with 5% SE-30 on Chromosorb W.
- 6.8 An electronic integrator or some other suitable method for measuring peak areas.
- 6.9 Tweezers.
- 6.10 Microliter syringes: 25-microliter.
- 6.11 Volumetric flasks: Convenient sizes for preparing standard solutions.
- 6.12 Pipets: Convenient sizes for preparing standard solutions, and 15-mL pipets for measuring the extraction medium.

7. Reagents

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

- 7.1 Methoxychlor.
- 7.2 Iso-octane.
- 7.3 Helium, purified.
- 7.4 Hydrogen, prepurified.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and 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 two-piece filter cassette holder and close firmly. The filter is supported by a backup pad.
 - 8.2.2 Remove the cassette plugs and attach the cassette to the personal sampling pump tubing. Clip the cassette to the worker's lapel.
 - 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 100 liters is recommended. Sample at a flow rate of 1.5 liter/minute. The flow rate should be known with an accuracy of 5%.

- 8.2.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading of greater than 2 mg of dust per sample or by the presence of oil mists or other liquids in the air, the 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 ambient temperature and pressure, sample flow rate, and collection time. If pressure reading is not available, record the elevation.
- 8.2.7 Cap each end of the filter cassette firmly.
- 8.2.8 Record the sample identity and all relevant sampling data.
- 8.2.9 The filter cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.
- 8.2.10 With each batch of ten samples, submit one 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 a blank.
- 8.2.11 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the collected samples.

8.3 Analysis of Samples

- 8.3.1 Each sample is analyzed separately.
- 8.3.2 Remove the glass fiber filter from the cassette filter holder and place it in a clean scintillation vial. Care must be taken to handle the filter with clean tweezers.
- 8.3.3 Pipet 15 mL of iso-octane into each vial. Swirl the contents in each vial occasionally for a period of 15 minutes.
- 8.3.4 Appropriate filter blanks must be analyzed at the same time as the samples.
- 8.3.5 GC Conditions. The typical operating conditions for the gas chromatograph are:

- 80 mL/minute helium carrier gas flow
- 80 mL/minute hydrogen flow through pyrolysis tube of the detector
- 225°C column temperature
- 250°C injector temperature
- 250°C transfer block temperature
- 820°C furnace temperature

The retention time of the p,p' isomer of methoxychlor is 6.0 minutes. The o,p' isomer will elute before the p,p' isomer.

- 8.3.6 Injection. The first step in the analysis is to inject the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, a solvent flush injection technique should be used. A 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe, the needle is removed from the solvent, and the plunger is pulled back about 1.0 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 15-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 before injection, the plunger is pulled back 2.0 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 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.

Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.3.5), it was found that 3.0 minutes was adequate to elute the solvent.

- 8.3.7 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.

9. Calibration and Standardization

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg methoxychlor/15 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 electrolytic conductivity response.

- 9.1 Prepare several stock standard solutions of methoxychlor in iso-octane.

9.2 From the above stock solutions, appropriate aliquots are withdrawn and dilutions are made in iso-octane. Prepare at least 5 working standards to cover the range of 0.15-4.5 mg/15 mL. This range is based on a 100-liter sample.

9.3 Prepare a standard calibration curve by plotting concentration of methoxychlor in mg/15 mL versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 mL of iso-octane 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 sample.

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

where:

$$\text{mg sample} = \text{mg found in sample filter}$$

$$\text{mg blank} = \text{mg found in blank filter}$$

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:

$$f = \text{flow rate sampled}$$

$$t = \text{sampling time}$$

$$P_1 = \text{pressure during calibration of sampling pump (mm Hg)}$$

$$P_2 = \text{pressure of air sampled (mm Hg)}$$

$$T_1 = \text{temperature during calibration of sampling pump (°K)}$$

$$T_2 = \text{temperature of air sampled (°K)}$$

10.4 The concentration of methoxychlor in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2)} \times 1000 \text{ (liters/cu m)}}{\text{Corr. Air Volume Sampled (liters) (Section 10.3)}}$$

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 Methoxychlor, prepared under NIOSH Contract No. 210-76-0123.

Methylcyclohexanol*

Analyte:	Methylcyclohexanol	Method No.: S374
Matrix:	Air	Range: 215-920 mg/cu m in a 12-L sample
OSHA Standard:	100 ppm (470 mg/cu m)	Precision ($\overline{CV}_T$): 0.063
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date: 1/20/78

1. Synopsis

- 1.1 A known volume of air is drawn through a tube containing activated coconut charcoal to trap methylcyclohexanol (Reference 11.1).
- 1.2 Methylcyclohexanol is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 This method was validated over the range of 215-920 mg/cu m at an atmospheric temperature of 25.5°C and atmospheric pressure of 761 mm Hg, using a 12-liter sample. This sample size is based on the capacity of the charcoal to collect vapors of methylcyclohexanol in air. 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 charcoal. This capacity may vary with the concentrations of methylcyclohexanol and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test gas mixture. A breakthrough test was conducted at a concentration of 942 mg/cu m and 85% relative humidity. Breakthrough occurred in 116 minutes at an average sampling rate of 0.190 liter/minute. This corresponds to a breakthrough capacity of 20.8 mg and volume of 22.4 liters.

* 50:50 mixture of the meta and para isomers of methylcyclohexanol

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 methylcyclohexanol 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 215-920 mg/cu m was 0.063. This value corresponds to a 30 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.
- 4.2 The Coefficient of Variation is a good measure of the accuracy of the method. Experiments performed in validation studies are described in Reference 11.3. In these experiments the desorption efficiency was greater than 0.919 for a loading of 2.710-11.31 mg on the sorbent. A correction was applied for this recovery. On the average the concentrations obtained at 0.5X, 1X, and 2X the OSHA standard level were 2.9% higher than the "true" concentration for 17 samples collected from dynamically generated test atmospheres. This difference does not represent a bias in the method, but rather a random variation from the experimentally determined "true" concentration. Storage stability studies indicated that the mean concentration of samples analyzed after 7 days compared within 0.2% to the mean concentration of samples analyzed immediately after collection. Thus, there are no known uncorrected sources of bias 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 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 methylcyclohexanol found on the backup section of the charcoal tube 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 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 recommended flow rate. Each personal sampling pump must be calibrated with a representative charcoal tube in the line to minimize errors associated with uncertainties in the volume sampled.
- 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 two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. 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 must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (12 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W.
- 6.5 An electronic integrator or some other suitable method of determining peak areas.
- 6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon caps.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-mL and other convenient sizes.
- 6.9 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

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

- 7.1 m-Methylcyclohexanol.
- 7.2 p-Methylcyclohexanol.
- 7.3 Methylene chloride.

7.4 Methylcyclohexanol Stock Standard Solution. Prepare a standard solution of a 50:50 mixture of the m- and p-isomers of methylcyclohexanol.

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, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.

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

8.2.3 The charcoal tube should be placed in a vertical direction during sampling 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 A sample size of 12 liters is recommended. Sample at a known flow rate of 0.01-0.2 liter/minute. Record the 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 The charcoal tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.2.8 With each 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 charcoal tubes should be shipped 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.

- 8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the collected samples.

8.3 Analysis of Samples

- 8.3.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-mL stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another sample container vial. These two sections are analyzed separately.
- 8.3.2 Desorption of Samples. Prior to analysis, 1.0 mL of methylene chloride is pipetted into each sample container. Desorption should be done for 20 minutes. Tests indicated 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. All work with methylene chloride should be performed in a hood.
- 8.3.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

60 mL/min (60 psig) nitrogen carrier gas flow
50 mL/min (24 psig) hydrogen gas flow to detector
500 mL/min (50 psig) air flow to detector
230°C injector temperature
230°C detector manifold temperature
140°C column temperature

A single peak for the meta and para isomers of methylcyclohexanol will be observed. A retention time of 5-6 minutes is to be expected for a mixture of the meta and para isomers of methylcyclohexanol under these conditions and using the column recommended in Section 6.4.

The method was validated for a mixture of the meta and para isomers of methylcyclohexanol. However, the response characteristics of the flame ionization detector and desorption efficiencies of the ortho isomer were found to be similar to the mixture of the meta and para isomers. Ortho-methylcyclohexanol elutes before the meta/para isomers and may appear as a shoulder peak in front of the meta/para peak. If this occurs, it may be necessary to alter chromatographic conditions to either merge the two peaks or separate them; this will be dependent on the concentration of the ortho isomer.

8.3.4 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. Three 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 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 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal 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 charcoal.

8.4.2 Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of a 50:50 mixture of the meta and para isomers of methylcyclohexanol is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The density of methylcyclohexanol is 0.914 at 20°C. The amount injected is equivalent to that present in a 12-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the methylcyclohexanol onto the charcoal. 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 8.4.

Two or three standards are prepared by injecting the same volume of methylcyclohexanol into 1.0 mL of methylene chloride with the same syringe used in the preparation of the samples. These are analyzed with the samples. These standards are used to confirm the calibration of the gas chromatograph.

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

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)} - \text{Blank (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of methylcyclohexanol collected on the charcoal. Plot the desorption efficiency versus weight of methylcyclohexanol 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 approximately 0.1 to 3 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/1.0 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 FID response.

9.1 From the stock standard solution (Section 7.4), appropriate aliquots are withdrawn and dilutions are made in methylene chloride. Prepare at least 5 working standards to cover the range of 0.56-16.8 mg/mL. This range is based on a 12-liter sample.

9.2 Analyze the standards as per Section 8.3.

9.3 Prepare a standard calibration curve by plotting concentration of methylcyclohexanol in mg/1.0 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 because the standard curve is based on mg/1.0 mL methylene chloride 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 front section of sample tube

mg blank = 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 weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

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

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.6 The concentration methylcyclohexanol in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 (L/mole) at 25°C and 760 mm Hg

M.W. = molecular weight (g/mole) of methylcyclohexanol

760 = standard pressure (mm Hg)

298 = standard temperature (°K)

11. References

- 11.1 White, L.D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).
- 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.
- 11.3 Backup Data Report for Methylcyclohexanol, prepared under NIOSH Contract No. 210-76-0123.

Methylcyclohexanone*

Analyte:	Methylcyclohexanone	Method No.: S375
Matrix:	Air	Range: 210-850 mg/cu m
OSHA Standard:	100 ppm (460 mg/cu m) - skin	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on Porapak Q, desorption with acetone, GC	Validation Date: 2/18/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a glass tube containing Porapak Q to trap methylcyclohexanone vapors.
- 1.2 Methylcyclohexanone is desorbed from the Porapak Q with acetone, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 213-852 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 759 mm Hg, using a 3-liter sample. This maximum sample size is based on the capacity of the Porapak Q to collect vapors of methylcyclohexanone in air at high relative humidity. 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 Porapak Q. This capacity may vary with the concentrations of methylcyclohexanone and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 150 mg of Porapak Q) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for three hours at an average sampling rate of 0.044 liter/minute and relative humidity of greater than 80% and temperature of 23°C. The breakthrough test was conducted at a concentration of 852 mg/cu m.

* Methylcyclohexanone is a mixture of isomers, primarily 3-methylcyclohexanone and 4-methylcyclohexanone.

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 methylcyclohexanone 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 213-852 mg/cu m was 0.057. This value corresponds to a 26 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 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1% higher than the "true" concentrations for 17 samples. 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 426 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 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 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 methylcyclohexanone found on the backup section of the Porapak Q tube 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 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.

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.

6.2 Porapak Q Tubes: Glass tube with both ends unsealed, 8.5-cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 50/80 mesh Porapak Q* separated by a 2-mm portion of urethane foam. The adsorbing section of the tube contains 150 mg of Porapak Q, and the backup section contains 75 mg. A plug of silylated glass wool is placed at the ends of the tube. The pressure drop across the tube must be less than 10 mm of mercury at a flow rate of 0.05 liter per minute. Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Porapak Q adhering to the walls of the glass tubes. The Porapak Q tubes are capped with plastic caps at each end.

Sorbent Washing Procedure: Prior to useage, Porapak Q is washed and dried to reduce or eliminate the effects of unreacted monomers, solvents, and manufacturer's batch to batch differences in production. A quantity of Porapak Q is placed in a sintered glass filter fitted to a large vacuum flask. Reagent grade acetone, equal to twice the volume of Porapak Q, is added to the sorbent and mixed, and a vacuum is applied. Repeat the operation of wash-mix-vacuum six times. The sorbent is then transferred to an evaporating dish and dried in a vacuum oven at 120°C under 25 inches mercury vacuum for four hours.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft long x 1/8-in O.D. stainless steel) packed with 50/80 mesh Porapak Q.

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

6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Polyseal** caps or equivalent.

6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.

6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.

6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.

6.10 Stopwatch.

* Porapak Q is a solid adsorbent which is manufactured by Waters Associates, Inc., and is commonly used as a gas chromatographic column packing material.

**The Polyseal Corp., Baltimore, Md.

6.11 Manometer.

7. Reagents

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7.1 Acetone, reagent grade.

7.2 3-Methylcyclohexanone, quantitative grade from Polyscience Corp., or equivalent.

7.3 4-Methylcyclohexanone, quantitative grade from Polyscience Corp., or equivalent.

7.4 n-Hexane, chromatographic quality.

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, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative Porapak Q tube in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.3)

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of Porapak Q is used as a backup and should be positioned nearer the sampling pump.

8.3.3 The tube should be placed in a vertical direction during sampling to minimize channeling through the Porapak Q.

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

8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record sampling time, flow rate, and type of sampling pump used.

- 8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The Porapak Q tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 With each 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.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Polyseal cap or equivalent. This sample should not be transported in the same container as the Porapak Q tubes. A minimum of 18 extra Porapak Q tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Porapak Q tube. Remove the glass wool plug and transfer the first (larger) section of Porapak Q to a 2-ml stoppered sample container. Remove the separating section of urethane foam and transfer the backup section of Porapak Q to another stoppered container. Analyze these two sections separately. Firm tapping of the tube may be necessary to affect complete transfer of the Porapak Q.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of acetone is pipetted into each sample container. Cap and shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the methylcyclohexanone is desorbed.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 50 ml/min (60 psig) nitrogen carrier gas flow
 - 65 ml/min (24 psig) hydrogen gas flow to detector
 - 500 ml/min (50 psig) air flow to detector
 - 200°C injector manifold temperature
 - 260°C detector manifold temperature
 - 190°C column temperature

A retention time of approximately 9 minutes is to be expected for methylcyclohexanone under these conditions and using the column recommended in Section 6.4. The acetone will elute from the column before the methylcyclohexanone. A single peak will be observed for the isomers.

8.4.4 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. Three 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. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Porapak Q.

8.4.5 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.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Porapak Q 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 Porapak Q.

8.5.2 Porapak Q equivalent to the amount in the first section of the sampling tube (150 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This Porapak Q must be from the same batch as that used in obtaining the samples. The open end is capped with Parafilm. A known amount of a hexane solution of a 50/50 mixture of 3-methylcyclohexanone and 4-methylcyclohexanone containing 345 mg/ml is injected directly into the Porapak Q with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is equivalent to that present in a 3-liter air sample at the

selected level. It is not practical to inject the neat liquid directly onto the Porapak Q, because the amounts to be added would be too small to measure accurately.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the methylcyclohexanone onto the Porapak Q. 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 8.4.

Two or three standards are prepared by injecting the same volume of methylcyclohexanone into 1.0 ml of acetone with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of methylcyclohexanone collected on the Porapak Q. Plot the desorption efficiency versus weight of methylcyclohexanone found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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 GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 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 FID response.

- 9.1 Prepare a stock standard solution containing 41.4 mg/ml of a 50/50 mixture of 3-methylcyclohexanone and 4-methylcyclohexanone in acetone.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in acetone. Prepare at least 5 working standards to cover the range of 0.138-4.14 mg/1.0 ml. This range is based on a 3-liter sample.
- 9.3 Prepare a standard calibration curve by plotting concentration of methylcyclohexanone in mg/1.0 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 because the standard curve is based on mg/1.0 ml acetone 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 front section of sample tube

mg blank = 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 weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

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

t = sampling time

P₁ = pressure during calibration of sampling pump (mm Hg)

P₂ = pressure of air sampled (mm Hg)

T₁ = temperature during calibration of sampling pump (°K)

T₂ = temperature of air sampled (°K)

10.6 The concentration of methylcyclohexanone in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

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 (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of o-methylcyclohexanone
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.2 Backup Data Report for Methylcyclohexanone, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Sodium Hydroxide

Analyte:	Sodium Hydroxide	Method No.:	S381
Matrix:	Air	Range:	0.75 - 3.9 mg/cu m
OSHA Standard:	2 mg/cu m	Precision: ($\overline{CV}_T$):	0.062
Procedure:	Filter Collection, extraction with aqueous acid, back titration with sodium hydroxide	Validation Date:	7/8/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a polytetrafluorethylene filter to trap the sodium hydroxide aerosol present.
- 1.2 The sodium hydroxide collected is extracted from the filter by addition of a known amount of excess hydrochloric acid and the resultant solution purged with a stream of nitrogen gas.
- 1.3 The excess hydrochloric acid is titrated with a standard solution of sodium hydroxide under a nitrogen atmosphere.
- 1.4 The amount of sodium hydroxide collected is calculated from the difference between the known amount of acid added and the amount of acid remaining after extraction of the filter.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.758-3.88 mg/cu m at an atmospheric temperature and pressure of 23°C and 758 mm Hg, using a 360-liter sample. For a sample size of 360 liters, the working range of the method is estimated to be 0.4-5.4 mg/cu m.
- 2.2 The method may be extended to higher concentrations by addition of larger aliquots of standard hydrochloric acid. The detection limit of the analytical method is estimated to be 28 µg of sodium hydroxide or 7×10^{-4} mmoles of alkalinity.

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 the method determines total alkalinity present in particulate form and thus is not specific to sodium hydroxide.

- 3.3 If the titration curve obtained in the analysis is not one of a titration of a strong acid with a strong base then the presence of an interfering species is indicated and the results should be confirmed by an alternate method of analysis.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.758 - 3.88 mg/cu m was 0.0622. This value corresponds to a 0.124 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 10.1. Details of the test procedures are found in Reference 10.2.
- 4.2 A collection efficiency of at least 99.0% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method -- the average recovery from the filters was 99.7%. In addition, the samples were found to be stable when stored on the filters for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable and involves no liquids. The filters are analyzed by means of a quick, instrumental method.
- 5.2 The method measures the toxic species, alkalinity, and is free from interference of other non-alkaline sodium compounds.
- 5.3 The method is not specific for sodium hydroxide but measures total alkalinity and the presence of any other alkaline species will present an interference.
- 5.4 Interference by carbon dioxide during collection has been minimized by virtue of the back titration used in the analytical procedure.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of aerosols has the following components:
- 6.1.1 Filter. The filter unit consists of the filter medium (Section 6.2) and 37-mm 3-piece cassette filter holder.
- 6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate is needed. The pump must be calibrated with a representative filter holder and filter in the line.

- 6.1.3 Thermometer.
- 6.1.4 Barometer.
- 6.1.5 Stopwatch.
- 6.2 A polytetrafluoroethylene (PTFE-Fluoropore) membrane filter, 1.0 micrometer pore size and 37-mm diameter. The filter is supported in the three-piece cassette by a cellulose backup pad.
- 6.3 Titration Assembly
 - 6.3.1 A pH meter equipped with pH electrodes and a recorder (recommended chart drive of 1.5 inches per minute).
 - 6.3.2 A titration vessel made from a 175-ml ointment jar (2.5 inches diameter) with two 5/8-inch holes drilled in the cap for the pH electrodes and two 3/8-inch holes for other inlets.
 - 6.3.3 A constant feed syringe drive and syringe (recommended delivery rate of 1 ml per minute).
 - 6.3.4 Magnetic stirrer and bar.
 - 6.3.5 Glass rod, 5-mm diameter and 15-cm long.
 - 6.3.6 Blunt-end Stainless Steel Needle, 10-cm long.

In the assembled apparatus the titration vessel contains the stirrer bar, solution to be titrated, the pH electrodes, nitrogen purge inlet and automatic syringe drive inlet all inserted through the cap and immersed in the solution. The vessel is positioned on top of the magnetic stirrer.

- 6.4 Pipets, 5 and 10 ml.
- 6.5 Balance, capacity of 1.000-100.000 g.
- 6.6 Ruler, graduated in millimeters.
- 6.7 Volumetric flasks, 100 and 1000 ml.
- 6.8 Glass bottle, 1 liter equipped with a stopper containing a trap filled with a suitable CO₂ absorbing material (recommended for storage of dilute sodium hydroxide solution).
- 6.9 Graduated Cylinder, 100 ml.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

- 7.1 Distilled water.
- 7.2 Standard stock hydrochloric acid solution, 0.1N.
- 7.3 Standard dilute hydrochloric acid, 0.01N. Prepare by diluting 10 ml of the stock solution into 100 ml.
- 7.4 Stock sodium hydroxide solution, 0.1N.
- 7.5 Working sodium hydroxide solution, 0.01N. Prepare by dilution of stock with distilled water through which nitrogen has been passed for 30 minutes.
- 7.6 Nitrogen gas.
- 7.7 Standard Buffer Solutions, pH 4 and pH 7.

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 PTFE 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 lay flat on the backup pad and 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.
 - 8.3.2 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 360 liters is recommended. Sample at a flow rate of 1.5 liters per minute for 4 hours. The flow rate should be known with an accuracy of at least $\pm 5\%$.
 - 8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy partic-

ulate 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 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 Set the pH recorder with the pH 4 and 7 buffers so that the range between pH 3 and 10 is recorded.

8.4.2 Add 75 ml of distilled water to the titration vessel.

8.4.3 Open the cassette filter holder and carefully remove the PTFE membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer the filter to the titration vessel with the collection side face down. Place the end of a glass rod in the center of the filter to maintain it completely below the liquid surface during the complete analytical procedure. Replace the titration vessel cover and place the pH electrode in place.

8.4.4 Pipet 5 ml of 0.01N hydrochloric acid into the vessel, start the magnet stirrer and a nitrogen purge of the solution.

8.4.5 After 15 minutes have passed, titrate the solution with 0.01N sodium hydroxide while maintaining a nitrogen purge in the system. Initiate the syringe drive at a known position on the chart recorder paper so that the amount of NaOH added may be determined from the distance elapsed to the inflection point of the titration curve.

8.4.6 Appropriate filter blanks should be analyzed by the same procedure used for the samples.

8.5 Calibration of Syringe Drive and Chart Recorder

8.5.1 The syringe drive must be calibrated so that the volume

of sodium hydroxide added can be known accurately. Fill the syringe with the titrating solution and connect the delivery tube to a weighing bottle which has been pretared. Activate the syringe drive for a period of time sufficient to allow the delivery rate in grams/min to be determined by weighing the amount of liquid collected.

- 8.5.2 Determine the syringe delivery rate in ml/min by converting the grams/min to volume/min using the density of the solution at the appropriate temperature.
- 8.5.3 Calibrate the chart speed on the recorder and accurately determine the speed (in mm/minute).
- 8.5.4 Using the calibrated syringe delivery rate and the recorder chart speed calculate the volume per mm on the chart paper.

$$\text{ml per mm} = \text{ml per minute/mm per minute}$$

8.6 Determination of Sample Recovery

- 8.6.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound from the collection device. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the true value.
- 8.6.2 Procedure for Determining Recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected is added to a representative PTFE membrane filter and air dried. The analyte is then recovered from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within $\pm 5\%$.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 360-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5, 1.0 and 2.0X the OSHA standard) were spiked accordingly by adding an aliquot of a solution of sodium hydroxide in methanol containing known amounts of alkalinity. A parallel blank filter was also treated in the same manner except that no sample was added to it. All the filters were then extracted and analyzed as described in Section 8.4. The average recovery value obtained was 0.997.

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

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}}$$

8.7 Standardization of the Titrating Solution

8.7.1 The sodium hydroxide titrating solution is standardized against the standard 0.0100N hydrochloric acid prepared by dilution of standard 0.1N hydrochloric acid.

8.7.2 The standardization is carried out according to the procedure described in Section 8.4 except for addition of a sample or a blank filter. The standardization is carried out in triplicate. The normality of sodium hydroxide is calculated as follows:

$$\text{Normality of sodium hydroxide} = \frac{(\text{Normality of hydrochloric acid}) \times (\text{Volume of hydrochloric acid added})}{(\text{mm on chart}) \times (\text{ml/mm for chart})}$$

9. Calculations

9.1 Determine the volume of sodium hydroxide needed to neutralize the excess hydrochloric acid present by multiplying the distance (in mm) elapsed from the initiation of the syringe drive to the endpoint in the titration by the conversion of ml per mm or:

$$\text{Volume of sodium hydroxide needed (ml)} = \text{mm to endpoint} \times \text{ml/mm}$$

9.2 The amount of sodium hydroxide (alkalinity) present on the filter is determined from the difference between the amount of hydrochloric acid added and the amount of sodium hydroxide needed in the back titration, or:

$$\text{mmoles of sodium hydroxide present} = (\text{Volume of hydrochloric acid added (ml)} \times \text{Normality of hydrochloric acid})$$

$$- (\text{Volume of sodium hydroxide added (ml)} \times \text{Normality of sodium hydroxide})$$

The amount of sodium hydroxide present is calculated using the molecular weight:

$$\mu\text{g sodium hydroxide sample} = \text{mmoles of sodium hydroxide present} \times 40,000.$$

9.3 Correction for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in blank filter}$$

9.4 Divide the total weight by the recovery to obtain the corrected μg sample.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total Weight } (\mu\text{g})}{\text{Recovery (Section 8.6)}}$$

9.5 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 = 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 ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

9.6 The concentration of the analyte in the air sampled can be expressed in mg/cu m . ($\mu\text{g/liter} = \text{mg/cu m}$)

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 9.4)}}{\text{Volume of Air Sampled in Liters (Section 9.5)}}$$

10. References

10.1 Memoranda, Kenneth A. Busch (Chief, Statistical Service, DLCD), to Deputy Director, DLCD, dated 1/6/77, 11/8/77, subject: Statistical Protocol for Analysis of Data from Contract CDC-99-74-45.

10.2 S381 Backup Data Report for Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, 7/8/77.

Tetraethyl lead

Analyte:	Tetraethyl lead (as Pb)	Method No:	S383
Matrix:	Air	Range:	0.045 - 0.20 mg/cu m (as Pb)
OSHA Standard:	8 hour TWA 0.075 mg/cu m (as Pb)	Precision ($\overline{CV}_T$):	0.087
Procedure:	Adsorption on XAD-2, desorption with pentane, GC/photoionization de- tection.	Validation Date:	3/18/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a XAD-2 tube to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.
- 1.2 The XAD-2 in each tube is transferred to a vial and the tetraethyl lead is desorbed with pentane and analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.045 - 0.20 mg/cu m (as Pb) at an atmospheric temperature of 22°C and atmospheric pressure of 767 mm Hg using a 120-liter sample volume. The sensitivity of this method is estimated to be at least 0.1 µg/ml. 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 tube. This capacity can vary with the concentrations of analyte and other substances in the air. (See Section 5.2)

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, temperature, etc.) must be changed to solve the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.05-0.20 mg/cu m (as Pb) was 0.087. 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 On the average, the concentrations "found" at the OSHA standard level using the overall sampling and analytical method were 5.5% higher than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.2). Any difference between the two concentrations does not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

The data are based on validation experiments using the internal standard method.

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 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When an atmosphere at 90% relative humidity containing 0.156 mg/cu m of tetraethyl lead was sampled at 1.0 liter per minute, 2.5% breakthrough was observed after 240 minutes (capacity is at least 264 liters or 40 μ g). The sample size recommended is less than the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard to minimize the probability of overloading the sampling tube.
- 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.

6. Apparatus

6.1 Sampling Apparatus

- 6.1.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.1.2 Resin tubes. Glass tube with both ends flame-sealed, 10-cm long with 6-mm O.D. and 4-mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin. The adsorbing section contains 100 mg of resin, the backup section 50 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute, it is necessary to avoid over-packing with glass wool.
- 6.1.3 Barometer.
- 6.1.4 Thermometer.
- 6.1.5 Stopwatch.
- 6.2 Gas chromatograph. The unit must be equipped with a photo-ionization detector.
- 6.3 Column. (10-ft. x 1/8-in. stainless steel) packed with 5% Carbowax 20M stationary phase on 80/100 mesh Chromosorb WAW.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Two milliliter sample containers with glass stoppers or Teflon lined caps. If an automatic injector is used the associated vials are acceptable.
- 6.6 Microliter syringes. 10, 20, 50, 100 and 250-microliter and other convenient sizes for preparing standards.
- 6.7 Pipet. 1-ml, delivery type.
- 6.8 Volumetric flasks. 10-ml or convenient sizes for making standard solutions and internal standard solutions.

7. Reagents

- 7.1 Pentane, reagent grade.
- 7.2 Tetraethyl lead.
- 7.3 Dodecane or other suitable internal standard. The appropriate solution of the internal standard is prepared in pentane.
- 7.4 Nitrogen, purified.
- 7.5 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Larger batches may be prepared by using a Giant extractor. Overnight (24 hours) extractions are then performed successively with water, methanol, diethylether and finally, n-pentane. Distilled-in-glass solvents are used in all cases. Resin has been prepared in this manner using charges of about 700g of resin and 1.5 liters of each solvent. The resin is dried by maintaining it under vacuum (1-10 torr) and mild heat for about 24 hours.

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 tube series in the line; the tube is described in Section 6.2. 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, break the two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The section containing 50 mg of resin is used as a backup and should be positioned nearest the sampling pump.
 - 8.3.3 The resin tube series should be placed in a vertical direction during sampling to minimize channeling through the resin.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the resin tube.

- 8.3.5 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 with an accuracy of at least $\pm 5\%$.
- 8.3.6 Record the ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 The resin tube 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 10 samples, submit one resin tube which has been handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped resin 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 resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the front 100-mg section is transferred to a 2-ml sample vial. The separating section of glass wool is removed and discarded. The second 50-mg section is transferred to another container. These two sections are analyzed separately.
- 8.4.2 Desorption of Sample. Prior to analysis, 1.0 ml of pentane is pipetted into each sample container. 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 1.0 ml of internal standard solution in pentane. For the validation studies a solution containing 0.1 μ l of dodecane per milliliter of pentane was used as an internal standard solution.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 20 ml/min (60 psig) nitrogen carrier gas flow
2. 185°C injector temperature
3. 200°C manifold temperature
4. 210°C photoionization detector temperature
5. 75°C column temperature

A retention time of approximately 4.5 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The internal standard elutes after the tetraethyl lead.

8.4.4 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 9.2.

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 XAD-2 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 resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at the OSHA standard level.

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 tetraethyl lead found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of tetraethyl lead found in the sample.

The analytical samples are prepared as follows: XAD-2, equivalent to the amount in the front section (100 mg), is measured into a 2-ml sample vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of tetraethyl lead in pentane (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- μ l 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 tetraethyl lead equivalent to that present in a 120-liter sample at the selected level. A stock solution containing 2.17 milligrams of lead (as tetraethyl lead) per milliliter of pentane was prepared. 2, 4, and 8-microliter aliquots of the solution were added to the XAD-2 resin tubes to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples were allowed to stand for at least overnight to assure complete adsorption of the analyte onto the resin. 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 experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5. Calibration standards are prepared by adding the appropriate volume of spiking solution to 1.0 ml of pentane with the same syringe used in the preparation of the samples. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of pentane containing a known amount of the internal standard.

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

$$\text{D.E.} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependent on the amount of tetraethyl lead collected on the resin. Plot the desorption efficiency versus weight of tetraethyl lead found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

9.1 Add 1.0 ml of pentane (or 1.0 ml of internal standard solution) to a 2-ml vial. The same solution of tetraethyl lead in pentane as described in Section 8.5.2 may be used to prepare calibration standards or alternatively microliter aliquots of pure tetraethyl lead could be diluted to the appropriate volume to standard concentration range of interest. The concentration of standards can be expressed in terms of μg of lead as tetraethyl lead in 1 ml of pentane.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in $\mu\text{g}/\text{ml}$.

For the internal standard method, use pentane containing a pre-determined amount of the internal standard. The internal standard concentration used was approximately 2-3 times the concentration of tetraethyl lead at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in $\mu\text{g}/\text{ml}$.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in photoionization detector response.

10. Calculations

10.1 Read the weight, in μg of lead, 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 pentane 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

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\mu\text{g sample} = \mu\text{g found in front (100-mg) sample section}$$

$$\mu\text{g blank} = \mu\text{g found in front (100-mg) blank section}$$

A similar procedure is followed for the backup (50-mg) section.

- 10.3 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

- 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 = sample flow rate

t = sampling time

P₁ = 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 ($^{\circ}\text{K}$)

T_2 = ambient temperature of air sampled ($^{\circ}\text{K}$)

- 10.6 The concentration of lead as tetraethyl lead in the air sampled can be expressed in mg per cu m which is numerically equal to μg per liter

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.4)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled

T = temperature ($^{\circ}\text{C}$) of air sampled

24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight

760 = standard pressure (mm Hg)

298 = standard temperature ($^{\circ}\text{K}$)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Tetraethyl lead, No. S383, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Tetramethyl lead (as Pb)

Analyte:	Tetramethyl lead	Method No: S384
Matrix:	Air	Range: 0.040-0.18 mg/cu m (as Pb)
OSHA Standard:	0.07 mg/cu m (as Pb)	Precision ($\overline{CV}_T$): 0.087
Procedure:	Adsorption on XAD-2, desorption with pentane, GC/photoionization de- tector	Validation Date: 4/15/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through a XAD-2 tube to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.
- 1.2 The XAD-2 in each tube is transferred to a vial and the tetramethyl lead is desorbed with pentane and analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.04-0.18 mg/cu m (as Pb) at an atmospheric temperature of 30°C and atmospheric pressure of 760 mm Hg using a 24-liter sample volume. For a 24-liter sample size, the working range of this method is estimated to be 0.02-0.2 mg/cu m. 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 tube. This capacity can vary with the concentrations of analyte and other substances in the air. (See Section 5.2)
- 2.3 The detection limit of this method is estimated to be at least 0.2 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, temperature, etc.) must be changed to solve the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.04-0.18 mg/cu m is 0.087. This value corresponds to a 0.006 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 concentrations "found" at the OSHA standard level using the overall sampling and analytical method were 0.9% lower than the "true" concentrations found for a limited number of samples analyzed by an alternate method (Reference 11.2). Any difference between the two concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

The data are based on validation experiments using the internal standard method.

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 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of micrograms that the tube will hold before overloading. When an atmosphere at 82% relative humidity containing 0.312 mg/cu m of tetramethyl lead was sampled at 0.2 liter per minute, no breakthrough was observed after 240 minutes (capacity is at least 48 liters or 15 μ g). The sample size recommended is less than the 5% breakthrough capacity at 82% R.H. for a test atmosphere at 2 times the OSHA standard to minimize the probability of overloading the sampling tube.
- 5.3 When the sample value obtained for the backup section of the sorbent tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

- 5.4 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.

6. Apparatus

6.1 Sampling Apparatus

- 6.1.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.1.2 Resin tubes. Glass tube with both ends flame-sealed, 10-cm long with 8-mm O.D. and 6-mm I.D., containing 2 sections of 20/50 mesh XAD-2 resin. The adsorbing section contains 400 mg of resin, the backup section 200 mg. A small wad of silylated glass wool is placed between the front adsorbing section and the backup section; a plug of silylated glass wool is also placed in front of the adsorbing section and at the end of the backup section. Since the pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute, it is necessary to avoid overpacking with glass wool.
- 6.1.3 Barometer
- 6.1.4 Thermometer
- 6.1.5 Stopwatch
- 6.2 Gas chromatograph. The unit must be equipped with a photo-ionization detector.
- 6.3 Column. (20 ft. x 1/8 in. stainless steel) packed with 10% Carbowax 20M stationary phase on 80/100 mesh Chromosorb WAW.
- 6.4 An electronic integrator or some other suitable method for measuring peak areas.
- 6.5 Four-milliliter screw cap vials with Teflon-lined caps.
- 6.6 Microliter syringes. 10, 25, 50, 100 and 250-microliter and other convenient sizes for preparing standards.
- 6.7 Pipet. 1 and 2-ml, delivery type.
- 6.8 Volumetric flasks. 10-ml or convenient sizes for making standard solutions and internal standard solutions.

7. Reagents

- 7.1 Pentane, reagent grade.
- 7.2 Tetramethyl lead.
- 7.3 Nonane or other suitable internal standard. The appropriate solution of the internal standard is prepared in pentane.
- 7.4 Nitrogen, purified.
- 7.5 Pre-cleaned resin: XAD-2 resin (20-50 mesh) can be obtained from the Rohm and Haas Company. XAD-2 resin is purified by charging an amount into a Soxhlet extractor. Larger batches may be prepared by using a Giant extractor. Overnight (24 hours) extractions are then performed successively with water, methanol, diethylether and finally, n-pentane. Distilled-in-glass solvents are used in all cases. 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 by maintaining it under vacuum (1-10 torr) and mild heat (70°C) for about 24 hours.

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 tube series in the line; the tube is described in Section 6.1.2. 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, break the two ends of the resin tube to provide an opening at least one-half the internal diameter of the tube (3 mm).
 - 8.3.2 The section containing 200 mg of resin is used as a backup and should be positioned nearest the sampling pump.
 - 8.3.3 The resin tube series should be placed in a vertical direction during sampling to minimize channeling through the resin.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the resin tube.
 - 8.3.5 A sample size of 24 liters is recommended. Sample at a flow rate of 0.2 liter per minute for 120 minutes. The flow rate should be known with an accuracy of at least $\pm 5\%$.

- 8.3.6 Record the ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.3.7 The resin tube 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 10 samples, submit one resin tube which has been handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped resin 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 resin tube is scored with a file in front of the first section of resin and broken open. The glass wool is removed and discarded. The resin in the front 400-mg section is transferred to a 4-ml vial. The separating section of glass wool is removed and discarded. The second 200-mg section is transferred to another vial. These two sections are analyzed separately. (see Section 5.3)
- 8.4.2 Desorption of Sample. Prior to analysis, 2.0 ml of pentane is pipetted into each 4-ml vial containing the 400 mg sections; 1.0 ml is added to the 200-mg backup sections. 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 internal standard solution prepared with pentane.
- If an automatic injector is used, the sample solutions are then transferred to the appropriate vials for analysis.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 17 ml/min (60 psig) Nitrogen carrier gas flow
2. 185°C injector temperature
3. 200°C manifold temperature
4. 210°C photoionization detector temperature
5. 75°C column temperature

A retention time of approximately 6 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The internal standard elutes after the tetramethyl lead.

8.4.4 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 XAD-2 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 resin used for sample collection and over the concentration range of interest. The desorption efficiency must be at least 75% at a sample loading equivalent to the OSHA standard level.

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 tetramethyl lead found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of tetramethyl lead found in the sample.

The analytical samples are prepared as follows: XAD-2, equivalent to the amount in the front section (400 mg), is measured into a 4-ml vial. This resin must be from the same batch as that used in obtaining the samples.

A known amount of a solution of tetramethyl lead in pentane (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 μ l 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 2 times the OSHA standard) were prepared by adding an amount of tetramethyl lead equivalent to that present in a 24-liter sample at the selected level. A stock solution containing 0.445 milligrams of tetramethyl lead (as lead) per milliliter of pentane was prepared. Two, 4, and 8 microliter aliquots of the solution were added to the XAD-2 resin tubes to produce samples equivalent to 24-liter collections at 0.5, 1 and 2 times the OSHA standard level. The analytical samples were allowed to stand for at least overnight to assure complete adsorption of the analyte onto the resin. 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 experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 ml of pentane with the same syringe used in the preparation of the samples. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 2.0 ml of pentane containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in μ g recovered from the tube divided by the weight in μ g added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}}$$

The desorption efficiency may be dependent on the amount of tetramethyl lead collected on the resin. Plot the desorption efficiency versus weight of tetramethyl lead found. This curve is used in Section 10.3 to correct for adsorption losses.

9. Calibration and Standards

9.1 Add 2.0 ml of pentane (or 2.0 ml of internal standard solution) to a 4-ml vial. The same solution in pentane as described in Section 8.5.2 may be used to prepare calibration standards or alternatively microliter aliquots of pure tetramethyl lead could be diluted to the appropriate volume. The concentration of standards can be expressed in terms of μg of tetramethyl lead (as lead) per 2 ml of pentane.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in $\mu\text{g}/2\text{ ml}$.

For the internal standard method, use pentane containing a pre-determined amount of the internal standard. The internal standard concentration used was approximately 4-5 times the concentration of tetramethyl lead at 2 times the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in $\mu\text{g}/2\text{ ml}$.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in photoionization detector response.

10. Calculations

10.1 Read the weight, in μg of tetramethyl lead (as lead) 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 pentane 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

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample} = \mu\text{g found in front (400-mg) sample section}$

$\mu\text{g blank} = \mu\text{g found in front (400-mg) blank section}$

A similar procedure is followed for the backup 200-mg section.

10.3 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section of the tube.

Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Weight (Front Section)}}{\text{D.E.}}$$

- 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 = 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 ($^{\circ}\text{K}$)

T_2 = ambient temperature of air sampled ($^{\circ}\text{K}$)

- 10.6 The concentration of tetramethyl lead (as lead) in the air sampled can be expressed in mg per cu m which is numerically equal to μg per liter

$$\text{mg}/\text{cu m} = \frac{\text{Corrected } \mu\text{g (see Section 10.4)}}{\text{Air Volume Sampled (liters)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg}/\text{cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

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
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."
- 11.2 Backup Data Report for Tetramethyl lead No. S384, prepared under NIOSH Contract No. 210-76-0123.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Vanadium, V₂O₅ Fume

Analyte:	Vanadium Oxides	Method No.: S388
Matrix:	Air	Range: 0.060-0.29 mg/cu m
OSHA Standard:	0.1 mg/cu m - Ceiling	Precision ($\overline{CV}_T$): 0.067
Procedure:	Filter collection, Alkali dissolution, Flameless AAS/HGA	Validation Date: 1/21/77

1. Principle of the Method

- 1.1 Vanadium oxides sample, collected on mixed cellulose ester membrane filter, is dissolved from the sample-containing filter by heating in a sodium hydroxide solution at 50° C for 15 minutes.
- 1.2 The solutions of samples and standards are analyzed by flameless atomic absorption spectrophotometry in a high temperature graphite atomizer (HGA). A hollow cathode lamp for vanadium is used to provide a characteristic vanadium line at 318.4 nm. The absorbance is proportional to the vanadium concentration.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.060-0.29 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 25-liter sample.
- 2.2 The OSHA standard for vanadium fume has a 15-minute ceiling value. Sampling at a nominal flow rate of 1.5 liters per minute for 15 minutes will yield 22.5 liters of air sample. For a sample size of 22.5 liters, the working range of the method is estimated to be 0.05-1 mg/cu m.
- 2.3 The method may be extended to higher values by further dilution of the sample solution; the absolute sensitivity of the method has not been established.

3. Interferences

- 3.1 There are no known spectral line interferences for the vanadium AAS assay.
- 3.2 The use of an alkaline dissolution method minimizes the potential interference of ferrovandium dust.
- 3.3 Vanadium exhibits self-absorption at 318.4 nm. It is necessary to operate the vanadium hollow cathode lamp at low currents to minimize self-absorption (Reference 11.1).

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV}_T$) for the combined analytical and sampling method in the range of 0.060-0.294 mg/cu m was 0.067. This value corresponds to a 0.007 mg/cu m standard deviation at the OSHA ceiling concentration. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2
- 4.2 A collection efficiency of at least 98.5% was determined for the collection medium; thus, no bias was introduced in the sample collection step. The analytical method recovery was found to be 94.3% with $CV_1 = 0.083$. Thus, CV_T is a satisfactory measure of both accuracy and precision. This is supported by data in which x-ray fluorescence was used as an independent method for determining generator concentration. (Reference 11.3).

5. Advantages and Disadvantages

- 5.1 The method is simple and specific for vanadium oxides (not vanadium metal).
- 5.2 The method does not distinguish the V_2O_5 dust.
- 5.3 The life of graphite tubes is limited due to high temperature atomization.
- 5.4 The calibration curve is non-linear above an absorbance of 0.3 units (ca. 75 ng V_2O_5) and in certain cases, depending on the graphite tube characteristics, it may be necessary to alternate samples with standards of similar response to obtain reliable results.

6. Apparatus

- 6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:
- 6.1.1 The filter unit, consisting of the filter media (section 6.2) and 37-mm 3-piece cassette filter holder.
- 6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

- 6.1.3 Thermometer
- 6.1.4 Barometer
- 6.1.5 Stopwatch
- 6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8 micrometer pore size.
- 6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have a high temperature graphite atomizer (HGA) and a deuterium arc background corrector.
 - 6.3.1 Vanadium hollow cathode lamp
 - 6.3.2 Deuterium arc lamp
 - 6.3.3 Purge gases: Argon (for HGA), Nitrogen (for Deuterium arc)
 - 6.3.4 Pressure regulators, two-stage, for each compressed gas tank used.
- 6.4 Glassware, borosilicate:
 - 6.4.1 50-ml beakers with watchglass covers.
 - 6.4.2 Pipetes, delivery or graduated, 1, 5, 10 ml and other convenient sizes for making standards.
 - 6.4.3 10-ml volumetric flasks
- 6.5 Water bath maintained at 50°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

- 7.1 Water, distilled or deionized
- 7.2 Sodium hydroxide, 0.01N.
- 7.3 Standard stock solutions containing 100 µg/ml of vanadium pentoxide. This solution can be prepared by dissolving 0.100 g V_2O_5 in 0.01N sodium hydroxide and diluting to 1.0 liter with 0.01N NaOH.
- 7.4 V_2O_5 working standard solution, 1.0 µg/ml. Prepare by appropriate dilution of above solution with 0.01N sodium hydroxide. Prepare fresh each day.

8. Procedure

8.1 Cleaning of Equipment

- 8.1.1 Before use, all glassware should be initially soaked in a mild detergent solution to remove any residual grease or chemicals.
- 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, 6M nitric acid, tap water and distilled or deionized water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

- 8.2.1 To collect V_2O_5 fume, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together with tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute for 15 minutes with face cap on and small plugs removed. After sampling, replace small plugs.
- 8.2.2 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 handling as for the samples except that no air is drawn through it. Label this as a blank.
- 8.2.3 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 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers. Transfer filter to a 50-ml beaker.
- 8.3.2 V_2O_5 dissolution. To ensure complete dissolution of V_2O_5 from the filter, add 5 ml of 0.01N NaOH to the beaker and heat in a water bath at 50°C for 15 minutes.
- 8.3.3 Cool solutions and quantitatively transfer the clear solutions into a 10-ml volumetric flask.

- 8.3.4 Rinse each beaker at least twice with 1-2 ml portions of 0.01N NaOH, and quantitatively transfer each rinsing to the solution in the volumetric flask.
- 8.3.5 Dilute all samples to 10 ml with 0.01N NaOH.
- 8.3.6 Inject 50 μ l of solution into a high temperature graphite atomizer. Dry at 125°C for 40 seconds, char at 500°C for 10 seconds and atomize at 2700°C for 20 seconds. Use the deuterium arc lamp to correct for "smoke" produced by the by the matrix. Record the absorbance at 318.4 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve if the graphite tube in use gives reproducible results.

NOTE: The characteristics of the graphite tubes can drastically influence the results. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible absorbance peak, it must be rejected and replaced because results so obtained are not reliable. Also, follow instrument manufacturer's recommendations for specific operating parameters. It is strongly recommended to use pyrolytically coated graphite tubes; these have significantly prolonged lifetime and enhance sensitivity about fivefold.

In case a calibration curve cannot be used because of the changing characteristics of the graphite tube, it is recommended that samples be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended would be as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, etc.

- 8.3.7 Appropriate filter blanks must be analyzed by the same procedure used for the samples.
- 8.4 Determination of Sample 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 should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the true value.

- 8.4.2 Procedure for determining recovery. An aliquot of a standard solution containing a known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within $\pm 5\%$.

For the validation study conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 25-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5x, 1X and 2X the OSHA ceiling standard) were spiked accordingly by adding an aliquot of a solution of vanadium pentoxide containing known amounts of vanadium. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 94.3%.

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

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ Recovered}}{\text{Weight } (\mu\text{g}) \text{ Added}}$$

9. Calibration and Standards

- 9.1 From the standard V_2O_5 working standard solution, prepare at least six calibration standards to cover the V_2O_5 concentration range from 0.5 to 7 μg per 10 ml. Prepare these calibration standards fresh daily and make all dilutions with 0.01N NaOH. (Express concentration as $\mu\text{g V}_2\text{O}_5$ per 10 ml.)
- 9.2 Proceed as in Section 8.3.7.
- 9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in $\mu\text{g}/10$ ml. See special comments in 8.3.6. Special care must be given to proper calibration due to irregular behavior of some graphite tubes.
- 9.4 In cases where a calibration curve could not be used reliably, determine the appropriate response factor. To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance and peak width readings during any given day.

10. Calculations

10.1 Read the weight, in μg , corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg per 10 ml. Or alternatively, determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor determined from the response of the calibration standard. All data are expressed as V_{205} .

10.2 Corrections for the blank must be made for each sample

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$$\begin{aligned}\mu\text{g sample} &= \mu\text{g found in sample filter} \\ \mu\text{g blank} &= \mu\text{g found in blank filter}\end{aligned}$$

10.3 Divide the total weight by the recovery to obtain the corrected μg sample.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 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:

$$\begin{aligned}f &= \text{sample flow rate} \\ t &= \text{sampling time} \\ P_1 &= \text{pressure during calibration of sampling pump (mm Hg)} \\ P_2 &= \text{pressure of air sampled (mm Hg)} \\ T_1 &= \text{temperature during calibration of sampling pump (°K)} \\ T_2 &= \text{temperature of air sampled (°K)}\end{aligned}$$

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).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Volume of Air Sampled in Liters}}$$

11. References

- 11.1 Christian, Gary and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., 1970
- 11.2 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99- 74-45."
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