NIOSH

NIOSH Manual of Analytical Methods

Volume 7

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

NIOSH MANUAL OF ANALYTICAL METHODS

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VOLUME 7

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
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National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering

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DISCLAIMER

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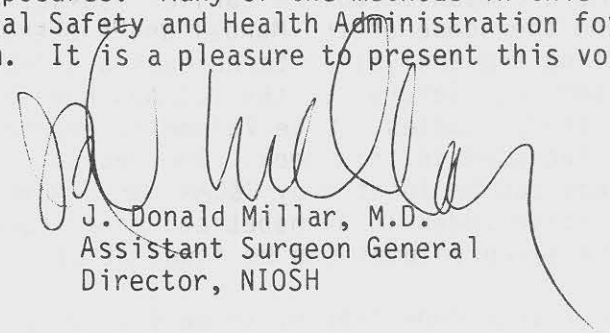
FOREWORD

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

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



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PREFACE

This volume of the NIOSH Manual of Analytical Methods presents 21 new methods for monitoring exposure to toxic substances in the workplace. The second edition of the Manual (Volumes 1-3) was published in 1977 and presents 337 methods. Volumes 4, 5 and 6 published in 1978, 1979 and 1980, supplement those methods with 152 new methods.

As a companion to the earlier books, Volume 7 presents methods that expand the scope of the Manual and together provide the largest set of sampling and analytical techniques available for industrial hygiene monitoring. Several of the methods have been improved and revalidated in laboratory studies. Like Volume 6, errata pages for earlier methods have been included in this book. The method numbering system is the same and methods can be located by P&CAM- or S-numbers in the Contents. Also, a Cumulative Index in alphabetical order covering all the chemical substances in the seven volumes can be found at the end of this book.

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

Copies of the previous volumes may be purchased by sending a self-addressed label with your order to: Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Stock Numbers: 017-033-00267-3 (Volume 1), 017-033-00260-6 (Volume 2), 017-033-00261-4 (Volume 3), 017-033-00317-3 (Volume 4), 017-033-00349-1 (Volume 5), and 017-033-00369-3 (Volume 6). Volumes 1 to 3 may also be ordered from the National Technical Information Service, Springfield, Virginia 22161. NTIS Stock Numbers: PB274-845 (Volume 1), PB276-624 (Volume 2), and PB276-838 (Volume 3).

ABSTRACT

This seventh volume of the Manual provides an additional 21 methods for monitoring toxic substances. The procedures give step-by-step instructions on how to sample as well as how to analyze for these compounds in the workplace.

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

CONTENTS OF VOLUME 7

Foreword iii
Preface to Volume 7 iv
Abstract v
Acknowledgments viii
Errata to Volumes 1-6 ix
Failure Reports xiii

	P&CAM No.
Particulate Nickel and Compounds (as Ni)	298*
p-Chlorophenol	337
Ethylene Glycol	338
Inorganic Acids	339
Acetone Cyanohydrin	340
Diborane	341
4,4'-Methylenebis(o-chloroaniline) [MOCA] in Urine	342
1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; and Pentachlorobenzene	343
Nickel Carbonyl	344
Welding and Brazing Fumes	345
Inorganic Arsenic	346
4,4'-Methylenebis(phenyl isocyanate) (MDI)	347
2,4,7-Trinitro-9-fluorenone	348
Vinyl Bromide	349
Lead Sulfide	350
Trace Elements	351
Formaldehyde	354

	SCP No.
Selenium Compounds (as Se)	S190*
Platinum and Inorganic Platinum Compounds	S191*
Tellurium	S204*
Lead and Inorganic Lead Compounds	S341*

CUMULATIVE INDEX (Volumes 1-7)

*Revision

ACKNOWLEDGMENTS

Each of the P&CAM-numbered methods has an author line following its references to recognize their contributions. The aid of Drs. Peter M. Eller, Larry K. Lowry, R. Alan Lunsford and Alexander W. Teass, and Messers Barry R. Belinky, Robert A. Glaser and John L. Holtz for monitoring contracts or supervising sections producing methods is acknowledged. Thanks are due to Patricia L. Combs, Helen Fley, Eleanor P. Robers and Anna B. Silvers for preparing portions of the manuscript. Special thanks go to Teri A. Slick for her suggestions and her dedication in updating and completing the entire manuscript for publication.

ERRATA TO VOLUMES 1-6

The following additions, changes or corrections to the methods appearing in Volumes 1-6 of the NIOSH Manual of Analytical Methods are given below. Other changes were presented in Volumes 4, 5, and 6.

Page Number; Section	Change
	Volume 1
209	See Dharmarajan, V. and Rando, R. J. "A Recommendation for Modifying the Standard Analytical Method for the Determination of Chlorine in Air," AIHA J, 40, 161(1979).
262-2; 7.5	Change "...cautiously, cool, and adjust..." to "...cautiously, cool, dilute to 1 L with distilled water, and adjust..."
125	Revised Standardization Procedure (see pages xi and xii in Volume 7).
235	Revised Standardization Procedure (see pages xi and xii in Volume 7).
	Volume 2
S59	See paragraph 1.5 of P&CAM 247 in Volume 1.
	Volume 4
S327	Revised Standardization Procedure (see pages xi and xii in Volume 7).
	Volume 5
173-1; 1.3	Change "Lead-S314" to "Lead-S341"
173-13; Table 1; d, e, and h	Change "1000 g/mL" to "1000 µg/mL"
299-1; Box	Change "thermal adsorption" to "thermal desorption"

Volume 6

Contents	Change " -Aminolevulinic Acid ... " to "δ-Aminolevulinic Acid ..."
318	Revised Standardization Procedure (see pages xi and xii in Volume 7).
329-3; 7.5	Add "60/100 mesh size. Deactivate by adding 3 g ultra-pure water to 97 g silica gel."
296-8; 11	Add "11.3 Woebkenberg, M. L.: A Sampling and Analytical Method for Hydrogen Sulfide, Measurement Systems Section Technical Report (January, 1979)."
Cumulative Index	Amines, aliphatic; Change "211" to "221"
Cumulative Index	Change "2,2-Bis 4-(2,3-epoxypropoxy) phenyl propane" to "2,2-Bis[4-(2,3-epoxypropoxy)-phenyl]propane
Cumulative Index	Change "Mevinphos" to "Mevinphos®"
Cumulative Index	Change "Phenyl ehter-biphenyl ..." to "Phenyl ether-biphenyl ..."
Cumulative Index	Change "3,3 Dichlorobenzidine" to "3,3'-Dichlorobenzidine"
Cumulative Index	2-Diethylaminoethanol; Change "270" to "270*" and change "S240" to "S140"
Cumulative Index	bis(2-Aminoethyl)amine; Remove "....328¢"
Cumulative Index	Silica, crystalline and Tridymite; Change "259" to "259(5)"

Revised Standardization Procedure for
Formaldehyde Methods P&CAM 125, P&CAM 235, P&CAM 318 and S327

This is an alternative to the procedure described in Section 9.1 of the subject methods for the standardization of the 1-mg/mL stock formaldehyde solution (formaldehyde standard solution "A"). This procedure is easier to follow and is more precise than that described in Section 9.1. The revised standardization procedure requires the additional apparatus and reagents as noted below.

6. Apparatus

6.a pH meter.
6.b Volumetric pipettes, 1-mL, 5-mL and 10-mL.
6.c Beaker, 50-mL.
6.d Burettes, 50-mL.
6.e Magnetic stirrer.

7. Reagents

7.a Sodium sulfite solution, 1.13 M. Dissolve 14.0 g of sodium sulfite in enough distilled water to make 100 mL of solution. It is best to prepare a fresh solution weekly and store it refrigerated.
7.b Sulfuric acid, 0.02 N, standardized.
7.c Sodium hydroxide, 0.01 N, standardized.

9. Standardization of Formaldehyde Standard Solution "A"

9.a Place 5.0 mL of 1.13 M sodium sulfite solution in a 50-mL beaker. An additional 5.0-mL aliquot of the sodium sulfite solution may be added to the beaker to immerse the pH meter electrode. Stir the solution using a magnetic stirrer. Measure the pH, which should be in the range between 7 and 9. Adjust the pH to within this range with 0.01 N sodium hydroxide or 0.02 N sulfuric acid, if necessary. Record the pH value.

9.b Pipette 10.0 mL of Formaldehyde Standard Solution "A" into the beaker. The pH should now be about 12.

9.c Using the pH meter, titrate the solution back to its original pH with 0.02 N H_2SO_4. Approximately 17 mL of acid will be needed. If the end point is overrun, the solution can be back titrated with the 0.01 N sodium hydroxide. This will require the use of the correction indicated in the formula shown below in 9.d.

9.d Calculate the concentration of formaldehyde. One milliliter of 0.02 N H_2SO_4 is equivalent to 0.6006 mg of formaldehyde. Thus:

$$C_s = \frac{30.0 \times [(N_a \times V_a) - (N_b \times V_b)]}{V_s}$$

where: C_s = Concentration of the standard formaldehyde solution (mg/mL)
N_a = Normality of sulfuric acid
V_a = Volume of acid used for titration
N_b = Normality of sodium hydroxide
V_b = Volume of base used for back titration if end pH was overrun
V_s = Volume of formaldehyde solution used in titration(10.00 mL)

11. References

11.a Walker, J. K. "Formaldehyde", R. E. Krieger Publishing Co., Huntington, N. Y., 1975, pp.486-7.

NIOSH Reports of Methods Not Validated Under the Joint NIOSH/OSHA Standards Completion Program (Failure Reports)

NIOSH attempted to develop and validate monitoring methods for 385 substances on the OSHA list of Permissible Exposure Levels between 1974-79 under the Standards Completion Program. Although 308 validated methods from this program have been published in this manual series, 77 failure reports were written. These failure reports indicate what laboratory testing was completed and makes recommendations for future efforts to develop a method. Some methods were developed after the failure report was written. These methods can be found in the Cumulative Index at the back of this volume. The failure reports listed below may be obtained using a request card attached to the back cover of this volume. Please indicate the individual report you want by number and name.

Method Number	Name
S21	Acrolein
S157	Acrylamide
S172	Allyl propyl disulfide
S277	Azinophos, methyl
S230	Boron trifluoride
S231	Bromine
S197	t-Butyl chromate
S196	Calcium arsenate
S322	Chlorine
S232	Chlorine dioxide
S233	Chlorine trifluoride
S59	∝-Chloroacetophenone
S154	o-Chlorobenzylidene malononitrile (OCBM)
S212	Chloropicrin
S353	Coal tar pitch volatiles
S355	Cotton dust
S177	Crotonaldehyde
S83	Cyclopentadiene
S235	Decaborane
S234	Diborane
S390	Dibutyl phosphate
S127	1,3-Dichloro-5,5-dimethylhydantoin
S282	Dichlorovos (DDVP)
S68	Diglycidyl ether
S207	Dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate
S34	Dimethyl phthalate
S359	Dimethyl sulfate
S136	Ethanolamine
S362	Ethyl mercaptan
S338	Ethylenimine

Method Number	Name
S145	Ethylenediamine
S363	Ferbam
S325	Fluoride in dust (as F)
S364	Fluorine
S263	Graphite
S265	Hydrogen peroxide
S238	Hydrogen selenide
S239	Iodine
S289	Lead arsenate
S202	Lithium hydride
S180	Maleic anhydride
S252	Methyl isocyanate
S373	Methyl mercaptan
S6	Methylenebis(phenyl isocyanate) (MDI)
S266	Mica
S377	Nickel carbonyl
S240	Nitrogen trifluoride
S221	1-Nitropropane
S222	2-Nitropropane
S192	Osmium tetroxide
S171	Oxalic acid
S251	Oxygen difluoride
S236	Pentaborane
S271	Perchloromethyl mercaptan
S241	Perchloryl fluoride
S159	p-Phenylene diamine
S331	Phosgene
S258	Phosphorous pentasulfide
S259	Phosphorous trichloride
S14	Pival
S268	Portland cement
S151	Propylene imine
S242	Selenium hexafluoride
S260	Silica, amorphous
S267	Soapstone
S270	Sulfur monochloride
S247	Sulfur pentachloride
S261	Talc, nonasbestiform
S304	Tetraethyl dithionopyrophosphate (TEDP)
S305	Tetraethyl pyrophosphate (TEPP)
S184	Tin, organic compounds
S344	Toluene-2,4-diisocyanate (TDI)
S226	Trinitrotoluene
S386	Uranium, insoluble compounds
S387	Uranium, soluble compounds
S307	Warfarin
S316	Zinc oxide fume

P&CAM METHODS

INORGANIC NICKEL, METAL AND COMPOUNDS (as Ni)

Methods Research Branch

Analytical Method

Analyte:	Nickel	Method No.:	P&CAM 298
Matrix:	Air	Range:	0.57 - 30.7 $\mu g/m^3$
Procedure:	Filter collection, acid digestion, graphite furnace, AAS	Precision:	0.075
Date Issued:	7/2/79		
Date Revised:	8/24/81	Classification:	B (Accepted)

1. Synopsis

   1.1 A known volume of air is drawn through a 0.8-µm pore size cellulose ester filter.

   1.2 The filter and sample are digested with a $HF-HNO_3$ mixture, taken to dryness, and diluted to a known volume with dilute HCl.

   1.3 The samples are analyzed by graphite furnace atomic absorption spectrophotometry.

2. Working Range, Sensitivity and Detection Limit

   2.1 This method was evaluated over the range 0.57 to 30.7 µg Ni/m^3 for a 400-L air sample collected at 20 °C and 750 torr, corresponding to 0.228 to 13.2 µg Ni per sample. The upper limit of the method may be extended by diluting the sample to a volume greater than 10.0 mL, so that 0.00010 µg Ni to 0.0040 µg Ni is injected into the graphite furnace.

   2.2 The instrumental sensitivity at 232.0 nm is 0.000625 µg Ni/0.0044 absorbance units.

   2.3 The 2σ detection limit at 232.0 nm is 0.000188 µg Ni/injection, corresponding to 0.094 $\mu g/m^3$ for a 400-L air sample dissolved in 10.0 mL of solution, and a 50-µL injection.

3. Interferences

3.1 Background absorption may be overcome by the use of a deuterium background corrector.

3.2 Iron is a positive interference in the analysis for nickel when present at high concentration ratios, beginning at about 100:1 Fe:Ni. When the approximate concentration of iron in a sample is known, it is advisable to add a corresponding quantity of iron to the calibration standard.

3.3 Nitrate, sulfate, copper, molybdenum, and calcium have been shown not to interfere with the determination at concentrations up to 200 times the nickel concentration.

4. Precision and Accuracy

4.1 The total precision of the sampling and analytical method is 7.48% RSD, based on six samples at each of three concentration levels.

4.2 The analytical method recovery was determined to be 101.9% at 0.5 times the OSHA standard. Collection efficiency was determined to be 1.00. In stability studies of generated samples, the mean of samples analyzed after fourteen days was the same as that of samples analyzed immediately after generation, at the 95% confidence level, the mean of samples analyzed by this method was the same as the mean of samples analyzed by instrumental neutron activation analysis. Details of this experiment are given in Reference 11.1.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable, and the samples easily collected.

5.2 The analytical method is extremely sensitive for nickel.

5.3 Samples may be analyzed quickly and easily.

5.4 Large iron concentrations will cause high results.

5.5 The analytical equipment required is relatively expensive.

6. Apparatus

6.1 Sampling equipment, consisting of a filter unit (0.8-μm cellulose ester membrane filter, and cellulose backup pad, 37-mm diameter, in a plastic cassette filter holder) and personal sampling pump capable of sampling at 1.5 to 2 L/min. The pump

must be calibrated with a representative filter in line, using a soap-bubble flowmeter or wet- or dry-test meter, and its flow rate must be known accurately to within ± 5%.

6.2 Atomic absorption spectrophotometer, equipped with a heated graphite atomizing rod, tube, or furnace. Reproducible control of times and temperatures during the drying, charring and atomizing cycles is essential, and a minimum atomization temperature of 2700 °C is required. Accessories needed for the spectrometer are: hollow cathode lamp for nickel, readout device (recorder or digital peak height or peak area analyzer), a gas control system for Ar purge gas, pipetting system (automatic or manual, 5 to 50 mL, as appropriate to atomizer size), and background correction system (simultaneous correction is preferred).

6.3 Glassware (borosilicate).

6.3.1 Volumetric pipettes, 1-, 2-, 3-, 4-, 5-, 6-, 10-, 15-, 20-, and 25-mL.

6.3.2 Volumetric flasks, 10-, 25-, 50-, 100-, 250-, and 1000-mL.

6.4 Teflon beakers, 100-mL, with watchglass covers.

6.5 Adjustable, thermostatically-controlled hotplate capable of reaching a surface temperature of 200 °C.

6.6 Steambath.

7. Reagents

All reagents used should be ACS reagent grade or better.

7.1 Distilled or deionized water.

7.2 Nitric acid, 70% (w/w), redistilled in glass.

7.3 Hydrochloric acid, 38% (w/w).

7.4 Hydrofluoric acid, 50% (w/w).

7.5 Dilute hydrochloric acid, 1% (w/w). Add 14 mL 70% HNO_3 to distilled or deionized water and dilute to 1000 mL.

7.6 Nickel stock standard solution, 1000 ppm Ni. Dissolve 1.000 gm pure Ni metal in a minimum volume of 70% HNO_3 and dilute to 1 L with 1% HCl. Alternatively, commercially prepared standard may be used.

7.7 Argon gas in compressed gas cylinder.

8. Procedure

8.1 Cleaning of Equipment. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in order, detergent solution, tap water, dilute nitric acid (soak four hours or longer), and distilled or deionized water.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.

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

8.2.3 Take the sample at an accurately known flow rate between 1.5 and 2.5 L/min. A sample size of 400 L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to Step 8.2.1.

8.2.5 Ship the cassettes so as to prevent excessive vibration or jarring to the cassettes.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter with tweezers and transfer it to a Teflon beaker. Discard the cellulose backup pad.

8.3.2 To each beaker containing a filter, add 10 mL 70% nitric acid. Cover with a watchglass and allow to sit on a hotplate at 150 °C for four hours or until the volume has been reduced to 1 mL. Rinse each watchglass with deionized water and add 4 mL of 1:1 70% HNO_3 to 50% HF to each beaker. Place the beakers on a steambath and allow the solution to go to dryness. Cool the solutions, redissolve the residue and dilute to 10.00 mL with 1% HCl. Sonicate for 30 minutes in an ultrasonic bath.

8.3.3 Inject samples into the graphite atomizer and operate in accordance with the manufacturer's instructions within the following limitations:

Aliquot Size:	10- or 50-µL, depending on the concentration of the sample.
Readout Mode:	Peak height in absorbance mode (3 x scale) is most precise.
Wavelength:	232.0 nm.
Background correction:	Simultaneous D_2 background correction is recommended.
Dry Cycle:	150 °C, 50 sec for a 50-µL aliquot.
Char Cycle:	1300 °C, 10 sec.
Atomize Cycle:	2700 °C, 10 sec.
Graphite Atomizer:	Pyrolytic tube.

9. Calibration and Standardization

9.1 A 10-ppm Ni standard solution is prepared by dilution of the 1000-ppm stock solution with 1% HCl. This solution is stable for several months if stored in polyethylene bottles and is used to prepare fresh weekly the working standards which should cover the range 0.01 to 0.04 ppm Ni (e.g., 0.01, 0.02, 0.03, 0.04, and 0.06 ppm Ni in 1% HCl for a 50-µL injection and 0.06, 0.10, 0.20, 0.30, and 0.40 ppm Ni in 1% HCl for a 10-µL injection).

9.2 The calibration curve is constructed from the absorbances measured for the standard solutions (Section 7.7) analyzed under the same instrumental conditions as the samples described in Section 8.3.3.

9.3 If the sample is known to contain iron at a concentration greater than 100 times the nickel concentration, iron should be added to the standard solutions to match the sample matrix.

10. Calculations

10.1 From the calibration curves obtained in Section 9, calculate for each sample the amount of nickel in µg.

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

$$W = S - B$$

where: W = net sample weight (µg)
S = weight found in sample filter (µg)
B = weight found in blank filter (µg).

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

$$V = \frac{f \times t}{1000} \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{1/2}$$

where: V = the corrected volume (cu m) of air sampled
f = flow rate sample (L/min)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K).

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

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

11. Reference

11.1 Backup Data Report for Inorganic Nickel, prepared under NIOSH Contract 210-79-0060.

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Mary Jamin, Ph.D.
George Colovos, Ph.D.
Rockwell International
NIOSH Contract No. 210-79-0060

Peter M. Eller, Ph.D.
NIOSH Project Officer
Inorganic Methods Development Section

p-CHLOROPHENOL

Methods Research Branch

Analytical Method

Analyte:	p-Chlorophenol	Method No.:	P&CAM 337
Matrix:	Air	Range:	0.910-23.4 mg/m^3
Procedure:	Adsorption on silica gel, desorption with acetonitrile, high performance liquid chromatography	Precision:	0.06
Date Issued:	9/19/80		
Date Revised:		Classification:	B (Accepted)

1. Synopsis

   1.1 A known volume of air is drawn through a silica gel tube to adsorb the p-chlorophenol vapor present.

   1.2 The silica gel in the tube is transferred to a small vial where the p-chlorophenol is desorbed with 1 mL of acetonitrile. Two mL of H_2O is added to the extract.

   1.3 An aliquot of the resulting solution is injected into a high performance liquid chromatograph.

   1.4 The area of the resulting peak for p-chlorophenol is determined and compared with the peak areas obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The overall method was evaluated by collecting 3-L samples of test atmospheres containing p-chlorophenol in the range of 0.910-23.4 mg/m^3 at 29°C and a relative humidity of greater than 80%. The amounts of p-chlorophenol collected ranged from 2.6-64 µg per 150-mg bed of silica gel. For the maximum allowable sampling volume of 40 L, the range is 0.064-1.6 mg/m^3.

2.2 The slope of the analytical calibration curve was 62 area counts/ng of p-chlorophenol with an HP 1084B liquid chromatograph.

2.3 The lowest analytically quantifiable level for this method was determined to be about 2.5 μg of p-chlorophenol per sorbent sample extracted with 1.00 mL of acetonitrile and then diluted to 3.00 mL with 2.00 mL of distilled, deionized water. The instrumental detection limit was about 0.1 μg/mL, a concentration of p-chlorophenol in 30% acetonitrile in water that gave a response that was about twice the noise level under the operating conditions specified below.

2.4 The breakthrough volume of the sorbent tube was found to be approximately 60 L with a sampling rate of 0.2 L/min at a p-chlorophenol concentration of about 70 mg/m^3, a sampling temperature of 43°C, and a relative humidity of greater than 80%.

3. Interferences

3.1 The chromatographic operating conditions described below will separate phenol, o-chlorophenol; 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dichlorophenol; o- and p-nitrophenol; 2,4-dimethylphenol; 2,4,5-trichlorophenol; 4-chloro-3-methylphenol; 2,4-dinitrophenol; 4,6-dinitro-2-methylphenol; and pentachlorophenol can be achieved; with comparable concentrations of the two in solution, the resolution was found to be 0.91.

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

3.3 Any substance that has the same retention time as p-chlorophenol with the chromatographic operating conditions described in this method can interfere with the analysis. Therefore, retention time data cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, changing the separation conditions (column type or temperature, solvent flow rate, solvent programming rate, etc.) may circumvent the problem.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for the replicate measurements was 6.1% over the range of 0.910-24.3 mg/m^3. The pooled RSD for the analytical method was 2.4% for 18 sorbent samples spiked with 2.54-48.0 μg of p-chlorophenol and stored for 24 hours.

4.2 The concentration of p-chlorophenol in test atmospheres was determined in control experiments by impinger sampling. The determinations with sorbent sampling gave values that averaged 98% of those determined by impinger sampling.

4.3 Samples of p-chlorophenol on silica gel were found to be stable at 25°C for seven days and for 29 days if stored at 0°C after the seventh day.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the analytical procedure. The samples are analyzed by means of a quick instrumental method.

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

6. Apparatus

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

6.2 Sorbent tubes. Pyrex tubes, 7-cm long with a 6-mm o.d. and a 4-mm i.d., flame-sealed at both ends. Each tube contains two sections of 20/40 mesh silica gel -- a 150-mg sorbing section and a 75-mg backup section. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated with a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.4 in H_2O (350 kPa) at a sampling rate of 0.2 L/min. This type of tube is available from SKC, Inc. (Eighty-Four, PA); its catalog number is 226-10.

6.3 High performance liquid chromatograph, such as the Hewlett-Packard 1084B or equivalent, with ultraviolet absorption spectrophotometric detector.

6.4 Reverse-phase liquid chromatographic column, C_{18} bonded to silica, such as the Varian MicroPak MCH-5, 5-μm particle size, 4-mm i.d. by 30-cm long.

6.5 Centrifuge tubes, 12-mL, glass with screw caps.

6.6 Vials, 1-mL, with crimp-on caps containing Teflon-lined silicone rubber septa.

6.7 Pipets, 1- and 2-mL, and convenient sizes for making dilutions.

6.8 Ultrasonic bath.

6.9 Centrifuge for 12-mL tubes.

7. Reagents

7.1 p-Chlorophenol, 99+% pure.

7.2 Acetonitrile, distilled in glass.

7.3 Water, distilled, deionized.

7.4 Hexane, distilled in glass.

8. Procedure

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

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break open the ends of the tube to provide openings that are at least 2-mm in diameter.

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

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

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

8.2.5 Sample the air at 0.05-0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 40 L at 0.2 L/min.

8.2.6 Record the temperature and pressure of the air being sampled and measured.

8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps.

8.2.8 To obtain a blank sample, process one unused silica gel tube in the same manner as the samples (break, seal, and transport) but do not sample air through this tube. Submit one blank sample tube for every ten samples with a minimum of three blank tubes.

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

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

8.2.11 Log samples as soon as they are received in the laboratory.

8.2.12 Refrigerate all samples stored longer than seven days.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the silica gel tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation on the cold sorbent material. Transfer each section of silica gel in a sorbent tube to a separate 12-mL centrifuge tube. Add the glass wool plug near the sorbent tube inlet to the centrifuge tube containing the sorbing section; add the two urethane foam plugs to the centrifuge tube containing the backup section.

8.3.2 Desorption of Samples. After the two sections of a sorbent tube are transferred, pipet 1 mL of acetonitrile into each centrifuge tube. Cap each tube immediately after the acetonitrile has been added. Extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature. Then add 2 mL of distilled, deionized water to each tube. Cap the tubes and mix the solutions well. Centrifuge the solutions for 10 min. Then transfer about 1 mL of the supernatant liquid in each tube to a separate 1-mL vial and seal the vial with a Teflon-lined septum.

8.3.3 Operating Conditions for the High Performance Liquid Chromatograph.

Solvent flow rate:	1 mL/min.
Solvent A:	Distilled, deionized water.
Solvent B:	Acetonitrile.
Solvent program:	30% B to 80% B in 20 min.
Column temperature:	30°C.
UV detector:	Analytical wavelength, 280 nm; reference wavelength, 430 nm.
Injection volume:	100 µL.
Under these conditions, the analyte elutes in approximately 11 min.	
Column cleanup procedure:	At the end of each working day, flush the column with approximately 50 mL of acetonitrile (Solvent B) at a flow rate of 1 mL/min.

8.3.4 Determination of Concentration. Determine the concentration of p-chlorophenol in the sample solution by comparing the peak area to the peak areas obtained with standard solutions as discussed in Section 9. Peak heights may also be used.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of silica gel. Also, for a given batch of silica gel the desorption efficiency may vary with the weight of contaminant adsorbed. The silica gel used for the study of this method gave an average desorption efficiency of 0.960 with a pooled RSD of 2.4% for loadings of 2.54-48.0 µg of p-chlorophenol on 150-mg beds of sorbent material.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve p-chlorophenol in hexane to give stock solutions with concentrations such that 2.5-48.0 µg of p-chlorophenol will be injected onto the sorbent in no more than 5 µL of a stock solution. Inject an aliquot of the appropriate solution into the front sorbing section of a sorbent tube while sampling 6 L of analyte-free air through the tube at 0.2 L/min. Cap the

tube and store it overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 3 mL of 30% (v/v) acetonitrile in water. Analyze the samples and standards as described in Section 8.3.

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

9. Calibration and Standardization

To make a stock solution, add 500 mg of p-chlorophenol to 25 mL of 30% (v/v) acetonitrile in water. By serial dilution with 30% CH_3CN/H_2O, prepare a series of working standards varying in concentration over the range of 0.5-100 µg/mL. Follow the dilution scheme presented below.

Initial concentration	Aliquot volume, mL	Final diluted volume, mL	Final concentration
20.0 mg/mL	1	10	2.0 mg/mL
2.0 mg/mL	5	10	1.0 mg/mL
1.0 mg/mL	1	10	100.0 µg/mL
100.0 µg/mL	5	10	50.0 µg/mL
100.0 µg/mL	1	10	10.0 µg/mL
10.0 µg/mL	1	10	1.0 µg/mL
1.0 µg/mL	5	10	0.5 µg/mL

Prepare fresh working standards daily; the same stock solution may be used indefinitely if stored in an airtight container. Analyze the five working standards under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve, plot the concentration of the standards in µg/mL versus peak area.

10. Calculations

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

10.2 Blank corrections are not expected to be necessary. If the analysis shows a blank correction is needed, make the correction as follows:

$$W_F = W_S - W_b$$

where: W_F = corrected amount (µg) on the front section of the silica gel tube.
W_S = amount (µg) found on the front section of the silica gel tube.
W_b = amount (µg) found on the front section of the blank silica gel tube.

Follow a similar procedure for the backup section.

10.3 Make a correction for desorption efficiency as follows:

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

where: M_F = corrected amount (µg) in the front section.
W_F = amount (µg) after blank correction.
D = desorption efficiency corresponding to the weight, W_F.

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

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

where: M_F = corrected amount (µg) of p-chlorophenol found on front section.
M_B = corrected amount (µg) of p-chlorophenol found on backup section.
V = volume (L) of air sampled.

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

$$C(ppm) = C(\mu g/L) \times \frac{24.45}{128.56} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.
T = temperature (°C) of air sampled.
24.45 = molecular volume (L/mol) at 25°C and 760 torr.
128.56 = molecular weight of p-chlorophenol.

11. Reference

11.1 Dillon, H. K.; Emory, M. B. "Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for p-Chlorophenol"; NIOSH Contract 210-78-0012; Southern Research Institute: Birmingham, Alabama; September, 1980.

H. Kenneth Dillon
Merry B. Emory
Southern Research Institute
NIOSH Contract No. 210-78-0012

ETHYLENE GLYCOL

Methods Research Branch

Analytical Method

Analyte:	Ethylene Glycol	Method No.:	P&CAM 338
Matrix:	Air	Range:	4.2-327 mg/m^3
Procedure:	Collection on filter and silica gel, GC	Precision:	0.084 (for aerosol) 0.065 (for vapor)
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 A known volume of air is drawn through a three-stage sampler consisting of a glass fiber filter followed by two sections of silica gel to collect ethylene glycol aerosol and vapor (Reference 11.1).

1.2 The glass fiber filter and two sections of silica gel are treated with 2:98 2-propanol-water (v/v) to remove the analyte.

1.3 The 2-propanol-water solutions are analyzed by gas chromatography with a flame ionization detector to determine the concentrations of ethylene glycol.

2. Working Range, Sensitivity, and Detection Limit

2.1 Ethylene glycol vapor in air at concentrations ranging from 4.2 to 327 mg/m^3 can be quantified for 3-L air samples. The lower quantitation limit for ethylene glycol aerosol in air is 3.3 mg/m^3 for a 3-L air sample if no evaporation of ethylene glycol from filters takes place. The upper quantitation limit for ethylene glycol aerosol in a 3-L air sample is unknown. The range useful for quantitation of ethylene glycol in solution is 10 to at least 1000 µg/mL.

2.2 The capacity of the silica gel tube for ethylene glycol is sufficient for collecting a 60-L air sample during a 5-hour period. In one experiment, an average of 20,650 µg of ethylene glycol was found on the front sections of two silica gel tubes

after a 23-hour sampling period; less than 10 µg of ethylene glycol was found on each of the two corresponding back sections of silica gel.

2.3 The calculated detection limit for ethylene glycol vapor in a 3-L air sample is 1.3 mg/m^3 when a desorption efficiency of 0.8 is assumed for 3.8 µg of ethylene glycol collected on silica gel. The detection limit for ethylene glycol in solution is approximately 3 µg/mL if 1-µL aliquots of a solution are injected.

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 A ghosting phenomenon is associated with analysis of ethylene glycol under gas chromatographic conditions for this method. If analysis of 100 ng of ethylene glycol in 1 µL of 2-propanol-water solution is followed by an injection of 1 µL of blank 2-propanol-water solution, a peak will appear which will correspond to roughly 4 ng of ethylene glycol (the ghost peak would be larger if the analysis of 100 ng of ethylene glycol were preceded by the analysis of a much larger quantity of ethylene glycol, a quantity such as 750 ng). Ghosting can be reduced by additional injections of blank 2-propanol-water solution (Reference 11.2).

3.3 Any compound which has the same retention time as that of ethylene glycol and is detected under the gas chromatographic conditions for this method is an interference.

4. Precision and Accuracy

4.1 The relative standard deviation for the sampling and analytical method for ethylene glycol aerosol at a concentration of 14.1 mg/m^3 was 0.084 for 6-L air samples. The pooled relative standard deviation for the sampling and analytical method for ethylene glycol vapor in the range from 45 to 84 mg/m^3 was 0.065 for 6-L air samples.

4.2 Average concentrations of ethylene glycol aerosol and vapor combined in controlled atmospheres based on the filter-silica gel tube method, 97.9, 53.6 and 44.9 mg/m^3, were 0.5% lower, 5.3% higher and 44.8% higher than corresponding average concentrations based on a reference method. The reference method involved sampling with bubblers of water, oxidation of ethylene glycol to formaldehyde with periodic acid and colorimetric analysis (Reference 11.3).

4.3 Average analytical method recoveries of ethylene glycol from filters stored in sealed vials for 0.5-hour periods were essentially quantitative at the following levels of ethylene glycol: 20, 300, and 900 µg. Average analytical method recoveries of ethylene glycol from silica gel tubes after application from the vapor phase were 0.82, 0.81, 0.85, 0.85 and 0.87 at the 20-, 60-, 300-, 900- and 3120-µg levels, respectively.

4.4 Ethylene glycol can evaporate from filters during air sampling at temperatures near 25 °C and enter the silica gel tubes. Thus, apparent concentrations of ethylene glycol aerosol may be low and apparent concentrations of ethylene glycol vapor may be high.

4.5 Collected samples of ethylene glycol are stable on silica gel at room temperature for at least 15 days. Ethylene glycol can evaporate from filters in sealed filter holders at room temperature and also at 2 °C; however, ethylene glycol from filters can be stored in 2:98 2-propanol-water (v/v) at room temperature.

5. Advantages and Disadvantages

5.1 The sampling device is small, light in weight, and convenient for personal sampling.

5.2 The analytical method is specific for ethylene glycol.

5.3 Standard solutions of ethylene glycol in 2:98 2-propanol-water (v/v) are stable for more than 1 year at room temperature.

5.4 One disadvantage is a time limitation for storage of ethylene glycol on filters in sealed filter holders. The following table presents information showing the effect of evaporation of ethylene glycol from filters in sealed filter holders.

Average Quantity Before Storage (µg)	Storage Time (hours)	Approximate Storage Temperature	Average Recovery
83	1	24 °C	98%
85	4	24 °C	51%
72	4	2 °C	84%

6. Apparatus

6.1 Sampling Equipment

6.1.1 Sampler. The sampler consists of three sections: a glass fiber filter followed by two sections of silica

gel. The glass fiber filter, free of binders, is a high-efficiency filter, 13 mm in diameter, and is contained in a 13-mm filter holder (Catalogue No. SX00 013 00, Millipore Corporation, Bedford, MA, or equivalent). The two sections of silica gel (20/40 mesh, 0.72 g/cm^3, 720-760 m^2/g) are contained in a glass tube approximately 8 cm in length when the sealed ends are broken off. The internal diameter and outside diameter of the glass tube are 6 and 8 mm, respectively. The front and back sections of silica gel, 520 and 260 mg in quantity, respectively, are separated by a plug of urethane foam. A portion of glass wool precedes the front section of silica gel. The filter holder is connected to the silica gel tube with two short pieces of plastic tubing, such as Tygon tubing. One of the pieces of plastic tubing is 7 mm long with an internal diameter of approximatey 3.5 mm and fits tightly around the tapered outlet of the filter holder. The ends of the second piece of plastic tubing, approximatey 1.7 cm in length with an internal diameter of approximatly 5 mm, fit tightly around the smaller piece of plastic tubing and the inlet of the silica gel tube. The assembly of the sampler may be completed immediately before sampling. Seal the ends of the filter holder with plastic tape for storage.

6.1.2 Calibrated personal sampling pump. The personal sampling pump should be calibrated for the recommended flow rate of 0.2 L/min with a representative sampler in line.

6.1.3 Stopwatch.

6.1.4 Thermometer.

6.2 Gas chromatograph equipped with a hydrogen flame ionization detector.

6.3 Glass column, 1.9-m x 2-mm internal diameter, packed with 3% Carbowax 20M on 80/100 mesh Chromosorb 101. Bake out the packing overnight at 200 °C with helium flowing through the column (Reference 11.4).

6.4 Column packing, 3% Carbowax 20M on 80/100 mesh Chromosorb 101. Add 19.4 g of 80/100 mesh Chromosorb 101 to a solution of 600 mg of Carbowax 20M in 60 mL of chloroform slowly with stirring during a period of 3 minutes. Stir the mixture for an additional 10 minutes. Spread out the mixture to form a shallow

layer and allow the mixture to stand in a fume hood while much of the chloroform escapes. The final product will appear dry and will be capable of flowing freely (Reference 11.4).

6.5 Syringes, 5-μL.

6.6 Glass vials, 1-mL, with rubber caps.

6.7 Volumetric flasks, 25-mL.

6.8 U-tube, glass.

6.9 Temperature bath.

7. Reagents

7.1 Ethylene glycol, analytical grade.

7.2 2:98 2-Propanol-water (v/v). Prepare this solution from freshly distilled water and analytical grade 2-propanol.

7.3 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 then distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break off the sealed ends of the silica gel tube in order to allow openings at least one half of the inside diameter of the tube. Remove the tape from the inlet and outlet of the filter holder. Assemble the sampler.

8.2.2 Connect the sampler to a calibrated personal sampling pump with flexible tubing.

8.2.3 Sample at a flow rate of 0.2 L/min for 15 minutes for ceiling concentrations or for 5 hours or less for time-weighted average concentrations.

8.2.4 Record pertinent data in regard to sampling, including sampling times and initial and final air temperatures. If atmospheric pressure data are not available, record the elevation.

8.2.5 After sampling, disassemble the sampler. Transfer the filter to a vial, add 1 mL of 2:98 2-propanol-water (v/v) and seal the vial. Seal the ends of the silica gel tube with plastic caps. If the transfer of the filter to a vial and addition of 2:98 2-propanol-water (v/v) is not performed soon after sampling, at least part of the ethylene glycol present on the filter at the end of sampling may evaporate and be lost.

8.2.6 For each set of samplers consisting of twenty or fewer samplers, label four samplers as "blank" samplers. Do not draw air through the "blank" samplers.

8.2.7 If a bulk sample of suspected material is to be submitted to the laboratory, place the sample into a glass container and seal the container with a cap lined with polytetrafluoroethylene.

8.2.8 Do not transport a bulk sample with the filter holders and silica gel tubes in the same container.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Agitate the vial containing the filter and 2:98 2-propanol-water solution occasionally during a 5-minute period. Remove from the silica gel tube the portion of glass wool. Transfer the front section of silica gel to a 1-mL vial. Transfer the back section of silica gel to another 1-mL vial. Add 1 mL of 2:98 2-propanol-water (v/v) and seal each vial. Agitate each vial occasionally during a 5-minute period.

8.3.2 GC Conditions. The operating conditions for gas chromatography are:

Carrier Gas:	Helium
Temperature of Column:	165 °C
Temperature of Injection Port:	250 °C
Temperature of Detector:	300 °C
Flow Rate of Helium:	31 mL/min
Flow Rate of Hydrogen:	44 mL/min
Flow Rate of Air:	304 mL/min
Retention Time:	Approximately 4 min
Column Efficiency:	Approximately 1000 theoretical plates for ethylene glycol

8.3.3 By means of the solvent-flush injection technique, inject a 1-µL aliquot of sample solution. Employ 1 µL of distilled water as solvent-flush behind the aliquot of sample solution.

8.3.4 If ghost peaks would interfere with the analysis of ethylene glycol in quantities near the detection limit, make injections of 2:98 2-propanol-water (v/v) until a chromatogram is obtained in which a ghost peak is not detected (see Section 3.2).

8.3.5 Analyze the "blank" samples with the field samples.

8.3.6 Measure peak heights or peak areas.

8.4 Determination of Analytical Method Recovery

8.4.1 Significance of Determination. The determination of analytical method recovery may provide information which would aid in correcting for bias in the analytical method (see Section 4.3). Sample recoveries should be determined in the ranges of interest.

8.4.2 Procedure for Determining Recovery from Filters. Place a glass fiber filter into a clean 1-mL vial. Add a known quantity of ethylene glycol in 5 µL of water solution to the filter. Seal the vial and allow the vial to stand for 0.5 hour. Prepare five additional samples in this manner. Analyze the filters with standards and three "blank" filters. Perform this procedure at two or more levels of ethylene glycol.

The analytical method recovery from filters is equal to the average quantity of ethylene glycol found corrected for the average blank and divided by the quantity of ethylene glycol applied.

8.4.3 Procedure for Determining Recovery from Silica Gel. Connect a U-tube to the inlet of a silica gel tube with a short piece of tubing in order that exposure of ethylene glycol vapor to the tubing will be minimal. Connect the outlet of the silica gel tube to a pump capable of drawing air at 0.2 L/min. Place a temperature bath at 75 °C under the U-tube and lower the U-tube until at least the bottom half of the U-tube is in contact with the bath. Add an appropriate quantity of ethylene glycol in 5 µL or

more of water solution to the U-tube, replace the stopcock, and immediately turn on the pump. Operate the pump for 30 minutes or longer. Prepare five additional samples in this manner. Analyze the silica gel tubes with standards and three "blank" silica gel tubes. Perform this procedure at two or more levels of ethylene glycol. Determinations of recovery of ethylene glycol from silica gel at levels above 5000 µg may be cumbersome and time-consuming.

The analytical method recovery from silica gel is equal to the average quantity of ethylene glycol found corrected for the average blank and divided by the quantity of ethylene glycol applied. Construct a curve of recovery versus average quantity of ethylene glycol found.

NOTE: The average recovery of ethylene glycol from silica gel after applications from the vapor phase may be different from the average recovery of ethylene glycol from silica gel after applications of ethylene glycol in water solution in the liquid phase.

9. Calibration and Standardization

Prepare a series of standard solutions of ethylene glycol in 2:98 2-propanol-water (v/v) in the range from 2 to 1000 µg/mL. Analyze the standards during the same period in which the samples are analyzed in order to minimize the effect of variations in the response of the hydrogen flame ionization detector. Construct a curve of either peak height or peak area versus concentration of ethylene glycol in µg/mL.

10. Calculations

10.1 Determine the quantity of ethylene glycol in µg found on the filter from the calibration curve.

10.2 Determine the quantity of ethylene glycol in µg found on the front section of silica gel from the calibration curve.

10.3 Determine the quantity of ethylene glycol in µg found on the back section of silica gel from the calibration curve.

10.4 Correct the quantities of ethylene glycol for corresponding "blank" values.

10.5 Correct the quantities of ethylene glycol found on sections of silica gel for analytical method recoveries according to the following equation:

$$Q' = \frac{Q}{R}$$

where: Q' = the corrected quantity of ethylene glycol in µg
Q = the uncorrected quantity of ethylene glycol in µg
R = the analytical method recovery (Determine R from a curve mentioned in Section 8.4.3.)

10.6 Add the corrected quantities of ethylene glycol found on the front and back sections of silica gel to find the total corrected quantity of ethylene glycol in the silica gel tube.

10.7 Calculate the concentration of ethylene glycol aerosol in the air sample in µg/L by dividing the corrected quantity of ethylene glycol in µg on the filter by the volume of air sampled in L. Concentrations in µg/L and mg/m^3 are numerically the same.

10.8 Calculate the concentration of ethylene glycol vapor in the air sample in µg/L by dividing the total corrected quantity of ethylene glycol in µg in the silica gel tube by the volume of air sampled in L.

10.9 Determine the total concentration of ethylene glycol in the air sample in µg/L by adding the concentration of ethylene glycol aerosol and the concentration of ethylene glycol vapor.

11. References

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11.2 Spitz, H. D., "Ghosting of Ethylene Glycol in GC," J. Pharm. Sci., 61, 1339-1340 (1972).

11.3 Taylor, D. G., NIOSH Method No. P&CAM 125, "Formaldehyde in Air" in NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 1, Dept. Health, Educ. Welfare, NIOSH, Cincinnati, Ohio (1977), DHEW (NIOSH) Publication No. 77-157-A.

11.4 Spitz, H. D., and J. Weinberger, "Determination of Ethylene Oxide, Ethylene Chlorohydrin, and Ethylene Glycol by Gas Chromatography," J. Pharm. Sci., 60, 271-274 (1971).

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Organic Methods Development Section

INORGANIC ACIDS

Methods Research Branch

Analytical Method

Analyte:	Inorganic acids (Table I)	Method No.:	P&CAM 339
		Range:	Table I
Matrix:	Air		
		Precision:	0.06-0.10
Procedure:	Silica gel tube collection, eluent desorption, ion chromatography		
Date Issued:	8/18/81		
Date Revised:		Classification:	D (Operational)

1. Synopsis

   1.1 A known volume of air is drawn through a silica gel sampling tube to collect the analyte. The samples are desorbed in an aqueous solution of 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 with heat. Solutions of samples and standards are analyzed by means of an ion chromatograph.

2. Working Range, Sensitivity, and Detection Limit

   2.1 For H_3PO_4, H_2SO_4, HNO_3, and HBr, the working range is based on a 48-L air sample and on a 15-L air sample for HCl. Refer to Table I.

   2.2 The sensitivity is expressed as µg per sample per mm chart deflection at a conductance setting of 10 µmhos full scale.

   2.3 With a 10-mL final solution volume and the instrumental parameters stated in the method, the lowest analytically quantifiable level (LAQL) is stated as µg/sample at 10% relative standard deviation. This lower limit may be extended through use of a more sensitive conductivity meter setting.

3. Interferences

3.1 Possible interferences in the method are SO_2 for H_2SO_4 and NO_2 for HNO_3. Their collection potential on silica gel and reduction during desorption have not been investigated.

3.2 Chlorine or hypochlorite ion may interfere with chloride up to 50% of its initial concentration, and bromine may give an interference of approximately 30% of its original concentration as determined from spiked samples. The collection potential of these substances on silica gel has not been investigated.

4. Precision and Accuracy

4.1 The precision is expressed as percent relative standard deviation for the overall sampling and analytical method over the range stated for each acid (Table I).

4.2 The collection efficiencies for each of the acids are based on samples at three concentration levels, 0.2, 1 and 2 times the OSHA permissible exposure limits.

5. Advantages and Disadvantages

5.1 The advantage of ion chromatography over other methods is its capability of separating the ions such that each of the acid anions may be identified and measured in a single sample.

5.2 The method is specific for the acid anions. Different oxidation states of the acids have different retention times, e.g., NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}.

5.3 The sampling device is a solid sorbent collection tube and involves no liquids.

5.4 The sampling device will collect five inorganic acids in both particulate and vaporous forms.

5.5 Because identification is based on retention time, interferences may not be easily identified.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Personal sampling pumps capable of operation at 0.2 L/min and calibrated to an accuracy of ±5% with a representative sampling tube in line.

6.1.2 Silica gel tubes. 7-mm o.d./4.8 mm i.d. glass tubes approximately 10 cm in length packed with 400 mg of 20/40 mesh washed silica gel in the front section and 200 mg in the backup section. Polyurethane foam plugs are placed between the sorbent sections and at the end. The front section of silica gel is held in place with a 5-mm diameter plug of thick glass fiber filter.

The silica gel is washed by the following procedure: Approximately a 200-mL volume of silica gel is placed in a 1-L beaker. 500-600 mL of deionized water is added slowly with stirring. When the exothermal reaction has subsided, the silica gel is heated in a 100 °C water bath for approximately 30 minutes with occassional stirring, decanted, and rinsed four to five times with deionized water. It is heated again in deionized water for 15-30 minutes, decanted, and rinsed thoroughly with deionized water. The silica gel is then dried overnight in a 100 °C oven until free flowing. If a blank of the silica gel shows any impurities, the washing procedure is repeated. Approximately 90% of the resulting silica gel will be 20/40 mesh.

6.1.3 Barometer.

6.1.4 Thermometer.

6.1.5 Hygrometer.

6.1.6 Stopwatch.

6.2 Ion chromatograph with a standard or fast run anion precolumn and separator column, a standard suppressor column, and conductimetric detector (Dionex Corp., Sunnyvale, CA, or equivalent).

6.3 Strip chart recorder.

6.4 Electronic integrator or some other suitable means of determining peak height (optional).

6.5 Centrifuge tubes, 15-mL, graduated.

6.6 Micropipettes with disposable tips for preparing standards.

6.7 Volumetric flasks, 100-mL and 25-mL or other convenient sizes for preparing standard solutions.

6.8 Syringes, 10-mL, polyethylene with luer tip.

6.9 In-line filter holders (Swinnex-type) with 25-mm membrane filters, 0.8 µm pore size, or Acrodisc in-line filters.

6.10 Parafilm.

6.11 Water bath maintained at 100 °C.

7. Reagents

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

7.1 Deionized, filtered water. Conductivity grade deionized water with specific conductance of 10 µmho/cm or less is needed for the preparation of eluents and other solutions used in the ion chromatograph. The water must be filtered before use to avoid plugging valves in the chromatograph.

7.2 Silica gel, 3/8 mesh, grade 01, thoroughly washed with deionized water (Sec. 6.1.2).

7.3 Sodium carbonate, Na_2CO_3.

7.4 Sodium bicarbonate, $NaHCO_3$.

7.5 Potassium chloride, KCl.

7.6 Monopotassium phosphate, KH_2PO_4.

7.7 Potassium sulfate, K_2SO_4.

7.8 Sodium nitrate, $NaNO_3$.

7.9 Sodium bromide, NaBr.

7.10 Stock standard solutions (1000 µg/mL). Dissolve salt in deionized, filtered water in a 100-mL volumetric flask, and dilute to volume with deionized, filtered water.

7.10.1 Chloride (1000 ppm Cl^-). Dissolve 0.2103 g KCl/100 mL.

7.10.2 Phosphate (1000 ppm PO_4^{3-}). Dissolve 1.433 g KH_2PO_4/100 mL.

7.10.3 Sulfate (1000 ppm SO_4^{2-}). Dissolve 0.1814 g K_2SO_4/100 mL.

7.10.4 Nitrate (1000 ppm NO_3^-). Dissolve 0.13707 g $NaNO_3$/100 mL.

7.10.5 Bromide (1000 ppm Br^-). Dissolve 0.1288 g NaBr/100 mL.

7.11 Eluent (0.003 M $NaHCO_3$/0.0024 M Na_2CO_3). Dissolve 1.008 g $NaHCO_3$ and 1.0176 g Na_2CO_3 in 4 L of deionized, filtered water.

8. Procedure

8.1 Cleaning of Equipment. Glassware and plasticware should be washed in detergent and thoroughly rinsed with deionized water. Acid cleaning is not recommended.

8.2 Collection and Shipping of Samples

8.2.1 Each personal sampling pump must be calibrated with a representative collection tube in line to assure accurately known sample volumes.

8.2.2 Immediately before sampling, break the ends of the collection tube to provide an opening of at least one half of the internal diameter of the tube.

8.2.3 Insert the tube in the sampling device with the glass fiber filter plug at the inlet. Place tube in a vertical position during sampling to minimize channeling through the sorbent.

8.2.4 Collect the sample at 0.2 Lpm. The air being sampled should not pass through any hose or tubing before entering the collection tube. A sample size of 48-L is recommended.

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

8.2.6 After sampling, label the collection tubes appropriately and cap the ends with plastic caps.

8.2.7 With each batch of up to 10 samples submit one blank collection tube which has been subjected to the same handling except that no air has been drawn through it.

8.3 Analysis of Samples

8.3.1 Place the silica gel and glass fiber plug from the front section of the collection tube into a 15-mL graduated centrifuge tube. (The backup section is analyzed separately.)

8.3.2 Add 5-6 mL of eluent solution (Section 7.7) and heat in a 100 °C water bath for 10 minutes. Allow to cool and dilute to a 10-mL volume with eluent. Cover with Parafilm and shake vigorously.

8.3.3 Pour the contents into a 10-mL plastic syringe fitted with an in-line filter and collect the filtrate in a second syringe or autosampler vial.

8.3.4 Inject 100-µL aliquots of the filtered sample into the ion chromatograph and record the sample identity and instrumental conditions. Typical operating conditions for inorganic acids are:

Eluent:	0.003 M $NaHCO_3$/0.0024 M Na_2CO_3
Flow Rate:	138 mL/hr (30% pump capacity)
Columns:	Standard Anion precolumn
	Standard Anion separator
	Standard Anion suppressor
Conductivity Meter Setting:	10 µmho full scale
Injection Volume:	100 µL
Recorder Speed:	30 cm/hr.

8.3.5 Measure and record peak height of each peak. The use of peak height is recommended over peak area for ion chromatography.

9. Calibration and Standardization

9.1 From the 1000 µg/mL acid stock solutions in Section 7.10, prepare mixed working standards in the concentrations of 0.5, 1, 2, 5, 10, 15, and 20 µg/mL in eluent solution (Section 7.7). The use of eluent eliminates the water dip in the chromatogram which occurs immediately before the elution of the chloride peak. These standards should be prepared fresh weekly and stored in polyethylene bottles.

9.2 With each set of samples analyzed, a complete calibration curve should be constructed. Plot peak height versus concentration.

10. Calculation

10.1 Read the concentration of each sample and blank from the calibration curve obtained in Section 9.2. Calculate the net concentration of each acid anion found

$$C_1 = C_2 - B$$

where: C_1 = acid anion concentration from air sample (µg/mL)
C_2 = total acid anion found on silica gel tube (µg/mL)
B = acid anion concentration from blank (µg/mL).

10.2 Calculate the concentration of acid in air sample.

10.2.1 Acid concentration in mg/m^3

$$C_A = \frac{F\ C_1\ D}{V}$$

where: C_A = acid concentration in air (mg/m^3)
C_1 = anion concentration in solution (µg/mL)
D = final volume of desorbed sample (mL)
V = volume of air sampled (L)
F = factor for converting anion to acid.

Acid	F
H_3PO_4	1.032
H_2SO_4	1.021
HNO_3	1.016
HBr	1.0125
HCl	1.028

10.2.2 Vapor-forming acid concentration in ppm. One gram molecular weight of a gas occupies 24.45 L at 25 °C and 760 mm Hg pressure

$$C_B = K \times C_A \times \frac{760 \times T}{298 \times P}$$

where: C_B = acid concentration in air (ppm)
C_A = acid concentration in air (mg/m^3)
T = absolute temperature at which the sample was taken (°K = °C + 273)
P = air pressure at which the sample was taken (mm Hg).

$$K = \frac{\text{vol. acid}}{\text{g-mol. wt. acid}}$$

Acid	K
HNO_3	0.3881
HBr	0.3022
HCl	0.6699

11. References

11.1 Cassinelli, M. E. and Taylor, D. G., Monitoring for Airborne Inorganic Acids, Symposium on Measurement and Control of Chemical Hazards in the Workplace Environment, ACS Symposium Series (1980).

11.2 Cassinelli, M. E., Ion Chromatographic Determination of Hydrogen Chloride - Hydrogen Bromide Mixtures, IMDS, MRB, Technical Report (1979).

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Table I

Acid	Useful Working Range mg/m³	Useful Working Range µg/sample	Validation Range mg/m³	Sensitivity µg/sample/mm	LAQL* µg/sample	Precision % RSD	Collection Efficiency %
H_3PO_4	0.06 - 2	3 - 100	0.5 - 2	1.0	1.9	9.6	88
H_2SO_4	0.06 - 2	3 - 100	0.5 - 2	1.7	2.7	8.7	90
HNO_3	0.06 - 10	3 - 500	1.0 - 10	1.7	2.8	8.5	102
HBr	0.06 - 20	3 - 960	2.0 - 20	1.4	2.0	7.4	102
HCl	0.03 - 14	0.5 - 200	0.14 - 14	0.25	0.5	5.9	100

*Lowest analytically quantifiable level.

ACETONE CYANOHYDRIN

Methods Research Branch

Analytical Method

Analyte:	Acetone Cyanohydrin	Method No.:	P&CAM 340
Matrix:	Air	Range:	0.33-16.7 mg/m^3 for a 3-L sample
Procedure:	Adsorption on Porapak QS, desorption with ethyl acetate, GC analysis via NPD	Precision:	0.093
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

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

2. Working Range, Sensitivity and Detection Limit

2.1 The method was evaluated by collecting 1-50 µg of acetone cyanohydrin at 0.2 L/min from U-tubes onto sorbent tubes containing Porapak QS over a one-hour period. The sample tubes were then exposed to humid air (relative humidity = 80%) at a temperature and pressure of 22°C and 740 torr for 15 minutes at 0.2 L/min.

2.2 The upper limit of the method is dependent upon the capacity of the Porapak QS to retain the analyte. A 1.0% weight breakthrough was observed when 100 µg of the analyte in 12 L of humid air (relative humidity = 80%) was collected onto a 100-mg bed of the sorbent at 0.2 L/min.

2.3 Levels as low as 0.1 μg/mL in ethyl acetate were analyzed using a nitrogen-phosphorous detector. At this level the precision of replicate injections was 6.3%.

3. Interferences

3.1 Any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Using a nitrogen-phosphorous thermionic detector, the following compounds have been found not to interfere with the analysis of acetone cyanohydrin: methanol, acetone, and methyl methacrylate. Retention time data on a single column cannot be considered as proof of chemical identity.

3.2 The analyte decomposes readily in the presence of water vapor. Since Porapak QS has an apparent capacity to collect water, it is necessary to refrigerate all samples collected from humid atmospheres immediately after sampling is completed. Tests have shown that samples of the analyte that have been spiked via evaporation from U-tubes onto sampling tubes containing the sorbent and exposed to 3 L of humid air (relative humidity = 80%) are stable for at least 5-7 days, if stored at 0°C.

4. Precision and Accuracy

4.1 The pooled relative standard deviation for the total sampling and analytical method in the range 0.33-16.7 mg/m^3 was 9.3%. At the 0.33-mg/m^3 level, this corresponds to a standard deviation of 0.031 mg/m^3. A 5% variation in pump flow is assumed in computing the pooled relative standard deviation.

4.2 Storage samples were collected from U-tubes and exposed to humid air for 15 minutes at 0.2 L/min. These samples were stored for periods ranging from 1 to 5 or 7 days. The 1-day samples were stored at ambient temperatures. The longer-term storage samples were maintained at 0°C. There was no statistical difference at the 95% level of confidence between the averages for the two groups.

5. Advantages and Disadvantages

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

5.2 Data suggest that at least 12 L of humid air can be sampled without danger of breakthrough of acetone cyanohydrin. However, when the amount of the cyanohydrin found on the backup section of the sampling tube exceeds 10% of that found on the front section, the probability of sample loss exists.

5.3 The samples must be refrigerated at 0°C as soon as possible after collection to prevent degradation of the analyte by co-adsorbed water vapor.

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

6. Apparatus

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

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

6.3 Gas chromatograph equipped with a nitrogen-phosphorous detector. The transfer lines from the injector to the column and from the column to the detector must be replaced with teflon tubing (as described in Figure 2).

6.4 GC column, 2-m long x 4-mm inside diameter teflon tubing packed with 5% OV-17 on Chromosorb T (40/60 mesh). The packing is prepared and loaded into the column using the techniques

*Porapak QS is a co-polymer of styrene-divinylbenzene which has been treated with a silylating agent. It is manufactured by Waters Associates.

described in Reference 2. The portion of the column to be inserted into the injection port should remain empty to preclude crushing the soft Teflon support and thereby plugging the front-end of the column.

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 Sohxlet extractor.

6.13 Parafilm.

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

6.15 Portable refrigerant, such as Koolit (PDC Pkg., Medford, MA), for refrigerating samples during shipment.

7. Reagents

7.1 Acetone, chromatoquality.

7.2 Acetone cyanohydrin, 98+% purity (Aldrich Chemical Co.).

7.3 Ethyl acetate, distilled in glass.

7.4 Nitrogen, purified.

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

7.7 Hexane, distilled in glass.

7.8 Methanol, distilled in glass.

8. Procedure

8.1 Cleaning of Equipment. Wash all glassware used for the laboratory analysis with detergent. Thoroughly rinse with tap water and distilled water. Allow to dry.

8.2 Collection and Shipping of Samples

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

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

8.2.3 Place the tube in a vertical position during sampling to minimize channeling through the Porapak QS.

8.2.4 Do not permit air being sampled to pass through any hose or tubing before entering the Porapak QS tube.

8.2.5 Sample 3 L of air at 0.2 L/min over a 15-minute period. At least 12 L of air can be sampled. Record the sampling time and the flowrate.

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

8.2.7 Seal the Porapak QS tube with plastic caps immediately after sampling. Do not use rubber caps.

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

8.2.9 Pack the capped tubes tightly. Pad them before they are shipped to minimize tube breakage. Ship the samples in an insulated container containing a portable refrigerant. Maintain the temperature at 0°C.

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

8.2.11 Refrigerate the Porapak QS tubes at 0°C as soon after sampling as possible.

8.3 Analysis of Samples

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

8.3.2 Desorption of Samples. Pipette 1.0 mL of ethyl acetate into each sample container. Allow samples to desorb in an ultrasonic bath for one hour. Analyses should be completed the same day that the samples are desorbed.

8.3.3 GC Conditions

	Flow Rates (mL/min)
Carrier gas (N_2)	33
Hydrogen	5
Air	175
	Temperatures (°C)
Injector	100
Detector	100
Column	70

The analyte has a retention time of approximately 3 minutes under these conditions using the column recommended in Section 6.4. The ethyl acetate will elute from the column before the analyte.

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

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

8.4 Determination of Desorption Efficiency

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

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

Six vials 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 acetone cyanohydrin onto the Porapak QS. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed as described in Section 8.3.

Prepare the standards by injecting the same volume of acetone cyanohydrin solutions into 1.0 mL of ethyl acetate with the same syringe as used in the preparation of the samples. These are analyzed with the samples.

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

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

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

9. Calibration and Standardization

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

9.2 From the stock solution, prepare at least five standards to cover the range 0.5-100 µg in 1.0 mL of ethyl acetate.

9.3 Analyze the standards with the samples.

9.4 Prepare a calibration curve by plotting the weight in µg of acetone cyanohydrin in the sample versus peak area.

10. Calculations

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

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

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

10.4 If the desorption efficiency (D) is determined to be 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 acetone cyanohydrin in the air sampled can be expressed in µg/L as follows:

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

where: V = volume of air sampled in liters (L).

This number is numerically equal to the concentration of acetone cyanohydrin in mg/m^3.

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

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

where: P = the pressure of air sampled in torr
T = the temperature of air sampled in °C
24.45 = the molar volume of an ideal gas in liters (L)
M = molecular weight (g/mole) of acetone cyanohydrin (85 g/mole)
760 = standard pressure in torr
298 = standard temperature in °K

11. References

11.1 R. A. Glaser and P. M. Fey. Development of a Quantitative Sampling and Analytical Method for Acetone Cyanohydrin. Report of research performed during fiscal years 1979 and 1980.

11.2 Supina, W. R. "The Packed Column in Gas Chromatography," Supelco Inc., Bellefonte, PA, 1974, pp. 91-94.

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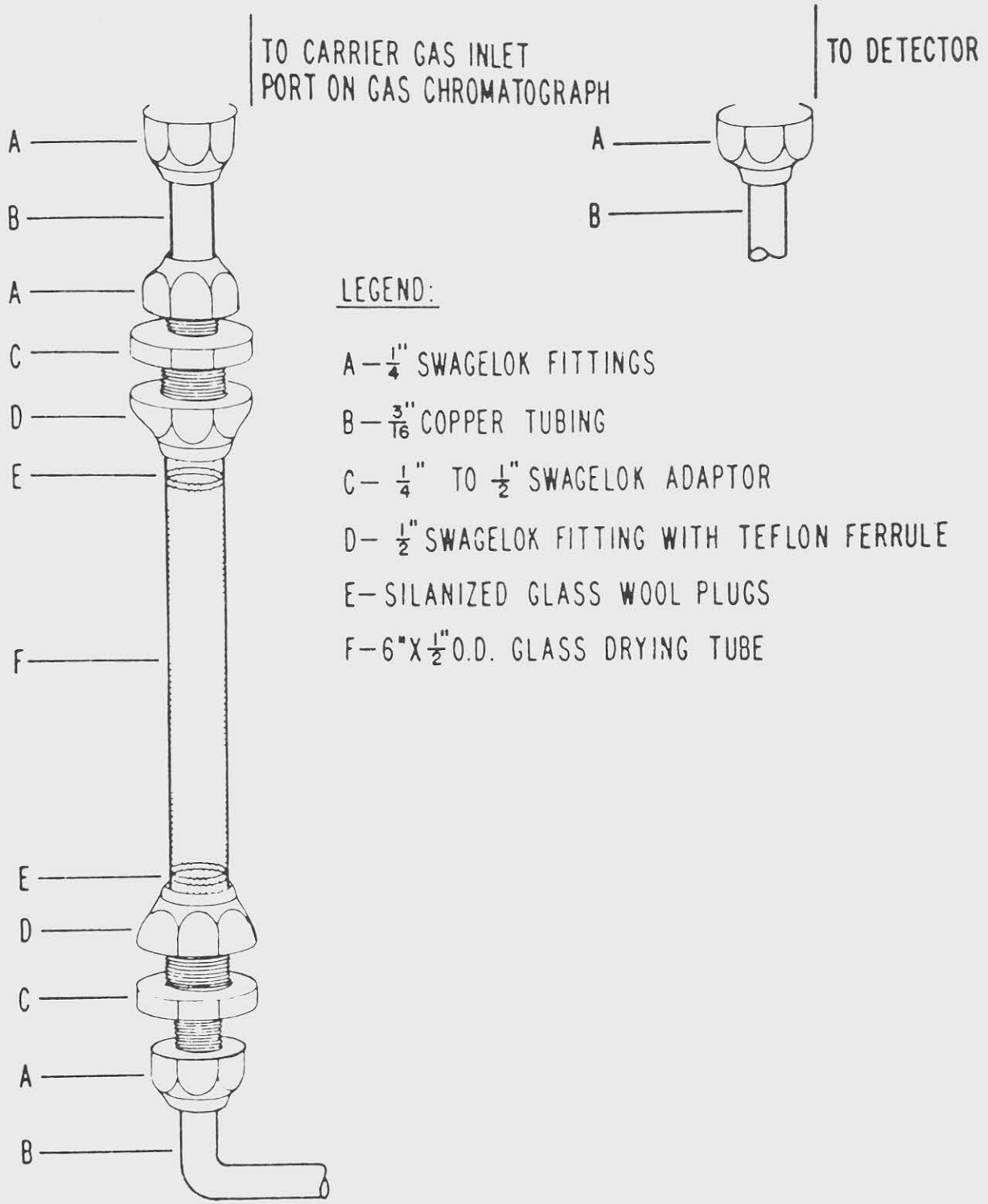

Figure 1. Purging system for porous polymers.

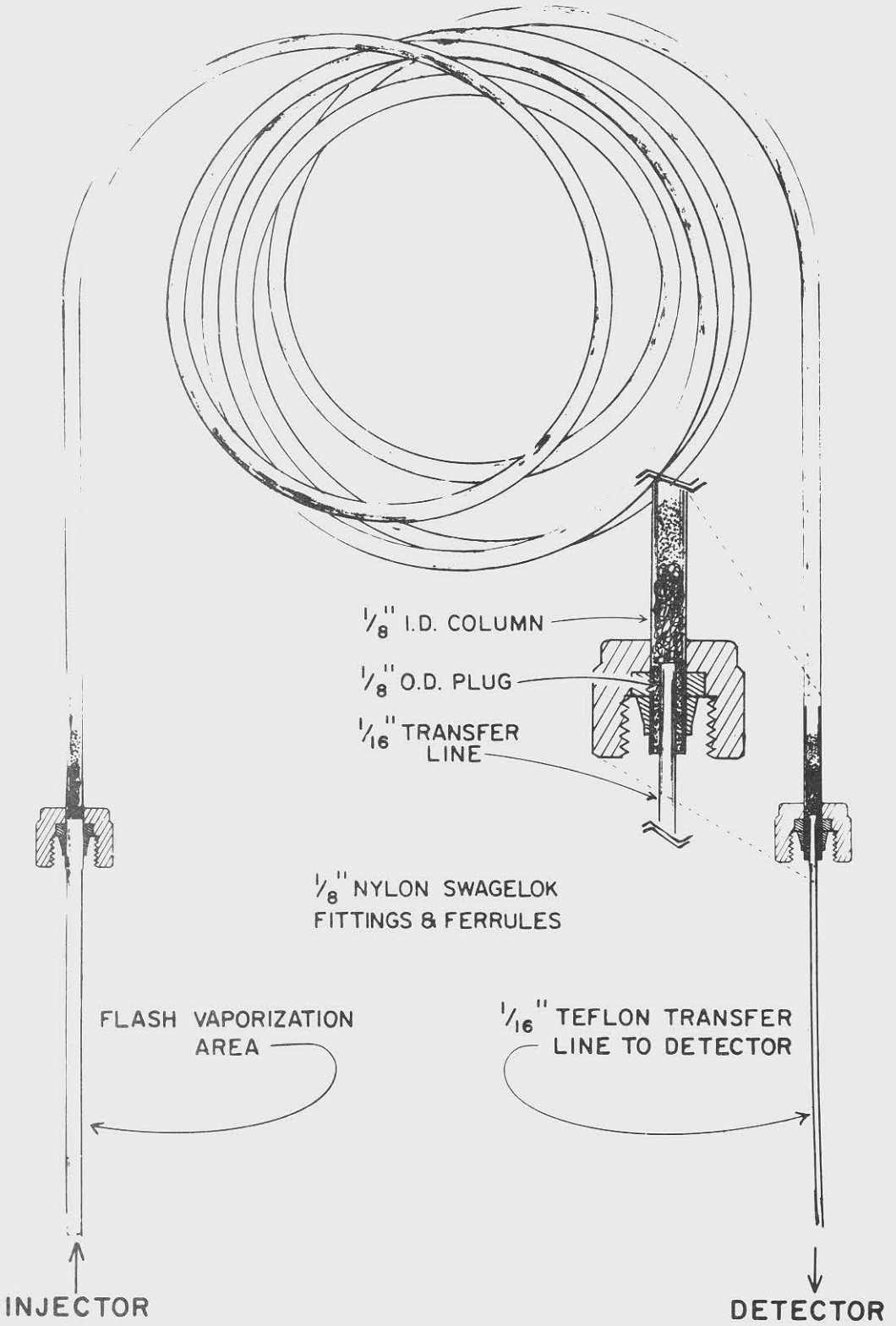

Figure 2. All Teflon gas chromatographic system used for the analysis of acetone cyanohydrin.

DIBORANE

Measurement Research Support Branch

Analytical Method

Analyte:	Boron	Method No.:	P&CAM 341
Matrix:	Air	Range:	0.051-0.216 mg/m^3
Procedure:	Adsorption on impregnated charcoal, desorption with 3% hydrogen peroxide, plasma emission spectrometry.	Precision:	0.07
Date Issued:	8/31/81	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

1.1 A known volume of air is drawn through a three-stage sampler consisting of a Teflon® filter cassette followed by a tube containing an oxidizer impregnated charcoal to trap the diborane vapors. The prefilter is used to remove interfering particulates. The sampling tube contains a front absorbing section and a backup section.

1.2 The charcoal in each tube is transferred to a plastic screw capped bottle and the diborane is desorbed with 3% hydrogen peroxide.

1.3 Solutions of samples and standards are analyzed for total boron by emission spectroscopy using a D.C. plasma excitation source. The intensity of the emission at 249.8 nm is proportional to the boron concentration.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 0.051 - 0.216 mg/m^3 at an atmospheric temperature of 21 °C and an atmospheric pressure of 764 mm Hg using a 120-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the impregnated charcoal. This capacity varies with the concentration of diborane and other substances in the air. When an atmosphere containing 0.35 mg/m^3 of diborane was sampled at 1 liter per minute, no breakthrough was detected after 235 minutes (capacity 80 µg). The sample size recommended is less than two-thirds of this volume, so the probability of overloading the sampling tube is minimal.

2.3 The detection limit of the analytical method is estimated to be 0.01 ppm or approximately 0.01 mg/m^3 based on calibration standards.

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 A prefilter is used to remove any boron containing particulates.

4. Precision and Accuracy

4.1 The relative standard deviation for the total analytical and sampling method in the range of 0.051 - 0.216 mg/m^3 was 0.07. This value corresponds to a 0.007 mg/m^3 standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

4.2 In validation experiments, this method was found to be capable of coming within $\pm$ 25% of the "true value" on the average of 95% of the time over the validation range. The concentrations measured by this method at 0.5, 1 and 2 times the OSHA standard were 5% lower than the dynamically generated test concentrations (n = 17). The desorption efficiency was determined to be 0.889, 0.964 and 0.994 for collector loadings of 6.7 µg, 13.4 µg and 26.8 µg, respectively. In storage stability studies, at low relative humidity, the mean of samples analyzed after seven days was within 5.8% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. The collected samples are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of diborane (boron) found on the backup charcoal section exceeds 25% of that found on the front section, the probability of sample loss exists.

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

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated sampling pump suitable for sampling at 1.0 liter per minute for 120 minutes. The pump must be accurate to within $\pm$ 5% at the recommended flow rate.

6.1.2 Sampling Filter. A two-piece filter cassette with fluoropore filter (Millipore FA or equivalent) should be positioned ahead of the sorbent tube to remove any aerosols or particulates in the atmosphere.

6.1.3 Sampling Tubes. The sampling tube consists of a glass tube, 7-cm long with a 6-mm O.D. and a 4-mm I.D., packed with two sections of type 580-20 impregnated charcoal (Barnebey-Cheney Co., Columbus, Ohio, or equivalent). The front absorbing section contains 100 mg and the backup section contains 50 mg. The two sections are separated by a portion of silylated glass wool. A plug of silylated glass wool is placed at each end of the sorbent tube. The impregnating material is proprietary information.

6.2 Spectraspan III plasma emission spectrometer with a D.C. plasma excitation source (Spectrametrics, Inc.) or equivalent.

6.2.1 Argon (for direct current plasma excitation source).

6.3 It is recommended that glassware be avoided due to the potential for borate interferences.

6.3.1 Pipettes in convenient sizes for making standards.

6.3.2 Nalgene®, or equivalent, volumetric flasks for standard solutions.

6.3.3 Nalgene®, or equivalent, 2-ounce screw top bottles for desorbing samples.

6.3.4 7-mL glass vials with screw on septum caps (or plastic if available).

6.4 Ultrasonic bath.

7. Reagents

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

7.1 Diborane gas, 1% (request an analysis from the supplier and confirm by emission spectroscopy).

7.2 Three percent hydrogen peroxide solution.

7.3 Boron reference standard solution certified for atomic absorption use (Fisher certified or equivalent).

8. Procedure

8.1 Cleaning of Equipment. All containers 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 assembly in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the seals at the ends of the tubes should be removed.

8.3.2 The section containing 50 mg of impregnated charcoal is used as a backup and should be positioned nearest the sampling pump. The charcoal tube should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should be passed through a fluoropore filter before entering the front section of the impregnated charcoal to remove any aerosols and/or particulates present.

8.3.4 A sample size of 120 liters is recommended. Sample at a known flow rate of 1.0 liter per minute. Set the

flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled.

8.3.5 One charcoal tube should be handled in the same manner as the sample tube, except for the taking of an air sample. This sample should be labeled as a blank. Submit one blank for every batch or partial batch of ten samples.

8.3.6 A minimum of six unused charcoal tubes should be available for use in desorption efficiency studies in conjunction with these samples, because desorption efficiency may vary from one batch of charcoal to another. Record the batch number of the charcoal used.

8.3.7 Capped sample tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. The filters may be discarded.

8.4 Analysis of Samples

8.4.1 Desorption of Sample. Prior to analysis, 10 mL of 3% hydrogen peroxide is pipetted into each plastic sample bottle. The charcoal is quickly added, and the bottle is capped immediately. Do not desorb the glass wool. The bottles are allowed to stand for thirty minutes, and then placed for twenty minutes in an ultrasonic bath. Each sample is then filtered through a 0.45 micron fluoropore membrane filter prior to analysis.

8.4.2 Spectrometer Conditions. The typical operating conditions for the Spectrospan III plasma emission spectrophotometer are:

249.8 nm boron emission line
50 x 300 mm entrance slits

Calibrate the instrument according to the manufacturer's instructions using a concentration of boron slightly higher than the concentration of the boron anticipated in the samples. Be sure the instrument response is linear over the concentration range chosen. For these experiments, a range of 0.1 ppm to 4.0 ppm boron was used.

8.4.3 Measurement of Signal. Record the sample concentrations from the instrument print-out.

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 impregnated charcoal to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of boron found in the samples.

The analytical samples are prepared as follows: 100 mg of impregnated charcoal is measured into a 7-mL glass vial equipped with a screw-on septum cap. The impregnated charcoal must be from the same batch used in obtaining the samples. A known volume of diborane gas is injected into the vial by means of a gas tight syringe through the septum.

Six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) are prepared by adding an amount of diborane equivalent to a 120-liter sample at the selected level. Aliquots (0.65, 1.3, and 2.6 mLs) of gas are added to the vials to produce samples at the 0.5, 1, and 2X levels. A parallel blank vial is treated in the same manner except that no sample is added to it. The vials are allowed to stand overnight.

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 from a certified boron reference standard. Standards should be prepared and analyzed at the same time the sample analysis is done.

The desorption efficiency (D) at each level is the ratio of the average amount measured (A_m) to the theoretical amount expected (A_t).

$$D = \frac{A_m}{A_t}$$

The desorption efficiency may be dependent on the amount of diborane collected on the sorbent. Plot the desorption efficiency versus weight of diborane found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of at least five standards varying in concentration over the range corresponding to 120-liter collections at 0.1 - 4 times the OSHA standard is prepared and analyzed during the same time period as the unknown samples. A calibration curve is established by plotting response versus concentration in µg/mL over the appropriate range (in this case 0.1 µg/mL to 4.0 µg/mL).

10. Calculations

10.1 Record the sample concentration, (C_S) in ppm of boron, from either the instrument print-out or manually constructed calibration curve as appropriate. Multiply the concentration by the total volume of the sample solution, usually 10 mL, to obtain the weight in µg of boron per sample (W_S).

$$W_S = 10\ C_S$$

10.2 Corrections for the sample blank (Section 8.3.5) must be made for each sample.

$$W = W_S - W_B$$

where: W = blank corrected sample weight (µg)
W_B = weight of blank (µg)

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 (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 amount (W_C, µg/sample).

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

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:

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

where: V_c = corrected volume
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 m^3 which is numerically equal to µg per liter

$$C_m = 1.280 \left(\frac{W_c}{V_c}\right)$$

where: C_m = concentration (mg diborane/m^3)
1.280 = ratio of MW of diborane to 2 equivalents of boron

Another method of expressing concentration is ppm (corrected to standard conditions of 25 °C and 760 mm Hg).

$$C_p = C_m \times \frac{24.45}{27.7} \times \frac{760}{P} \times \frac{T + 273}{298}$$

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
27.7 = molecular weight of diborane
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 Diborane, prepared under NIOSH Contract No. 210-80-0099.

Christine Jones
Doris Wilson
Arthur D. Little, Inc.
NIOSH Contract No. 210-80-0099

Barry R. Belinky
Project Officer
Measurement Development Section

4,4'-METHYLENE-BIS-(o-CHLOROANILINE) [MOCA] IN URINE

Division of Biomedical and Behavioral Science

Analytical Method

Analyte:	MOCA	Method No.:	P&CAM 342
Matrix:	Urine	Range:	4-250 µg/L
Procedure:	Acid hydrolysis, ether-hexane extraction, derivatization, gas chromatography, ECD	Precision:	0.212
Date Issued:	8/31/81		
Date Revised:		Classification:	D (Operational)

1. Synopsis

A urine specimen is hydrolyzed with acid and then a known volume is made alkaline. The MOCA and metabolites are then extracted into an organic solvent and the extractant is concentrated for derivatization to the pentafluoropropionyl derivative in the presence of triethylamine. The pentafluoropropionyl derivative is analyzed by gas chromatography using electron capture detection. A further cleanup of the pentafluoropropionyl derivative using 10% deactivated Florisil column chromatography can allow detection of 1.0 µg MOCA/L of urine. This procedure is adapted from the one developed by the Michigan Department of Public Health (Ref. 11.1).

2. Working Range, Sensitivity and Detection Limit

2.1 The working range is from 4-250 µg of MOCA/L of urine.

2.2 The electron capture detector (^{63}Ni) has a linear response up to 250 µg of MOCA/L of urine.

2.3 The detection limit of this analytical procedure is 1.0 µg of MOCA/L of urine.

3. Interferences

3.1 Imipramine and any other compound having a chromatographic elution time identical to that of MOCA under the same GC operating conditions described in this method can interfere. However, this type of interference may be overcome by changing the operating conditions of the instrument.

3.2 Water in the extractant can be detrimental to the packing in the GC column and will cause plugging.

4. Precision and Accuracy

4.1 The precision for eleven replicate spiked urine samples was 21.2% (relative standard deviation).

4.2 Absolute recoveries calculated from data were found to range from 89% for samples containing 100 µg of MOCA/L of urine to 79% for samples containing 4 to 25 µg of MOCA/L of urine when derivatized and passed through a Florisil column.

5. Advantages and Disadvantages

5.1 Citric acid solution added to the collecting container prior to urine collection stabilizes the MOCA in the urine.

5.2 Although the method is time consuming, it can be used to detect 4 µg of MOCA/L in urine without the Florisil cleanup. Some specimens may require Florisil cleanup at levels of MOCA of less than 8 µg/L.

5.3 The detection limit of this method is 1.0 µg of MOCA/L of urine on the basis of nondetectable MOCA urine specimens spiked at that level. This represents a 40-fold increase in sensitivity when compared to the current NIOSH method for MOCA determination in urine (Ref. 11.2).

6. Apparatus

6.1 Gas chromatograph equipped with an electron capture detector.

6.2 A mechanical or electronic integrator for determining peak areas.

6.3 Glass column (3-m x 2-mm i.d.) packed with 3% OV-1 on 100-120 mesh Gas Chrom Q.

6.4 Pasteur pipets, disposable.

6.5 Graduated centrifuge tubes (15-mL), glass-stoppered or equivalent.

6.6 Rotary mixer designed to accommodate 20-mm culture tubes, which can be operated at 50-60 rpm.

6.7 Chromatography column, 7-mm i.d. x 200-mm, with a 25-mL reservoir and Teflon stopcock.

6.8 pH paper, wide range.

6.9 Nitrogen manifold for evaporating organic solutions.

6.10 Vortex mixer.

6.11 Culture tubes, 20 x 150-mm, screw cap, Teflon-lined.

6.12 10-mL pipets, disposable.

6.13 Centrifuge, table top, clinical.

6.14 Glass syringes, 10-µL and 50-µL.

6.15 Water bath with temperature range 30-100 °C.

6.16 Volumetric flasks, 100-mL and 250-mL or convenient sizes for making standards.

6.17 Glass wool.

7. Reagents

All reagents should be of analytical or spectroquality grade. Solvents are distilled in glass.

7.1 Hexane.

7.2 Diethyl ether.

7.3 Methanol.

7.4 Benzene.

7.5 Sodium sulfate, granular, anhydrous.

7.6 4,4'-Methylene-bis-(o-chloroaniline) [MOCA]. Stock standard: Accurately weigh 50 mg of MOCA, dissolve in a small quantity of methanol, and dilute to 250 mL with hexane.

7.7 4,4' Methylene dianiline [MDA], internal standard, 10 µg/mL hexane.

7.8 NaOH.

7.9 Triethylamine [TEA], 0.05 M stock solution in hexane.

7.10 Pentafluoropropionic anhydride [PFPA].

7.11 KH_2PO_4.

7.12 Citric acid, monohydrate, granular.

7.13 Florisil®, PR grade, 60 to 100 mesh, activated by the manufacturer at 650 °C.

7.14 Nitrogen, prepurified.

7.15 P-5 gas, 5% methane in argon.

7.16 Urine control sample or Hycel® urine control (Hycel Co., Houston, Tx).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 All glassware used for the laboratory analysis should be detergent washed and rinsed with tap water followed by a chromic acid treatment and thoroughly rinsed with distilled water.

8.2 Collection and Shipping of Samples

8.2.1 The urine sample is collected in a 4-oz polyethylene screw cap bottle containing 3 mL of 30 percent citric acid solution.

8.2.2 Immediately after the urine specimen has been collected (around 100 mL), close the container and swirl gently.

8.2.3 If analysis is to be postponed for more than 48 hours, the urine should be frozen, and shipped packed in dry ice in an insulated shipping container.

8.3 Analysis of Samples

CAUTION: Ethyl ether and hexane are extremely flammable. Handle with care in a well ventilated hood.

8.3.1 Defrost sample (control urines are analyzed with each set of samples).

8.3.2 Adjust the pH of the urine in the sample bottle to 3 with 30% citric acid.

8.3.3 Pipet a 10-mL sample into a clean culture tube (20 x 150 mm).

8.3.4 Adjust the pH to 10 using 10N NaOH (approximately 0.1 mL).

8.3.5 Add 3 mL of methanol and mix well.

8.3.6 Add 5 mL of 1:1 diethyl ether:hexane and shake steadily for two minutes to extract the MOCA and other metabolites.

8.3.7 Centrifuge to separate phases and transfer the organic phase with the aid of a Pasteur pipet to a clean disposable culture tube. Emulsions are possible and can be broken by methanol addition and/or repeated centrifugation. Combine organic phases.

8.3.8 Repeat steps 8.3.6 and 8.3.7 two more times, combining the organic phases.

8.3.9 Concentrate the extractant to approximately 1 mL under a gentle stream of nitrogen.

8.3.10 Add 50 µL of TEA, 50 µL of PFPA and 10 µL of MDA to the concentrated extract and mix well in a well ventilated hood.

8.3.11 Secure the cap loosely and heat in a water bath at 50 °C for 15 minutes.

8.3.12 Remove from water bath and add 2 mL hexane and 5 mL of pH 6 KH_2PO_4 buffer. Mix well.

8.3.13 Centrifuge to separate the organic and aqueous phases completely. Transfer the organic layer containing the derivative with the aid of a Pasteur pipet into a clean 15-mL centrifuge tube without disturbing or transferring the aqueous phase.

8.3.14 Add 2 mL hexane to the aqueous buffer and mix well. Repeat step 8.3.13 but transfer the organic layer to the same 15-mL centrifuge tube.

8.3.15 Dilute the organic solution to 5 mL using hexane. Add 0.2 g Na_2SO_4 and mix.

8.3.16. The parameters of the Perkin-Elmer Model 3920 gas chromatograph equipped with a Nickel-63 electron capture detector are as follows:

P-5 carrier gas flow:	40 mL/min
^{63}Ni ECD temperature:	300 °C
Injector temperature:	220 °C
Interface temperature:	250 °C
Column temperature:	220 °C
Retention time for the pentafluoropropionyl derivative:	~9 min

8.3.17 Inject 5 µL of the hexane extract containing the derivative into the gas chromatograph using the solvent flush injection technique. The 10-µL syringe is first flushed with hexane to wet the barrel and plunger. Three µL of solvent are first drawn into the syringe, then the plunger is pulled back about 0.3 µL to separate the solvent flush from the sample. The needle is then immersed in the sample and a 5 µL aliquot is withdrawn, taking into consideration the volume of the needle (approximately 0.8 µL). After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle.

8.3.18 The area of the sample peak is measured by an electronic integrator and compared with the area of the internal standard.

8.3.19 If MOCA cannot be detected, proceed to the Florisil cleanup procedure below.

8.4 Micro Florisil Column Cleanup

8.4.1 Separate the hexane extract from the Na_2SO_4; then concentrate the extract to approximately 0.5 mL under a gentle stream of N_2 at 30 °C in the water bath.

8.4.2 Florisil is heated to 130 °C for 24 hours.

8.4.3 10% deactivated Florisil is prepared in a 50-mL culture tube by addition of 10% w/w H_2O and mixed on a rotary mixer for 2 hours at 50 rpm. The deactivated Florisil should not be kept for more than a week.

8.4.4 Place a small glass wool plug in a chromatographic column and add 1.6 g of the deactivated Florisil. Top with 2 cm of anhydrous Na_2SO_4.

8.4.5 Pre-rinse the packed column with 10 mL of hexane.

8.4.6 Transfer the 0.5 mL of derivatized extract to the column with the aid of a Pasteur pipet. Add the extract just as the level of hexane rinse is even with the Na_2SO_4 layer. Quickly rinse the extract tube with several additional small quantities of hexane.

8.4.7 Do not allow the level of rinse to fall below the Na_2SO_4 layer. Discard the eluted pre-rinse.

8.4.8 Elute the column with 10 mL of 40% benzene/hexane (v/v). The solvent mixture should not fall below the Na_2SO_4 layer; the eluate is discarded.

8.4.9 Elute the column with 10 mL of 100% benzene and save the eluate. The pentafluoropropionyl derivative elutes in this fraction which can be concentrated to 1 mL for subsequent analysis by gas chromatography.

8.4.10 The parameters of the gas chromatograph are the same as described before (see 8.3.16) except the column and injection temperatures are set at 240 °C. The retention time for the pentafluoropropionyl derivative for these conditions is approximately 5 minutes.

8.4.11 Inject 2 µL of the concentrated benzene fraction using the sample flush technique described previously (see 8.3.17), except use benzene instead of hexane as the flush solvent.

8.4.12 The area of the MOCA peak is measured and compared with the area of the internal standard.

9. Calibration and Standardization

CAUTION: Laboratory Operations Involving Carcinogens. MOCA and benzene are carcinogens regulated by the Occupational Safety and Health Administration. Therefore, handling of these chemicals must be in compliance with 29 CFR 1910.1005 and 29 CFR 1910.1028, respectively.

9.1 Using the stock standard (see 7.6) and a urine control, prepare a series of standards ranging from zero to 200 µg MOCA/L of urine.

9.2 Ten mL of each urine standard is extracted under the same conditions used for the urine specimens (see 8.3).

9.3 The calibration curve is established by plotting MOCA concentrations (µg/L) versus the ratio of the peak areas of MOCA to the peak areas of MDA (internal standard).

10. Calculations

10.1 The concentration of MOCA in urine can be determined from the calibration curve or calculated as shown below. No volume correction is needed because the volume of sample injected is identical to the volume of standards injected.

$$M = \frac{(A)(R)}{(A_{IS})}$$

where:
- M = the concentration of MOCA in urine expressed as µg/L of urine
- A = the area of the sample MOCA peak
- R = the ratio of MOCA standard (concentration divided by its area) times the area of the internal standard
- A_{IS} = the area of the sample internal standard peak.

10.2 MOCA in urine specimens can be adjusted or "normalized" using a creatinine correction. For this correction to be valid, urine creatinine must be determined by a separate method and the concentration of creatinine must exceed 0.4 g/L. The concentration of MOCA in urine, corrected for creatinine excretion (M_C), expressed as µg MOCA/g creatinine is as follows:

$$M_C = \frac{M}{(C_{cre})}$$

where:
- M = the urine MOCA concentration expressed as µg/L of urine.
- C_{cre} = the urine creatinine concentration expressed as as g/L of urine.

10.3 Specific gravity corrections are invalid due to the high specific gravity of the urine preservative (30% citric acid).

11. References

11.1 Micro method for the analysis of Curene 442® in Urine by Electron Capture Chromatography. Michigan Department of Public Health Analytical Method, Environmental Epidemiology Laboratory, September 1979 (unpublished).

11.2 Special Hazard Review with Control Recommendations for 4,4'-methylenebis(2-chloroanaline). DHEW (NIOSH) Publication No. 78-188, September 1978.

William Tolos
Clinical and Biochemical Support Section

1,2,4-TRICHLOROBENZENE; 1,2,4,5-TETRACHLOROBENZENE; AND PENTACHLOROBENZENE

Methods Research Branch

Analytical Method

Analyte:	1,2,4-Trichlorobenzene (1,2,4-TCBz); 1,2,4,5-tetrachlorobenzene (1,2,4,5-TCBz); and pentachlorobenzene (PCBz)	Method No.:	P&CAM 343
		Range:	In 10-12 L of air, 0.002-100 mg/m^3 for 1,2,4-TCBz; 0.003-31 mg/m^3 for 1,2,4,5-TCBz; and 0.008-22 mg/m^3 for PCBz
Matrix:	Air		
Procedure:	Collection on Teflon filter and Amberlite XAD-2, elution with hexane, analysis by GC/ECD	Precision:	0.093 for 1,2,4-TCBz 0.097 for 1,2,4,5-TCBz 0.098 for PCBz
Date Issued:	8/31/81		
Date Revised:		Classification:	B (Accepted)

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1. Synopsis

1.1 A known volume of air is drawn through a two-stage sampler consisting of a Teflon fiber mat filter followed by a tube containing two sections of Amberlite XAD-2 sorbent material to collect the analytes as aerosols or vapors.

1.2 The Teflon filter and sorbent sections are each transferred to a separate vial where the analytes are desorbed with 2 mL of hexane.

1.3 Aliquots of the resulting solutions are injected into a gas chromatograph equipped with an electron capture detector (GC/ECD).

1.4 The height or area of the peak corresponding to each analyte is determined and compared with the peak heights or areas obtained from the injection of standard solutions of the analytes in hexane.

2. Working Range, Sensitivity, and Detection Limit

2.1 The overall method was validated by collecting 10 to 12-L samples of test atmospheres containing the three analytes in the following concentration ranges: 0.002 to 100 mg/m^3 for 1,2,4-trichlorobenzene; 0.003 to 31 mg/m^3 for 1,2,4,5-tetrachlorobenzene; and 0.008 to 22 mg/m^3 for pentachlorobenzene. In these evaluations, the temperature of the test atmosphere was 28 to 30 °C and the relative humidity was > 80%. The corresponding average quantities of the analytes recovered from the sampling devices in these tests ranged as follows: 0.023 to 1200 µg of 1,2,4-tetrachlorobenzene; 0.028 to 280 µg of 1,2,4,5-tetrachlorobenzene; and 0.076 to 231 µg of pentachlorobenzene.

2.2 With a Perkin-Elmer Model 910 gas chromatograph, the slopes of the analytical calibration curves (peak height as a function of quantity injected) were as follows on an instrument attenuation of one: 2.5 mm/pg of 1,2,4-trichlorobenzene; 4 mm/pg of 1,2,4,5-tetrachlorobenzene; and 4.5 mm/pg of pentachlorobenzene.

2.3 The lowest analytically quantifiable level (LAQL) of each analyte was determined to be about 0.02 µg when extracted from the 100-mg sorbent section of the sampler with 2 mL of hexane. The LAQL would correspond to a concentration of about 0.002 mg/m^3 in a 12-L air sample. (Neither the filter nor the filter holder sorbed significant quantities of the analytes when exposed to the analytes at the .02 µg level.) The instrumental detection limit was found to be about 20 pg of each analyte, corresponding to a solution concentration of 10 ng/mL with a 2-µL injection volume. At this concentration level, a relative standard deviation of about 10% was obtained for replicate injections. The ratio of the peak height to the background noise was about 5:1. The ratio was about 2:1 at concentrations near 1 ng/mL (2 pg injected).

2.4 The breakthrough volume of the 100-mg sorbent section of the sampler for 1,2,4-trichlorobenzene (the most volatile of the three analytes) was found to be approximately 24 L with a sampling rate of 0.2 L/min at a 1,2,4-trichlorobenzene concentration of about 45 mg/m^3, a sampling temperature of 40 °C, and a relative humidity of > 80%. During the determination of this capacity, the other two analytes were also present in the test atmosphere. Their concentrations were 22 mg/m^3 of 1,2,4,5-tetrachlorobenzene and 15 mg/m^3 of pentachlorobenzene. The capacity of the 100-mg sorbing section was not specifically determined for these two analytes; however, their breakthrough volumes were greater than 24 L.

3. Interferences

3.1 The gas chromatographic operating conditions described below will separate the three analytes from each other and from all but one of the nine remaining isomers of the chlorinated benzenes. No set of operating conditions nor alternate packed column could be found that would separate 1,2,4,5-tetrachlorobenzene from 1,2,3,5-tetrachlorobenzene.

3.2 When substances other than the analytes are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because these substances may interfere with the determination of the analytes.

3.3 Any substance that has the same retention time as one of the three analytes with the chromatographic operating conditions described in this method can interfere with the analysis. Therefore, retention time data cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, changing the separation conditions (column packing, temperature, carrier flow, detector, etc.) may circumvent the problem.

4. Accuracy and Precision

4.1 For the overall sampling and analytical method, the pooled relative standard deviations (RSD's) for six replicate measurements of each analyte in six or seven separate tests in the specified concentration ranges were as follows:

Analyte	Concentration, mg/m^3	RSD, %
1,2,4-Trichlorobenzene	0.002 - 100	9.3
1,2,4,5-Tetrachlorobenzene	0.003 - 31	9.7
Pentachlorobenzene	0.008 - 22	9.8

The pooled RSD's for the analytical method obtained with 36 samplers, each spiked with all three analytes in the specified ranges and stored for one day prior to analysis, were as follows:

Analyte	Quantity, µg	RSD, %
1,2,4-Trichlorobenzene	0.0189 - 502	4.4
1,2,4,5-Tetrachlorobenzene	0.0209 - 506	4.2
Pentachlorobenzene	0.0209 - 513	5.7

4.2 The concentrations of the analytes in the test atmospheres were determined in control experiments primarily by impinger

sampling. The average ratios of the determinaions with the developed sampler to the determinations by impinger sampling were 0.96 for 1,2,4-trichlorobenzene; 1.01 for 1,2,4,5-tetrachlorobenzene; and 0.97 for pentachlorobenzene.

4.3 Thirty-five nanograms of 1,2,4-trichlorobenzene; 63 ng of 1,2,4,5-tetrachlorobenzene; and 43 ng of pentachlorobenzene were found to be stable at room temperature (25 to 30 °C) for at least 14 days.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the analytical procedure. The samples are analyzed by means of a quick instrumental method.

5.2 Another advantage is that the two-stage sampling device may be used to collect both particulate and gaseous air contaminants.

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

5.4 Another disadvantage of the method is that the quantities of the vapors of the analytes that can be sampled are limited by the capacity of the sorbent tube. When the quantity of an analyte that is found on the backup section of the sorbent tube exceeds 20% of that found on the front section, the possibility of sample loss exists.

6. Apparatus

Disclaimer: Mention of company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

6.1 Personal sampling pump capable of accurate performance (± 5%) at 0.025 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Two-stage sampler: The sampler is described schematically in the figure; the assembled unit consists of a 13-mm Teflon fiber mat (the Millipore Type LS [Mitex] filter disc, Catalog No. LSWP01300) in a stainless steel filter holder (the Millipore Swinny Stainless Disc Filter Holder, Catalog No. XX3001200) in tandem with a Pyrex sorbent tube (7 cm long with a 6.4-mm [0.25 in] o.d. and a 4-mm i.d.). The filter holder and tube are

coupled with a nylon Swagelok union (Crawford Fitting Company, Catalog No. NY-400-6). To attach the outlet of the filter holder to the union, a Teflon Swagelok reducing ferrule (Alltech Associates, Catalog No. RF-400/200-T) is bored out to 4-mm (0.156 in) i.d. and the filter holder outlet is inserted into the ferrule. Standard 0.25 in o.d. front and back Teflon Swagelok ferrules (Crawford Fitting Company, Catalog Nos. T-404-1 and T-403-1) are used to attach the sorbent tube to the union; however, the union is bored out to 7.1 mm (0.28 in) to allow the insertion of the end of the tube for a butt-to-butt fit with the reducing ferrule. The sorbent tube contains two sections of 20/50-mesh Amberlite XAD-2 -- a 100-mg sorbing section and a 50-mg backup section. The sorbent sections are separated by a 4-mg plug of silanized glass wool. Two additional 4-mg plugs of the glass wool, one near each end of the sorbent tube, serve to hold the sorbent sections in place. The sampling device is sealed at each end, first with Teflon tape and then with plastic caps. The pressure drop across an assembled sampler is typically 4 in H_2O (1 kPa) at a sampling rate of 0.2 L/min. The filter disc and sorbent tube are disposable; the filter holder, connector, and plastic caps are reusable.

Before sorbent tubes are packed, bulk quantities of the Amberlite XAD-2 are cleansed of impurities by Soxhlet extraction in a 4:1 (v/v) mixture of acetone and methanol for 4 h followed by Soxhlet extraction in hexane for 4 h. The washed material is then dried overnight at 70 to 100 °C under vacuum.

Commercially available sorbent tubes containing Amberlite XAD-2 may not exhibit as high a capacity for the analytes as do sorbent tubes prepared as described above.

6.3 A gas chromatograph equipped with a ^{63}Ni electron capture detector.

6.4 A 2.0 m by 2 mm i.d. nickel column containing 10% Carbowax 20M-TPA on 80/100-mesh Chromosorb W AW.

6.5 Vials, 5-mL, with crimp-on caps containing Teflon-lined silicone rubber septa.

6.6 Pipets, 2.00-mL and convenient sizes for making dilutions.

6.7 Volumetric flasks, 5.00-mL and convenient sizes for making dilutions.

6.8 Ultrasonic bath.

6.9 Syringes, 10-µL.

7. Reagents

7.1 1,2,4-trichlorobenzene, 98% pure.

7.2 1,2,4,5-tetrachlorobenzene, 98% pure.

7.3 Pentachlorobenzene, 98% pure.

7.4 Hexane, distilled in glass.

7.5 Ultra high purity nitrogen (99.999%) for GC carrier and purge gas.

7.6 Stock standard solution. Prepare a stock standard solution containing each of the three analytes in hexane as follows: Add an accurately weighed quantity (about 500 mg) of each analyte to a 5-mL volumetric flask. Add hexane to the mark and dissolve the compounds. Store in an airtight container. The solution is stable indefinitely.

8. Procedure

8.1 Cleaning of Equipment. All nondisposable glassware used for the laboratory analysis, empty sorbent tubes, and the components of the stainless steel filter holders and nylon unions should be thoroughly cleaned and rinsed with 5% nitric acid, tap water, distilled water, acetone, and hexane (in that order). The materials should then be dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the plastic caps and Teflon tape from the ends of the sampler.

8.2.2 Connect the outlet of the sorbent tube to the sampling pump with Tygon or rubber tubing.

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

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

8.2.5 Sample the air at 0.025 to 0.2 L/min. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 12 L.

8.2.6 Record the temperature and pressure of the air being sampled.

8.2.7 Immediately after sampling, separate the filter holder from the sorbent tube and seal the ends of each device with Teflon tape and plastic caps. Save the union for future usage.

8.2.8 To obtain a blank sample, process one unused sampler in the same manner as the exposed samplers (open, seal, and transport) but do not sample air through this sampler. Submit one blank sampler for every ten exposed samplers with a minimum of three blank samplers.

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

8.2.10 Ship nine to twelve Teflon filter discs and sealed sorbent tubes so that desorption efficiency studies can be performed on the same type and lot of Teflon filters and Amberlite XAD-2 used for sampling.

8.2.11 Refrigerate all samples stored longer than seven days.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the sealed filter holders and sorbent tubes from the refrigerator and permit them to equilibrate to room temperature to prevent water condensation inside the devices. Transfer each section of Amberlite XAD-2 in a sorbent tube to a separate 5-mL vial. Add the glass wool plug near the sorbent tube inlet to the vial containing the sorbing section; add the other two glass wool plugs to the vial containing the backup section. Transfer each Teflon filter to a separate 5-mL vial.

8.3.2 Desorption of Samples. To each vial add 2.00 mL of hexane. Cap each vial immediately with a Teflon-lined silicone rubber septum. Extract the sealed samples in an ultrasonic bath for 30 min at room temperature. Also, wash the inside surfaces of the filter holder with 2-3 mL of hexane. Transfer the washings of the filter holder to a 5-mL volumetric flask and dilute to the mark with hexane.

8.3.3 Operating Conditions for the Gas Chromatograph.

Carrier glas flow rate:	30 mL/min of nitrogen.
Detector purge gas flow rate:	90 mL/min of nitrogen.
Injection port temperature:	220 °C.

Column temperature: 160 °C.
Detector temperature: 300 °C.
Injection volume: 2 µL.

Under these conditions, the analytes elute with the following retention times:

Analyte	Retention Time (min)
1,2,4-trichlorobenzene	2.0
1,2,4,5-tetrachlorobenzene	3.3
pentachlorobenzene	7.5

8.3.4 Injection. Inject a 2-µL aliquot of a sample extract or standard into the gas chromatograph by the solvent flush technique. Use 1 µL of hexane as the solvent flush. Maintain a 1 µL air gap between the solvent flush and the 2-µL aliquot.

8.3.5 Measurement of Peak Height. The product of peak height and attenuation setting is linear over the concentration range of about 10-100 ng/mL of each analyte in hexane. The peak height is multiplied by the attenuator setting necessary to keep the peak on scale. Results are read from a standard curve prepared as discussed in Section 9. If peak heights indicate an apparent concentration above about 100 ng/mL, dilute the sample solution appropriately for reanalysis.

8.4 Determination of the Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiencies of the three chlorinated benzenes can vary from one laboratory to another and also from one batch of samplers to another. It is necessary to determine the fraction of each analyte that can be recovered from the samplers. In laboratory tests, the mean overall desorption efficiencies for the three analytes when extracted from exposed samplers were found to be as follows: 0.908 for 1,2,4-trichlorobenzene; 0.901 for 1,2,4,5-tetrachlorobenzene; and 0.917 for pentachlorobenzene.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels of each of the three analytes with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve all three of

the analytes in hexane to give stock solutions with concentrations such that 20 ng to 500 µg of each compound will be injected onto the sampler in no more than 5 µL of a stock solution. Inject an aliquot of the appropriate solution onto the filter in an assembled sampler while drawing 12 L of analyte-free air through the sampler at 0.2 L/min to volatilize the analytes and flush their vapors onto the 100-mg sorbing layer. Separate the filter holder and the sorbent tube, seal each device with Teflon tape and plastic caps, and store the devices overnight at room temperature, then extract the components of the sampler as described in Section 8.3. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 2 mL of hexane. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is taken to be the ratio of the sum of the average amounts of each analyte found on the various components of the samplers to the total amount spiked. The quantities of the analytes found on the backup sorbent sections should be negligible and, therefore, should make a negligible contribution to the computation of the desorption efficiency. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve for each analyte is constructed by plotting the total amounts of each compound found in the samplers versus the desorption efficiency.

9. Calibration and Standardization

By serial dilution of the stock standard solution with hexane, prepare a series of five working standards varying in concentration over the range of 10-100 ng/mL of each analyte. Prepare fresh working standards daily. Analyze the five working standards under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve, plot the concentration of the standards in µg/mL versus peak height or area.

10. Calculations

10.1 Determine the weight of each analyte in a sample (µg) from the standard curve. If the sample solution was diluted for analysis, use the appropriate dilution factor.

10.2 Blank corrections are not expected to be necessary. If the analysis shows a blank correction is needed, make the correction as follows:

$$W_i = W_S - W_b$$

where: W_i = corrected amount (µg) of the analyte of interest on the ith component of the sampler, either the filter, filter holder, or a sorbent section.
W_S = amount (µg) actually found.
W_b = amount (µg) found on the corresponding component of a blank sampler.

Follow a similar procedure for each component of the sampler and for each analyte.

10.3 Make a correction for desorption efficiency as follows:

$$M_F = \frac{\sum_i W_i}{D}$$

where: i = the index summed over the components of the sampling device excluding the backup sorbent section.
M_F = the sum of the corrected amounts (µg) of the analyte of interest on the components of the sampler excluding the backup sorbent section.
W_i = amount (µg) of the analyte of interest on the ith component of the sampler after blank correction.
D = desorption efficiency corresponding to the weight ($\sum_i W_i$).

Follow an analogous procedure for the backup sorbent section.

10.4 Express the concentration, C, of each of the three analytes in mg/m^3, which is numerically equal to µg/L.

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

where: M_F = the sum of the corrected amounts (µg) of the analyte of interest found on the components of the sampling device excluding the backup sorbent section.
M_B = corrected amount (µg) of the analyte found on the backup sorbent section.
V = volume (L) of air sampled.

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

$$C(ppm) = C(mg/m^3) \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.
T = temperature (°C) of air sampled.
24.45 = molecular volume (L/mole) at 25 °C and 760 torr.
M.W. = molecular weight of the analyte of interest (181.46 for 1,2,4-trichlorobenzene; 215.90 for 1,2,4,5-tetrachlorobenzene; and 250.35 for pentachlorobenzene).

11. References

11.1 Dillon, H. K.; Bryant, M. L. "Analytical Methods Evaluation and Validation for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; Pentachlorobenzene; and Polychlorinated Terphenyls: Research Report for 1,2,4-Trichlorobenzene; 1,2,4,5-Tetrachlorobenzene; and Pentachlorobenzene," NIOSH Contract No. 210-79-0102, Southern Research Institute, Birmingham, AL, May 1981.

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NICKEL CARBONYL

Methods Research Branch

Analytical Method

Analyte:	Nickel	Method No.:	P&CAM 344
Matrix:	Air	Range:	2 to 60 μg/m^3
Procedure:	Collection on charcoal, graphite furnace AAS	Precision:	0.099
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

Nickel carbonyl is collected on acid-washed charcoal. Nickel is desorbed with dilute nitric acid and analyzed by graphite furnace atomic absorption spectrometry.

2. Working Range, Sensitivity, and Detection Limit

2.1 For an 80-L air sample, the approximate working range is 2 to 60 μg $Ni(CO)_4/m^3$ (0.29 to 8.6 ppb at 25 °C). For lower concentrations, aliquots larger than 20 μL may be injected, or larger air volumes may be taken. For higher concentrations, smaller air volumes may be taken.

2.2 The analytical sensitivity is approximately 1% absorption (0.0044 A) per 0.15 ng Ni/injection. For a 1-mL desorbed sample volume, 20-μL injection volume, and 80-L air volume, this corresponds to 0.27 μg $Ni(CO)_4/m^3$ (0.039 ppb at 25 °C). Both the analytical sensitivity and detection limit are stated for optimized instrumental conditions, but may be improved by nearly a factor of two by using pyrolytically coated graphite tubes.

2.3 The detection limit, for an 80-L air sample and 20 μL injection volume, is approximately 0.3 μg $Ni(CO)_4/m^3$ (0.043 ppb at 25 °C). This corresponds to a final solution concentration for the desorbed sample of 0.01 μg Ni/mL.

3. Interferences

Particulate nickel compounds will interfere unless a prefilter is used.

4. Precision and Accuracy

4.1 The relative standard deviations of the analytical measurements on sample tubes spiked with 0.08, 0.20, and 0.50 μg Ni as $Ni(NO_3)_2$ were 0.038%, 0.021%, and 0.025% respectively. Accuracy at these levels, which represent 0.4X, 1.0X, and 2.5X the OSHA standard for a 83-L sample averages 93.4% desorption efficiency.

4.2 The relative standard deviation and accuracy for sampling and analysis are

5. Advantages and Disadvantages

5.1 The method utilizes a solid sorbent, involved minimal sample manipulation, and is very sensitive.

5.2 The analysis requires expensive equipment and special care to prevent contamination.

6. Apparatus

6.1 Air Sampling Equipment

6.1.1 Sorbent tubes: glass tube with both ends flame sealed, 8 cm long with 6 mm o.d. and 4 mm i.d., containing two sections of acid washed activated charcoal (7.5), a 2-cm absorbing section (120 mg) and a 1-cm backup section (60 mg), separated by a 2-mm piece of urethane foam. A 3-mm piece of urethane foam is placed behind the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube shall be less than one inch of mercury at a flow rate of 0.2 L/min.

6.1.2 Prefilter unit, consisting of a 37-mm, 0.8-μm cellulose ester filter and cellulose backup pad in a plastic filter holder. The prefilter must be used when particulate nickel is present in the air to be sampled. Connect the prefilter holder to the sorbent tube with a short section of plastic tubing.

6.2 Atomic Absorption Spectrometer

6.2.1 Atomic absorption spectrometer, equipped with a heated graphite atomizing rod, tube or furnace. Reproducible

control of times and temperatures during the drying, charring and atomizing cycles is essential and a minimum atomization temperature of 2700°C is required. Accessories needed for the spectrometer are: readout device (recorder or digital peak height or peak area analyzer), pipetting system (automatic or manual, 5-50 µL, as appropriate to atomizer size) and background correction system (H_2 or D_2 simultaneous correction is preferred but manual correction using a nonabsorbing line is sufficient).

6.2.2 Hollow cathode lamp for nickel.

6.2.3 High-purity argon purge gas in a cylinder equipped with a two-stage regulator, set to deliver 20 psig to the instrument. Nitrogen cannot be used as purge gas because of the formation of uv-absorbing cyanogen.

6.3 Microliter syringes, various sizes, for standard solutions.

6.4 Volumetric flasks, various sizes, for standard solutions.

6.5 Vials, 2-mL, with screw caps

6.6 Volumetric pipette, 1 mL

6.7 Ultrasonic water bath.

7. Reagents (ACS Reagent Grade or Better)

7.1 Double-distilled or deionized water ("distilled water").

7.2 Nitric acid, 70% HNO_3, redistilled in glass.

7.3 Stock standard nickel solution, 1000 µg/mL Ni. Dissolve 1.000 g pure Ni metal in a minimum volume of 70% HNO_3 and dilute to 1 liter with 2% HNO_3. Alternatively, commercially prepared standard may be used.

7.4 Dilute nitric acid, 2% (w/w) HNO_3. Add 29 mL 70% HNO_3 (7.2) to distilled water and dilute to 1 L.

7.5 Charcoal, acid-washed, activated. Acid-wash a sufficient quantity of petroleum-based charcoal, which has a blank value of less than 0.02 µg Ni/200 mg, by soaking overnight in dilute nitric acid (7.4). Rinse several times with distilled water. Pour off excess water, cover with a watch glass, and activate by heating in air at 600°C for 1-1/2 hours.

7.6 Argon gas in compressed gas cylinder.

8. Procedure

8.1 Cleaning of Equipment. New glassware must be cleaned by soaking in hot, concentrated nitric acid followed by thorough rinsing with distilled water. Then, after each use, the glassware should be washed with, in order, detergent solution, tap water, diluted nitric acid (soak four hours or longer) and distilled water.

8.2 Collection and Shipping of Samples

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

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

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

8.2.4 Air being sampling should not be passed through any hose or tubing before entering the tube, except that a cellulose ester membrane filter must precede the sorbent tube to remove particulate nickel compounds if they are present.

8.2.5 Sample at 0.05 to 0.2 L/min. A sample size of 50 to 100 L is recommended. Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 250 L.

8.2.6 Record the temperature and pressure of the air being sampled.

8.2.7 Immediately after sampling, seal the two ends of the tube with plastic caps.

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

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

8.2.10 Store the samples at or below room temperature.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Transfer the sorbing section to a 2-mL vial and the backup section to a separate 2-mL vial. Discard the glass wool plug and the foam plugs.

8.3.2 Desorption of samples: After the two sections of a tube are transferred to vials, pipet 1.00 mL of 2% nitric acid (7.4) into each vial. Cap each vial and extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature.

8.3.3 Inject samples into the graphite atomizer and operate in accordance with the manufacturer's instructions within the following limitations:

Aliquot size: 5-50 µL, depending on atomizer dimensions.

Inert gas flow: Increased sensitivity will be obtained if flow is interrupted during atomization step.

Readout mode: Peak height (analog or digital) is more precise on some spectrometers. The peak is fast and narrow (ca. 3 sec).

Wavelength: Either 232 nm or 341.5 nm may be used; 232 nm is more sensitive.

Background correction: Use D_2 or H_2 lamp (simultaneously or sequentially with Ni lamp) or a nonabsorbing line (231.5 for the 232 nm Ni line).

Dry cycle: 30 sec at 110°C. Longer time and ramp program may be needed for larger aliquots.

Ash (char) cycle: 15 sec at 800°C.

Atomize cycle: 10 sec at 2700-3000°C. Do not atomize below 2600°C, as atomization is too slow for reproducible atomization. A "maximum-power" feature will increase sensitivity if used.

Graphite atomizer: May be either non-pyrolytic or pyrolytic; better sensitivity with pyrolytic.

8.3.4 Analyze a series of standards before and after each set of samples and analyze one mid-range standard after each ten samples. Analyze all solutions in triplicate and take the mean absorbance as proportional to concentration. Sorbent tube blanks and reagent blanks should also be analyzed in the same manner.

9. Calibration and Standardization

9.1 Working standards. Prepare a 100 µg/mL Ni standard solution by dilution of the 1000 µg/mL stock solution with 2% HNO_3 (7.4). This solution is stable for several months if stored in a polyethylene bottle and is used to prepare fresh daily the working standards which should cover the range 0.05-0.3 µg/mL Ni (e.g., 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 µg/mL Ni in 2% HNO_3).

9.2 Analyze the working standards along with the samples (8.3.4). Construct a calibration curve, plotting peak height versus µg/mL Ni.

10. Calculations

10.1 Read the concentration of the sample or blank solution from the calibration curve. Express concentration in µg Ni/mL.

10.2 Multiply the sample or blank concentration by the volumetric dilution factor (e.g., 1.0 mL) to obtain total µg Ni/sample.

10.3 Subtract from the sample concentration the appropriate blank concentration.

$$W_F = W_S - W_O$$

where: W_F = corrected amount of Ni (µg) on the front section of the sorbent tube.
W_S = amount of Ni (µg) found on the front section of the sorbent tube.
W_b = amount of Ni (µg) found on the front section of the blank sorbent tube.

Follow a similar procedure for the backup section to find W_B, the corrected amount of Ni (µg) on the backup section of the sample tube.

10.4 Express the concentration, C, of nickel carbonyl in the air in $\mu g/m^3$:

$$C = \frac{W_F + W_B}{V} \times \frac{170.75}{58.71}$$

where: V = volume (m^3) of air sampled.
170.75 = molecular weight (g/mol) of nickel carbonyl.
58.71 = molecular weight (g/mol) of nickel.

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

$$C(ppb) = C(\mu g/m^3) \times \frac{24.45}{170.75} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where: P = pressure (torr) of air sampled.
T = temperature (°C) of air sampled.
24.45 = molar volume (L/mol) at 25°C and 760 torr.

11. References

11.1 Begnoche, B. C. and T. H. Risby: Determination of Metals in Atmospheric Particulates Using Low-Volume Sampling and Flameless Atomic Absorption Spectrometry, Anal. Chem., 47, 1041-1045 (1975).

11.2 Arthur, J. L.: Special Occupational Hazard Review and Control Recommendations for Nickel Carbonyl. U.S. Dept. of Health, Education and Welfare Publ. (NIOSH) 77-184.

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WELDING AND BRAZING FUMES

Methods Research Branch

Analytical Method

Analytes:	Cr, Mn, Fe, Ni, Cu, Zn, Cd	Method No:	P&CAM 345
Matrix	Air	Range:	See Table 1
Procedure:	Filter collection, X-ray fluorescence analysis	Precision:	0.06-0.07
Date Issued:	8/31/81		
Date Revised:		Classification:	See Table 1

1. Synopsis

1.1 A known volume of air is drawn through a close-faced filter cassette containing a cellulose acetate membrane filter. The elements are determined by x-ray fluorescence spectometry.

1.2 The elemental constitution of metal fumes from welding and brazing operations is dependent on the nature of the base metal, flux, and welding material (rod or wire) used. However, mild steel welding typically contains iron and manganese; stainless steel welding fumes may contain iron, nickel, chromium, and manganese; and brazing fumes can contain cadmium, zinc, and copper (Reference 11.1).

2. Working Range, Sensitivity, and Detection Limit

2.1 The method was developed using welding (shielded metal arc welding on stainless and mild steels) and brazing (Sta-Flo 45 brazing wire on copper) fume samples having loadings of 30-280 µg/filter (as oxides). The method was validated for iron, nickel, chromium, and manganese (Reference 11.2). Copper, zinc, and cadmium were also evaluated but not validated. A 120-liter sample will provide sufficient deposition to detect the above-mentioned elements at air concentrations of one-half the current TLV for the compounds. This will generally provide a sample within the recommended loading of < 1 mg.

2.2 The detection limit, range, sensitivity, precision, and bias of the various elements determined are given in Table 1.

3. Interferences

3.1 Absorption and enhancement effects, penetration of the fume into the filter, and particle size effects (Reference 11.3) have been evaluated and found to be not significant in the analysis of welding and brazing fumes (Reference 11.2).

3.2 The background intensity will contain the analyte-line emission for the elemental components of the spectrometer and associated apparatus (e.g., the filter holder). This intensity is subtracted out in the determination of the analyte line intensity (Section 8.3.2).

3.3 Line overlap occurs when two elements fluorescence at the same or nearly the same wavelength. Significant line overlap occurs in wavelength-dispersive XRF spectrometers with the pairs Se/Pb, Ti/V, Cr/Mn, Ba/Ti, Br/As, V/Cr, and Cd/Ag (interferent/analyte). The overlap can be corrected by reference to the spectra of the pure element (Section 8.4.2). Line overlap interference is considerably more severe with energy-dispersive spectrometers; refer to the instrument instructions for correction procedures.

4. Precision and Accuracy

4.1 The accuracy and precision of this method varies with the element. Table 1 provides this information for the welding station fume filters. The pooled relative standard deviation from the analysis of generated welding fumes was 6-7% for the various elements (Reference 11.4).

4.2 The data in Table 1 demonstrate that the method is accurate to 4-7% except for chromium, which has an average bias of 12.3%. The biases are due to inaccuracies in the calibration curve slopes, and consequently cannot be used as correction factors.

4.3 Collection efficiency is 1.0 for iron, manganese, nickel, and chromium. Penetration of the fume through the filter is not likely to be a significant factor in fume monitoring with membrane filters (Reference 11.2).

5. Advantages and Disadvantages

5.1 The significant advantage to the x-ray fluorescence method is the minimal sample preparation, the speed of the analysis (2 minutes/element), and the lack of sample destruction.

Additional analyses are possible because the sample is not destroyed during analysis. Corrections for particle size, self-absorption, and filter absorption effects are not necessary for surface deposition of fumes on membrane filters.

5.2 The main disadvantage is the difficulty in proper standardization. Proper standards require careful preparation (Section 9.1).

5.3 Commercial standards, which have been shown to result in unacceptably poor accuracy for welding fume analysis, are available. If used, they should be identical to the field sample filters in construction material and area of deposition. Disadvantages of commercial standards include expense and fragility after exposure to intense x-rays (i.e., they may break after three or four uses).

5.4 The laboratory-made filter standards described herein can be economically produced; however, their production requires some technical skill. In addition, they will become fragile after three or four exposures to intense x-rays.

6. Apparatus

6.1 Apparatus for Sampling

6.1.1 A filter unit consisting of a 37-mm, 0.8-μm mixed cellulose acetate membrane filter and cassette.

6.1.2 A calibrated personal sampling pump, capable of maintaining an accuracy of ± 5% at the recommended flow rate (1 L/min).

6.1.3 An integrated volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Apparatus for Analysis

6.2.1 Suction device consisting of a Buchner funnel and filtering apparatus (Millipore Corporation) and vacuum source.

6.2.2 Freezer-mill (Spex Industries, Metuchen, N.J.).

6.2.3 Ultrasonic bath apparatus (Buehler Ltd., Evanston, Ill).

6.2.4 Flask, 1-L or larger.

6.2.5 Powder sieve, 10 mm (±2 mm) pore size. (Buckbee Maers, St. Paul, Minn.).

6.2.6 Ion-exchange filter paper (Gelman Acropor SA-6404, C-10 resin, or equivalent).

6.2.7 Mylar film (Spex Industries, Metuchin, N.J.).

6.2.8 An energy- or wavelength-dispersive x-ray fluorescence spectrometer.

6.2.9 Atomic absorption spectrometer for initial calibration of standards.

7. Reagents

7.1 Powdered element standard containing only elements of interest. (Spex Industries, Metuchen, N. J.). Multielement powders containing hard-to-solubilize elemental compounds should not be used (e.g., Spex Mix 1000). This powder is freezer-milled, and sieved with isopropanol (10 μm sieve) in the ultrasonic bath.

7.2 Cobalt atomic absorption standard solution (1000 ppm).

7.3 Isopropanol.

7.4 Deionized water.

8. Procedure

8.1 Cleaning of Equipment. Acid clean all glassware and associated apparatus in nitric acid before use.

8.2 Collection and Shipment of Samples

8.2.1 The monitor cassette should be equipped with a 0.8 μm membrane filter with backup pad. The cassette is connected to the personal monitoring pump with tygon tubing or equivalent.

8.2.2 Personal sampling takes place in the breathing zone of the welder, i.e., inside the welders' helmet. Secure the end of a length of tygon tubing to the inside the welders' helmet and attach the other end to the inlet of the cassette.

8.2.3 Sampling takes place with tip or plugs of closed-faced cassettes removed. Use a flow rate of 1.0 L/min. Sampling time is 2 hours. Visually inspect the samples to avoid too heavy a deposition on the filter. Terminate sampling before a highly colored deposition develops. A heavily deposited filter is prone to destruction of the deposition because the depositions will not sufficiently adhere to the filter. In addition, a heavy deposition may necessitate a non-linear calibration curve due to XRF shadowing.

8.2.4 Immediately after sampling, remove the cassette and place caps over the inlet and exit orifices of the cassette. Return the cassettes to the laboratory for analysis. The depositions on the filter are somewhat fragile and should be treated with care.

8.3 Preparation of Internal Standard Filter

8.3.1 Place the ion-exchange filter paper in the Buchner filtration assembly. Wet the paper by pouring approximately 50 mL of water into the Buchner filter assembly, apply a low vacuum, and collect the water in a second 100 mL beaker. Add 200 µL of cobalt atomic absorption standard solution to the collected water, pour into the Buchner filter device, and draw the liquid again through the filter with a low vacuum. Collect the liquid with the first beaker and repeat, passing the liquid through the filter seven times. When completed, remove the filter to dry.

8.3.2 A cobalt-impregnated ion-exchange filter is made for every position in the sample changer of the spectrometer. These filters should have exactly the same amount of cobalt deposited on them. Prior to their use, analyze the cobalt-impregnated filters for cobalt by XRF to determine their similarity. They should give the same XRF analyte-line intensity for cobalt within normal statistical variation (that is, the analyte-line intensity of no filter should differ from any other by an amount equal to the square root of the intensity in counts/second).

8.4 Analysis of Filters

8.4.1 Obtain a qualitative scan of one of the filters to establish which elements are present in the samples. The XRF spectrometer parameters are then set for analysis of these elements, and including cobalt,

according to the manufacturer's specifications (Parameters for Philips AXS wavelength-dispersive spectrometer are given in Table 2). Any required line overlap correction factors should be determined as described in Section 8.4.2.

8.4.2 Line overlap correction factors are to be determined as described in this example. It is known that Cr Kβ emission interferes with the Mn Kα analyte line. From the spectrum of pure Cr, a factor F is found which relates the intensity of the Cr Kβ line (at the Mn Kα wavelength), to the intensity of the Cr Kα line:

$$F = \frac{\text{Cr K}\beta \text{ (at Mn K}\alpha \text{ wavelength)}}{\text{Cr K}\alpha \text{ (at Cr K}\alpha \text{ wavelength)}}$$

For the determination of the Mn Kα emission intensity, Cr is measured at Cr Kα, and the product of (Cr Kα emission) x F is subtracted from the intensity measured at Mn Kα. The result is a measure of the Mn Kα intensity without the line overlap interference of chromium.

8.4.3 The cobalt-impregnated ion-exchange filters are placed in the sample holders of the spectrometer. They are used as internal standards and as support for the field sample filters.

8.4.4 The cassettes should be opened carefully and the filters placed into the XRF sample holders, on top of the cobalt-impregnated filters. Mylar covers do not absorb x-rays of elements above atomic number 20 and may be used to retain heavily overloaded fumes; however, they may damage the depositions and should be used only when needed.

8.4.5 A filter blank should be included for every ten field samples. Blanks for the standards (Section 9.1.5) are also included.

8.4.6 The samples and standards are loaded into the XRF instrument and analyzed. The standards are generally analyzed first. The field samples are analyzed soon afterwards, in order to minimize the effects of instrument drift.

8.4.7 All analyses are performed with cobalt as the internal standard. Cobalt is analyzed on every filter sample, and all other element analyte-line intensities are divided by the cobalt analyte-line intensity.

9. Calibration and Standardization

9.1 Preparation of Standard Filters

9.1.1 A set of standard filters is made in duplicate, at four levels of the elements of interest (eight filters), covering the approximate range of the method. An identical set of eight filters is made, wet-ashed, and analyzed by atomic absorption (or an equivalent technique) to provide the initial calibration of the elemental loading on the XRF standard filters.

9.1.2 Make up a liquid suspension from the prepared elemental powder standard. Approximately 0.5 gram is added to 1 L of ispropanol. The suspension is ultrasonicated 1/2 hour before using. During use, stir the solution with a Teflon®-coated mixing bar.

9.1.3 Place an alcohol-resistant membrane filter (e.g., Gelman GA-6) in the Buchner filtration apparatus. Place approximately 50 mL of isopropanol above the filter. Measure an aliquot of 2 mL of stirred suspension with a pipette and add to the isopropanol above the filter. Carefully stir this solution with the pipette and rinse the outside of the pipette with isopropanol solution afterwards. Add a few mL of isopropanol to the pipette to wash out any remaining suspension. Apply a low vacuum so that the suspension is slowly drawn through the filter. After all the solution has passed through the filter, remove and dry it.

9.1.4 Repeat the process until four identical filters have been produced. The variation in these filters should be < 5% RSD. Repeat the process with 2 mL, and again with 3 mL.

9.1.5 Obtain four blank filters, two for wet-ashing and analysis, and two for use as XRF standards.

9.1.6 Wet-ash and analyse two filters from each set by a suitable method (e.g., atomic absorption) to determine the quantities of the elements on the filters. The other two filters of each set are used in the XRF analysis.

9.2 Analyze the samples and standards by x-ray fluorescence spectrometry according to the procedure described in

Section 8.4. Following analysis, subtract the appropriate blank values from the analyte-line intensity of the samples and standards.

10. Calculations

10.1 After the samples have been analyzed and the blank values subtracted, plot the XRF analyte-line intensities of the standards versus the deposition of the standards (µg) determined by atomic absorption. A straight line calibration curve is sufficient for recommended loadings (< 1µg). Convert the analyte-line XRF intensities of the samples into mass concentrations, according to the formula:

$$M = K(I-B-X)$$

where: M = mass of the analyte (µg)
K = slope in µg/(cts/sec) of the standard calibration curve
I = relative XRF analyte-line intensity (ratioed to the cobalt intensity)
B = corrections for XRF analyte-line background intensity and line overlap, if needed (ratioed to the cobalt intensity)
X = relative XRF intensity of the filter blank (divided by the cobalt intensity)

10.2 For personal sampling pumps with rotameters only, the following volume correction should be made.

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

where V = the corrected volume (m^3) of air sampled
f = flow rate of sample (liters/min)
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).

10.3 To determine the airborne concentration of an element in $\mu g/m^3$

$$C = \frac{M}{Vs}$$

where: Vs = volume of air sampled in cubic meter at standard conditions of 25 °C and 760 mm Hg (1000 liter = 1 m^3; volume = flow rate x sampling time).

11. References

11.1. T. Carsey, "Feasibility Study of X-ray Fluorescence for Analysis of Welding and Brazing Fumes," available through NTIS (in press).

11.2 T. Carsey, "Standardization Techniques in X-ray Fluorescence," DHHS (NIOSH) Internal Report, 1981.

11.3. E. P. Bertin, "Principles and Practice of X-ray Spectrometric Analysis," 2nd Edition, Plenum, N.Y., 1975.

11.4 D. G. Taylor, R. E. Kupel, and J. M. Bryant, "Documentation of the NIOSH Validation Tests," U.S. Department of Health, Education, and Welfare, 1977, Cincinnati, Ohio, DHEW (NIOSH) Publ. No. 77-185, p. 10.

11.5. "Threshold Limit Values for Chemical Substances and Physical Agents in the Workplace Environment with Intended Changes for 1981," American Congress of Governmental Industrial Hygienists, Cincinnati, 1981.

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Inorganic Methods Development Section

Table 1

Analytical Results for Welding Fume Elements

Element	Method Class	Range[1] (mg/m³)	Detection Limit[2] (µg)	RSD (%)	Average Bias[3] (%)	TLV[4] (mg/m³)	Sensitivity[5] (rel int/µg)
Iron	B	0.05-0.50	1.5	7.0	5.9	1	178.1
Manganese	B	0.04-0.29	2.7	6.7	4.6	1	168.1
Chromium	E	0.04-0.42	1.8	6.8	12.3	0.5[6]	21.1
Nickel	B	0.02-0.14	1.5	7.1	6.8	1	47.2
Copper[7]	E	0.01-0.03	---	11.7	----	0.2	------
Zinc	E	0.05-0.06	---	4.3	----	5	-------
Cadmium	E	0.3 - 5.0	---	6.3	----	0.05	--------

1. Based on a 120-L sampling volume. The upper limit given here was defined by the range of the validation samples. This may be extended up to approximately 2 mg/m³ without danger of a non-linear calibration curve.

2. Detection limit (mg/m³) computed as $DL = 3A(I^{1/2})/120L$ where I is the filter blank intensity, and A is the slope of the analyte calibration curve [(AI) = Concentration in µg].

3. This quantity is the average of the four biases (100x[AAS-XRF]/AAS), where AAS is the amount of metal determined by atomic absorption spectroscopy, from the four deposition levels.

4. Threshold Limit Values from Reference 11.4.

5. Sensitivity defined as [analyte-line intensity/cobalt line intensity]/ [µg/filter], the latter determined by AAS.

6. Chromium (VI) compounds have a TLV of 0.05 mg/m³ (Reference 5).

7. Teflon filter holder required.

Table 2

XRF Instrument Parameters

El	KV,MA	Crystal	Collim	Detector	Peak 2θ	Bkgr 2θ	Overlap Factor, F
Cr	60,40	LiF200	Coarse	Fl (+)	69.36	68.00	--
Mn	60,40	LiF200	Coarse	Fl (+)	63.08	65.00	Cr;F=.006
Fe	60,40	LiF200	Coarse	Fl,Sc (+)	57.56	58.50	--
Ni	60,40	LiF200	Fine	Fl,Sc (+)	48.70	49.50	--
Cu	60,40	LiF200	Fine	Fl,Sc (+)	45.08	46.50	--
Zn	60,40	LiF200	Fine	Fl,Sc (+)	41.83	42.50	--
Cd	60.40	LiF200	Fine	Fl,Sc (+)	15.26	15.55	--

In Table 2, Fl is the gas flow detector, Sc is the scintillation counter detector, (+) designates the differential pulse height counting, and PET denotes the pentaerythritol crystal. Kα emission is always used.

INORGANIC ARSENIC

Methods Research Branch

Analytical Method

Analyte:	Arsenic	Method No.:	P&CAM 346
Matrix:	Air	Range:	0.67-32.2 $\mu g/m^3$
Procedure:	Treated filter collection, wet digestion, graphite furnace, AAS	Precision:	0.075
Date Issued:	8/31/81		
Date Revised:		Classification:	D (Operational)

1. Synopsis

   1.1 A known volume of air is drawn through a Na_2CO_3-impregnated 0.8-µm pore size cellulose ester filter and cellulose backup pad to collect vaporous and particulate arsenic.

   1.2 The filter-backup pad pair is digested with HNO_3-H_2O_2 and nickel nitrate is added for matrix modification.

   1.3 The samples are analyzed by graphite furnace atomic absorption spectrophotometry.

2. Working Range, Sensitivity and Detection Limit

   2.1 The method was evaluated over the range 0.670 to 32.2 $\mu g/m^3$ for a 400-L air sample collected at 20 °C and 750 torr, corresponding to 0.268 to 12.8 µg/sample. The upper limit of the method may be extended by diluting the sample to a volume greater than 10.0 mL, such that 0.0005 to 0.008 µg As is injected into the graphite furnace.

   2.2 The instrumental sensitivity at 193.7 nm is 0.000066 µg As/0.0044 absorbance units.

   2.3 The 2σ detection limit at 193.7 nm is 0.0003 µg As/injection, corresponding to 0.15 $\mu g/m^3$ for a 400-L air sample dissolved in 10.0 mL of solution, and a 50-mL injection.

3. Interferences

3.1 Background absorption is overcome by the use of a deuterium background corrector.

3.2 Copper (II), nitrate, chloride, and sulfate have been shown specifically not to interfere with the determination at concentrations up to 50 times the As concentration.

4. Precision and Accuracy

4.1 The relative standard deviation for the total sampling and analytical method in the range of 0.67 to 32.2 $\mu g/m^3$ was 0.075l. Details of the statistical treatment may be found in Reference 11.1.

4.2 The analytical method recovery was determined to be 1.005 ± 0.020 at 6.5 $\mu g/m^3$. Collection efficiency for arsenic trioxide vapor was better than 0.939 in all cases. In stability studies of generated samples, the mean of samples analyzed after fourteen days was the same as that of samples analyzed after one day at the 95% confidence level.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable, and the samples are easily collected.

5.2 With the base-treated filters, total arsenic, both particulate and vapor-phase, is collected and analyzed.

5.3 Samples may be analyzed quickly and easily.

5.4 The method is extremely sensitive for arsenic. Extreme care must be exercised in all stages of the analysis.

5.5 The analytical instrumentation required is relatively expensive.

5.6 No extended period of radio-frequency ashing is required.

6. Apparatus

6.1 Sampling equipment, consisting of a filter unit (37-mm/0.8-μm cellulose ester membrane filter and cellulose backup pad treated with Na_2CO_3/glycerol solution) and personal sampling pump capable of sampling at 1.5 to 2.5 L/min. The impregnated filters may be prepared up to one week ahead of time. The pump must be calibrated with a representative filter in line and its flow rate must be known to within ± 5%. The pump must be

capable of maintaining a maximum pressure drop of 20 inches of water across the impregnated filter-backup pad pair during a sampling period of four hours.

6.2 Atomic absorption spectrophotometer, equipped with a graphite furnace atomizer. Reproducible control of times and temperatures during the drying, charring, and atomization cycles is essential. Required accessories include an electrodeless discharge lamp for arsenic and EDL power supply, readout device (recorder or digital peak height analyzer), a gas control system for argon purge gas, pipetting system (automatic or manual) and simultaneous deuterium background corrector.

6.3 Glassware (borosilicate).

6.3.1 Volumetric pipettes, 1.0-, 2.0-, 4.0-, 6.0-, 8.0-, 10.0-, and 100.0-mL.

6.3.2 Volumetric flasks, 100.0-, and 1000.0-mL.

6.3.3 Beakers, 50-mL.

6.4 Steambath.

7. Reagents

All reagents used should be ACS reagent grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, 70% (w/w), redistilled in glass.

7.3 Hydrogen peroxide, 30%.

7.4 1000 µg/mL Ni^{++} in 1% HNO_3 solution. Dilute 4.95 gm $Ni(NO_3)_2$ to 1.0 L with 1% HNO_3. Alternatively, use a commercially prepared Ni standard prepared in 1% HNO_3.

7.5 Arsenic stock standard solution, 1000 µg/mL As. Use a commercially prepared standard.

7.6 Argon gas in a compressed gas cylinder.

7.7 9:1 1 M Na_2CO_3:glycerol solution. Dissolve 9.5 g sodium carbonate, Na_2CO_3, in 90 mL distilled water and add 10 mL pure glycerol.

8. Procedure

8.1 Cleaning of Equipment. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in the following order, detergent solution, tap water, dilute nitric acid (soak four hours or longer), and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Remove the top plug from the cassette and inject 300-µL of 9:1 1 M Na_2CO_3:glycerol solution. Replace the plug, rotate the cassette carefully to completely cover the surface of the filter with solution, and allow the filter to dry overnight.

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

8.2.4 Take the sample at an accurately known flow rate between 1.5 and 2.5 L/min. A sampling size of 400 L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.5 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to steps 8.2.1 and 8.2.2 of this procedure.

8.2.6 Ship the cassette so as to prevent excessive vibration or jarring to the cassettes.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the filter and backup pad with tweezers; transfer both to a 50-mL beaker.

8.3.2 To each beaker, add 15 mL HNO_3. Cover with a watchglass and allow to sit on a hotplate at 150 °C until the volume has been reduced to about 1 mL. Rinse each watchglass with deionized water and add 6 mL 30% H_2O_2 to each beaker. Place each beaker on a steambath and allow the solution to go to dryness. Cool the beakers; add 10.0 mL of 1000 µg/mL Ni^{++} 1% HNO_3 solution and sonicate for 30 minutes in an ultrasonic bath.

8.3.3 Inject samples into the graphite furnace and operate in accordance with the manufacturer's instructions with the following limitations:

Aliquot Size:	10 or 50-µL, depending on the concentration of the sample.
Readout Mode:	Peak height in absorbance mode (3 x scale) is most precise.
Wavelength:	193.7 nm.
Background correction:	Simultaneous D_2 background correction is recommended.
Dry Cycle:	100 °C, 70 sec.
Char Cycle:	1300 °C, 30 sec.
Atomize Cycle:	2700 °C, 10 sec.
Graphite Atomizer:	Non-pyrolytic tube.

9. Calibration and Standardization

9.1 Dilute stock (1000 µg/mL) arsenic standard solution 1:100 with 1000 µg/mL Ni in 1% HNO_3. The resulting standard solution contains 10 µg/mL As.

9.2 Make a further 1:10 dilution of the 10 µg/mL As solution with 1000 µg/mL Ni in 1% HNO_3 solution to give a 1 µg/mL As stock.

9.3 Make working standards by dilution of these two stock solutions with 1000 µg/mL Ni in 1% HNO_3 solution (e.g., 2:100, 4:100, 6:100, and 8:100 dilutions of the 1 µg/mL As stock will give 0.02, 0.04, 0.06, and 0.08 µg/mL As working standards for a 50-µL injection of sample). Working standards for a 10-µL injection of sample are prepared by 2:100, 4:100, 6:100, and 8:100 dilutions of the 10 µg/mL As stock, giving concentrations of 0.20, 0.40, 0.60, and 0.80 µg/mL As. These working standards should be prepared weekly.

9.4 The calibration curve is constructed from the absorbance measured for the working standard solutions analyzed under the same instrumental conditions as the samples.

10. Calculations

10.1 From the calibration curves obtained in Section 9, calculate for each sample the amount of arsenic in µg.

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

$$W = S - B$$

where: W = net sample weight (µg)
S = weight found in sample filter (µg)
B = weight found in blank filter (µg).

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

$$V = \frac{f \times t}{1000} \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{1/2}$$

where: V = the corrected volume (cu m) of air sampled
f = flow rate sample (L/min)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K).

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

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

11. Reference

11.1 Backup Data Report for Inorganic Arsenic, prepared under NIOSH Contract 210-79-0060.

Dan Garland
Mary Jamin, Ph.D.
George Colovos, Ph.D.
Rockwell International
NIOSH Contract No. 210-79-0060

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4,4'-METHYLENEBIS(PHENYL ISOCYANATE) (MDI)

Methods Research Branch

Analytical Method

Analyte:	A urea derivative of MDI	Method No:	P&CAM 347
Matrix:	Air	Range:	4.4 to 800 µg/m^3
Procedure:	Collection and derivatization on impregnated filter, HPLC	Precision:	0.078
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 A known volume of air is drawn through a glass-fiber filter impregnated with a reagent, N-p-nitrobenzyl-N-propylamine, to collect MDI. MDI reacts with the reagent to form N,N"-(methylenedi-4,1-phenylene)bis[N'-[(4-nitrophenyl)methyl]-N'-propylurea] (MDIU) as a derivative. (Reference 11.1)

1.2 The impregnated filter is treated with dichloromethane to recover the urea derivative.

1.3 The dichloromethane solution is analyzed by high pressure liquid chromatography (HPLC) with an ultraviolet detector set at 254 nm to determine the concentration of MDIU.

1.4 The concentration of MDI in air is calculated from the quantity of MDIU on the filter and the volume of air sampled.

2. Working Range, Sensitivity and Detection Limit

2.1 MDI in air can be quantified at concentrations ranging from 4.4 to 800 µg/m^3 for 180-L air samples and at ceiling concentrations ranging from 80 to 1000 µg/m^3 for 10-L air samples. The range useful for quantitation of the urea derivative (MDIU) in solution is equivalent to 0.8 to more than 150 µg MDI per mL of solution when 50-µL aliquots are injected into the HPLC.

2.2 The impregnated filter can collect more than 298 μg of MDI (greater than 99.3% of the MDI) at a concentration of 500 μg/m^3 during a 10-hour sampling period at 1 L/min when the air temperature is 18 °C.

2.3 It has been estimated that MDI at a concentration of 0.6 μg/m^3 could be detected in a 180-L air sample. The detection limit of MDIU in solution is equivalent to approximately 0.1 μg of MDI per mL if a 50-μL aliquot is injected into the HPLC.

3. Interferences

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

3.2 N-p-Nitrobenzyl-N-propylamine on glass fiber filters is unstable in the presence of light and is unstable to a smaller degree during storage in the dark at room temperature. Interference during HPLC analysis may result if impregnated filters in filter holders are exposed to light for an excessive period or are stored in the dark at room temperature for an excessive period. Exposure of two impregnated filters inside filter holders to fluorescent lighting for 25 hours gave rise to interferences during HPLC analysis which corresponded to roughly 2 μg of MDI per filter. Storage of three impregnated filters for 41 days in the dark (33 days at room temperature and 8 days at -21 °C) gave rise to interferences which corresponded to an average of roughly 0.4 μg MDI per filter. Storage of six impregnated filters for 42 days in the dark at -21 °C gave rise to no interferences during HPLC analysis.

3.3 The following compounds would not interfere with the analysis of MDI in this method: toluene-2,4-diisocyanate (2,4-TDI), toluene-2,6-diisocyanate (2,6-TDI), and hexamethylene diisocyanate (HDI).

3.4 Any compound which has the same retention time as that of MDIU and is detected under the HPLC conditions indicated in this method is an interference.

4. Precision and Accuracy

4.1 The pooled relative standard deviation for the sampling and analytical method in the approximate range from 170 to 800 μg/m^3 was 0.060 when critical orifices were used to maintain sampling rates near 1 L/min. The relative standard deviation for the sampling and analytical method in the same approximate range of concentrations would be 0.078 if a pump error of 0.05 is assumed for personal-sampling pumps.

4.2 Average recoveries of MDIU from impregnated filters ranged from 0.96 to 0.99 over the range 0.8 to 67 μg of MDI per filter. The pooled relative standard deviation for the average recoveries was 0.030.

4.3 MDIU on impregnated filters is stable during storage at room temperature in the dark for at least 15 days.

5. Advantages and Disadvantages

5.1 Advantages of tne method are: (a) the sampler is small, portable and convenient for personal sampling; (b) the sampler can collect MDI in both vapor and aerosol forms; and (c) the analytical method is specific for MDI.

5.2 Disadvantages of the method are: (a) a time limitation of approximately 21 days for storage of impregnated filters at room temperature in the dark because of the instability of the reagent, N-p-nitrobenzyl-N-propylamine; (b) a need to protect impregnated filters from light; and (c) a need to wash the HPLC column when N-p-nitrobenzyl-N-propylamine causes a large detector response (see Sections 3.2 and 8.3.6).

6. Apparatus

6.1 Sampling Equipment

6.1.1 Samplers. Each sampler contains a glass-fiber filter, 13 mm in diameter, which has been impregnated with N-p-nitrobenzyl-N-propylamine. The impregnated filter is housed in a 13-mm filter holder (Catalogue No. SX00 013 00, Millipore Corporation, Bedford, MA, or equivalent). The internal diameter of the inlet of the filter holder is 4 mm. The filter holders may be wrapped with black tape in order to help protect the impregnated filters from light. Seal the inlets and outlets of the filter holders with plastic tape for storage. The samplers may be stored at -21 °C in the dark for at least 6 weeks. Limit the storage time of the samplers at room temperature in the dark to approximately 21 days (see Section 3.2).

6.1.2 Impregnated Filters. Place 300 mg (0.0013 mole) of N-p-nitrobenzyl-N-propylamine hydrochloride into a 125-mL separatory funnel. Add 25 mL of deionized water and shake the mixture until all of the hydrochloride has dissolved. Cause free amine to separate from the solution by adding 15 mL of 1 N NaOH solution and shaking the mixture. Extract the N-p-nitrobenzyl-N-propylamine with 50 mL of hexane.

Place six glass-fiber filters which are free of binders and 6 mL of the hexane solution into a 50-mL beaker. In dim light, allow hexane to evaporate from the beaker with the aid of a stream of nitrogen. Occasionally swirl the mixture. The filters are sufficiently dry when they no longer cling to the beaker. It has been estimated that there is 4.5 mg of N-p-nitrobenzyl-N-propylamine on each impregnated filter.

6.1.3 Calibrated Personal-Sampling Pump. The personal sampling pump should be calibrated for the recommended flow rate of 1 L/min with a representative sampler in line.

6.1.4 Stopwatch.

6.1.5 Thermometer.

6.2 High pressure liquid chromatograph with an ultraviolet detector set at 254 nm.

6.3 HPLC column, 25-cm x 4.6-mm internal diameter, packed with Partisil 10 (a porous silica packing; diameter, 10 µm; surface area, 400 m^2/g; Whatman, Inc., Clifton, NJ).

6.4 Frits, 0.5-micrometer pore diameter, for use in front of the packing in the HPLC column.

6.5 Partisil 10 or other silica packing for use in replacing packing which may be lost from the HPLC column (see Section 8.3.7).

6.6 Spectrophotometer set at 555 nm.

6.7 Quartz cells for spectrophotometer, 5-cm path length.

6.8 Glass vials, 1-mL, with caps lined with polytetrafluoroethylene.

6.9 Volumetric flasks, 5-mL and other convenient sizes.

6.10 Graduated cylinders, 10-, 25-, 100-, and 1000-mL.

6.11 Tweezers.

7. Reagents

Except where otherwise indicated, each reagent should be of ACS reagent grade or better.

7.1 4,4'-Methylenebis(phenyl isocyanate) (MDI), practical grade or better.

7.2 N-p-Nitrobenzyl-N-propylamine hydrochloride.

7.3 Dichloromethane, distilled in glass.

7.4 Solution of MDI in dichloromethane. Mix 2.0 g of MDI with 200 mL of dichloromethane. Filter the solution with a glass frit of fine porosity. Determine the concentration of MDI according to Section 9.1.

7.5 Water, deionized.

7.6 MDIU. Mix 1.500 g (0.00650 mole) of N-p-nitrobenzyl-N-propylamine hydrochloride with 25 mL of deionized water in a 125-mL separatory funnel. Cause free amine to separate from the solution by adding 15 mL of 1 N NaOH and shaking the mixture. Extract the N-p-nitrobenzyl-N-propylamine with 50 mL of hexane. Determine the volume of the solution prepared according to Section 7.4 which would contain 577 mg (0.00231 mole) of MDI, and add 577 mg of MDI in solution to 40 mL of the hexane solution. Reduce the volume of the mixture to approximately 25 mL with a rotary evaporator. Collect the solid by filtration. Wash the solid with several portions of hexane. Recrystallize the product from benzene by dissolving the product in hot benzene, filtering the solution quickly, and allowing the filtrate to cool. Collect the crystals in a Buchner funnel, and dry the product *in vacuo* at 80 °C. Melting point = 161-162 °C. (Reference 11.2)

NOTE: Benzene is a carcinogen and should be handled with care in a ventilated fume hood.

7.7 4,4'-Methylenedianiline, high purity.

7.8 Acetic acid, glacial.

7.9 Standard solution of 4,4'-methylenedianiline. Dissolve 238 mg of 4,4'-methylenedianiline in 700 mL of glacial acetic acid. Dilute the solution to 1 liter with deionized water.

7.10 Hydrochloric acid, 12 M.

7.11 Hydrochloric acid-acetic acid solution. Add 35 mL of 12 M hydrochloric acid and 22 mL of glacial acetic acid to 600 mL of deionized water. Dilute the solution to 1 liter with deionized water.

7.12 Sodium nitrite-sodium bromide solution. Dissolve 3.0 g of sodium nitrite and 5.0 g of sodium bromide in deionized water and dilute the solution to 100 mL. Discard the solution after 1 week.

7.13 Sulfamic acid solution. Dissolve 10.0 g of sulfamic acid in 100 mL of deionized water.

7.14 Sodium carbonate solution. Dissolve 16.0 g of anhydrous sodium carbonate in deionized water and dilute the solution to 100 mL. Discard the solution after 1 week.

7.15 N-(1-Naphthyl)ethylenediamine dihydrochloride solution. Dissolve 1.0 g of N-(1-naphthyl)ethylenediamine dihydrochloride in 50 mL of deionized water, add 2 mL of 12 M hydrochloric acid, and dilute the solution to 100 mL. Discard the solution after 1 week.

7.16 N,N-Dimethylformamide-hydrochloric acid solution. Mix 90 mL of N,N-dimethylformamide with 10 mL of 6 M hydrochloric acid. Discard the solution after 1 week.

7.17 2-Propanol, distilled in glass.

8. Procedure

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

8.2 Collection and Shipping of Samples

8.2.1 In each set of samplers consisting of six or fewer samplers, label two samplers as "blank" samplers. The "blank" samplers and the corresponding samplers used in actual air sampling should contain impregnated filters from the same batch (Section 6.1.2).

8.2.2 Handle the "blank" samplers and other samplers under the same conditions of temperature, light exposure and storage time. Do not unseal and do not draw air through the "blank" samplers.

8.2.3 Immediately before sampling, unseal the inlet and outlet of the sampler.

8.2.4 Connect the sampler to a calibrated personal-sampling pump with flexible tubing.

8.2.5 Sample at a flow rate of 1 L/min for 10 hours or less if the maximum air temperature will be 18 °C or less. (Experiments were performed at air temperatures near 18 °C, and 12 hours of sampling was borderline for breakthrough to occur. Breakthrough volumes would be expected to decrease with increases in concentration

of MDI vapor, and the maximum vapor concentration of MDI would increase with temperature. Maximum sampling periods should be decreased with increases in air temperature.) Sample at 1 L/min for 5.5 hours or less if the maximum air temperature will be between 18 °C and 29 °C. Sample at 1 L/min for 3 hours or less if the maximum air temperature will be between 29 °C and 40 °C.

8.2.6 Record pertinent data in regard to sampling including sampling time, air temperatures, and atmospheric pressures. If pressure data are not available, record the elevation.

8.2.7 After sampling, seal the inlets and outlets of the samplers with plastic tape. Store these samplers and the "blank" samplers in the dark and, if practical, at -21 °C until analyses are performed. If the samplers are stored at room temperature, limit the total storage time at room temperature to approximately 21 days. Consider storage time before sampling as part of the total storage time. The samplers may be stored in the dark at -21 °C for at least 6 weeks.

8.2.8 If a bulk sample of material suspected to contain MDI is to be submitted to the laboratory, place the bulk sample into a glass container, and seal it with a cap lined with polytetrafluoroethylene. Secure the cap in place with tape.

8.2.9 Do not transport the bulk sample and the air samples in the same container.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Remove the impregnated filter from the filter holder with tweezers, and place the filter into a 1-mL glass vial. Place 1 mL of dichloromethane into the vial. Seal the vial with a cap lined with polytetrafluoroethylene. Shake the vial vigorously for approximately 1 minute.

8.3.2 HPLC Conditions. Operating conditions for high pressure liquid chromatography are:

Column temperature:	Room temperature
Mobile phase:	1.4:98.6 2-Propanol-dichloromethane (v/v)
Flow rate:	2.0 mL/min
Detector:	UV (254 nm)

Injection volume:	50 µL
Column efficiency:	Approximately 300 theoretical plates for MDIU

Compound*	Adjusted Retention Volume (V_R')	Capacity Factor (k')
MDIU	4.1 mL	1.9
2,4-TDIU	11.1 mL	5.0
2,6-TDIU	>18.4 mL	>8.3
HDIU	>30 mL	>13.6

*2,4-TDIU, 2,6-TDIU, and HDIU are the corresponding urea derivatives of toluene-2,4-diisocyanate (2,4-TDI), toluene-2,6-diisocyanate (2,6-TDI), and hexamethylene diisocyanate (HDI), respectively.

NOTE: If HPLC conditions are employed which are different from those mentioned for this method, "blank" impregnated filters should be analyzed after storage of such filters and after exposure of such filters to light in order to help determine possibilities of interference.

8.3.3 Inject a 50-µL aliquot of sample solution into the high pressure liquid chromatograph, and determine the size of the peak corresponding to MDIU.

8.3.4 If the quantity of MDIU is above the lower quantitation limit, analyze another aliquot of the sample solution with two standards at concentrations above and below that of the MDIU in the sample solution. Precede and follow an injection of sample solution with an injection of standard solution.

8.3.5 Analyze the "blank" samples with the field samples.

8.3.6 After an aliquot of sample solution has been injected into the liquid chromatograph, N-p-nitrobenzyl-N-propylamine will emerge eventually from the HPLC column and cause a large response in the detector. Wash the column periodically to remove excess N-p-nitrobenzyl-N-propylamine by pumping 50:50 2-propanol-dichloromethane (v/v) at 2 mL/min through the column for at least 1 minute. Then pump 1.4:98.6

2-propanol-dichloromethane (v/v) at 2 mL/min through the column for 15 minutes before the next injection.

8.3.7 Replace the frit in front of the column packing when pressure becomes excessive (see Section 6.4). If a small quantity of packing is lost, replace the lost packing with fresh Partisil 10 or other silica packing.

8.3.8 Measure either peak heights or peak areas.

8.3.9 Construct a calibration curve for each sample based on the two adjacent standards (see Section 8.3.4).

8.4 Determination of Analytical-Method Recovery

8.4.1 Significance of Determination. The determination of analytical-method recovery may provide information which would aid in correcting for bias, if any, in the analytical method. Analytical-method recoveries should be determined at three levels of MDI which span the range of interest.

8.4.2 Procedure. Prepare three solutions of MDI in dichloromethane at concentrations appropriate for the application of approximately 10-µL aliquots to filters (a solution at a concentration of 0.08 µg/µL would be appropriate for the application of 0.8 µg of MDI per filter). Determine the concentrations of MDI according to Section 9.2. Place 18 impregnated filters (six filters for each level of MDI) into separate 1-mL glass vials, and add a known quantity of MDI in approximately 10 µL of dichloromethane solution to each filter. Seal each vial with a cap lined with polytetrafluoroethylene, and store each vial at room temperature in the dark for several hours. Analyze the samples and nine "blanks" (three "blanks" for each level) according to Section 8.3.

The analytical-method recovery for a level of MDI equals the average quantity of MDIU found in the samples corrected for the average blank and divided by the quantity of MDIU corresponding to the quantity of MDI applied.

Construct a curve of recovery versus average quantity of MDIU found.

9. Calibration and Standardization

9.1 Determination of Concentration of MDI in Dichloromethane Solution by a Colorimetric Method. (Reference 11.3)

9.1.1 Mix 10 mL of the standard solution of 4,4'-methylenedianiline (Section 7.9) with 35 mL of 12 M hydrochloric acid and 15 mL of glacial acetic acid, and dilute the solution to 1 liter with deionized water.

9.1.2 Prepare a series of standards in the range from 1.2 to 12 µg 4,4'-methylenedianiline per 15 mL of solution by diluting aliquots of the diluted standard solution (Section 9.1.1) with hydrochloric acid–acetic acid solution (Section 7.11).

9.1.3 Take 15 mL of hydrochloric acid–acetic acid solution (Section 7.11) as a blank.

9.1.4 Mix 0.5 mL of sodium nitrite–sodium bromide solution with 15 mL of each standard solution prepared according to Section 9.1.2 and with the blank (Section 9.1.3).

9.1.5 Add 1 mL of sulfamic acid solution to each mixture, stir each mixture for 0.5 minute, and allow each mixture to stand for 2 minutes.

9.1.6 Add 1.5 mL of sodium carbonate solution to each mixture, and stir each mixture.

9.1.7 Add 1 mL of N-(1-naphthyl)ethylenediamine dihydrochloride solution to each mixture, and stir each mixture.

9.1.8 Transfer a portion of each solution to a 5-cm cell 15 minutes after the addition of N-(1-naphthyl)ethylenediamine dihydrochloride solution, and measure the absorbance of each solution within 15 minutes after transfer. Water may be placed into the reference cell.

9.1.9 Construct a calibration curve of absorbance versus quantity of 4,4'-methylenedianiline in µg per 15 mL of solution.

9.1.10 Mix four 0.5-mL samples of the solution of MDI in dichloromethane with quantities of N,N-dimethylformamide–hydrochloric acid solution

(Section 7.16) in 10-mL graduated cylinders sufficient to make 9.5 mL of solution for each sample.

9.1.11 Add 10 µL of each solution prepared according to Section 9.1.10 to a separate 14-mL quantity of hydrochloric acid-acetic acid solution (Section 7.11), and dilute each solution to 15 mL with hydrochloric acid-acetic acid solution.

9.1.12 Analyze each sample solution according to Sections 9.1.3 through 9.1.8.

9.1.13 Determine the quantity of 4,4'-methylenedianiline in each 15-mL quantity of the sample solution (Section 9.1.11) from the calibration curve.

9.1.14 Calculate the concentration, D, of MDI in each sample of dichloromethane solution in mg/mL according to the following equation:

$$D = 2.39 \times B$$

where: 2.39 = a value based on three volumes (9.5 mL, 10 µL and 0.5 mL) specified in Sections 9.1.10 and 9.1.11 and the molecular weights of MDI and 4,4'-methylenedianiline (250.26 and 198.27, respectively)

B = quantity of 4,4'-methylenedianiline in µg in 15 mL of solution according to the calibration curve (see Section 9.1.13).

9.1.15 Calculate the average concentration of MDI.

9.2 Determination of Concentration of MDI in Dichloromethane Solution by an HPLC Method.

9.2.1 Mix four 10-µL aliquots of the solution of MDI in dichloromethane with separate volumes of a solution of N-p-nitrobenzyl-N-propylamine in hexane sufficient to make 1-mL quantities of solution (see Section 6.1.2 for preparation of a solution of N-p-nitrobenzyl-N-propylamine in hexane).

9.2.2 Analyze each solution according to Section 8.3.

9.2.3 Determine each concentration of MDIU from a calibration curve (see Section 8.3.9).

9.2.4 Calculate the concentration of MDI in each sample of dichloromethane solution, D', in μg/μL according to the following equation:

$$D' = 0.0392 \times J$$

where: 0.0392 = a value based on the 10-μL aliquot of solution of MDI and the molecular weights of MDI and MDIU (250.26 and 638.73, respectively)

J = the concentration of MDIU in μg/mL.

9.2.5 Calculate the average concentration of MDI.

9.3 Construction of Calibration Curve. A calibration curve will be an aid in selecting standards to be analyzed with samples. Prepare 5 mL of a dichloromethane solution containing 50 mg of MDIU. Prepare a series of standard solutions at concentrations ranging from 0.3 to 380 μg MDIU per mL of solution. Analyze 50-μL aliquots of the standards according to the HPLC conditions indicated in Section 8.3. Construct a calibration curve of either peak height or peak area versus concentration of MDIU.

10. Calculations

10.1 Determine the quantity of MDIU in μg found on the impregnated filter from the appropriate calibration curve (see Section 8.3.9).

10.2 Correct the quantity of MDIU for the corresponding "blank" value.

10.3 Determine the value of the recovery, R, from the recovery curve (see Section 8.4.2).

10.4 Correct the quantity of MDIU for recovery by dividing the quantity by R.

10.5 Calculate the concentration of MDI, C, in $\mu g/m^3$ in the air sample according to the following equation:

$$C = \frac{392 \times Q}{V}$$

where: 392 = a value based on 1000 liters/m^3 and the molecular weights of MDI and MDIU (250.26 and 638.73, respectively)

Q = the corrected quantity of MDIU in μg

V = the volume of air sampled in liters.

11. References

11.1 Tucker, S. P., and J. E. Arnold, "Sampling and Analytical Methods for Toluene-2,4-diisocyanate and 4,4'-Methylenebis(phenyl isocyanate) in Air" (report in preparation).

11.2 Hastings Vogt, C. R., C. Y. Ko and T. R. Ryan, "Simple Ureas Derived from Diisocyantes and Their Liquid Chromatography on a 5-cm Column," J. Chromatogr., 134, 451-458 (1977).

11.3 Method No. P&CAM 142, "p,p- Diphenylmethane Diisocyanate (MDI) in Air," in NIOSH Manual of Analytical Methods, Vol. 1, Second Ed., D. G. Taylor, Ed., National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1977. DHEW (NIOSH) Publication No. 77-157-A.

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2,4,7-TRINITRO-9-FLUORENONE

Methods Research Branch

Analytical Method

Analyte:	2,4,7-Trinitro-9-fluorenone	Method No.:	P&CAM 348
		Range:	0.48-8.0 µg/m³
Matrix:	Air		
Procedure:	Collection on teflon filters, extraction with toluene, analysis by HPLC	Precision:	0.056 (Analytical)
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known volume of air is drawn through a polytetrafluoroethylene membrane filter to collect the particulate present. The filter is transferred to a small screw cap test tube and extracted with toluene. After the sample is agitated in an ultrasonic bath, it is centrifuged to separate insoluble material. An aliquot of the solution is injected into a high performance liquid chromatograph equipped with a UV detector capable of detection at 280 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was evaluated over the analytical range 0.2-4.0 µg per filter sample, using 2 mL of extraction solvent and 100-µL injections into the HPLC. This corresponds to 0.5-8.0 µg/m³ for 500 L of air sampled.

2.2 Over the range of 120-800 ng/mL, the slope of the analytical calibration curve was 257 area units mL/ng when peak areas were plotted as a function of the concentration of trinitrofluorenone in the aliquot injected.

2.3 The minimum detectable quantity for trinitrofluorenone was 40 ng in a filter sample, corresponding to 0.08 µg/m³ for 500 L of air sampled.

3. Interferences

3.1 Any substance that has the same retention characteristics as trinitrofluorenone under the operating conditions described and exhibits ultraviolet absorption at 280 nm will be an interference.

3.2 The conditions described below separated trinitrofluorenone from substances present in samples containing copy machine toner.

4. Precision and Accuracy

4.1 The analytical precision of the method has been determined to be 5.6% relative standard deviation. This value is the pooled relative standard deviation for eleven groups of samples containing at least six samples per group and covering the range 0.2-4.0 µg per filter sample.

4.2 The average recovery of trinitrofluorenone was determined to be 95% over a range 0.2-4.0 µg per filter sample.

4.3 Polytetrafluoroethylene filters loaded with 0.4 µg of trinitrofluorenone were successfully stored for two weeks at room temperature with no loss of trinitrofluorenone.

5. Advantages and Disadvantages

5.1 The extraction and preparation of the samples collected on filters is straightforward and simple.

5.2 The trinitrofluorenone is measured directly by a quick instrumental technique.

5.3 The equipment for analysis is relatively expensive.

6. Apparatus

6.1 Sampling Equipment

6.1.1 Filter. The filter unit consists of a 37-mm diameter, 0.5-µm pore size, polytetrafluoroethylene membrane filter (Millipore FH or equivalent) and back-up pad.

6.1.2 Filter holder, 37-mm, three-piece cassette.

6.1.3 Personal sampling pump calibrated at a flow rate of 2 L/min with a representative filter unit in line.

6.2 High performance liquid chromatograph equipped with an ultraviolet detector monitoring 280 nm.

6.3 Waters RCM 100 Radial Compression Module equipped with a Radial Pak B column (packed with 10-µm silica) or equivalent.

6.4 Syringe or autosampler for injection into the HPLC.

6.5 Recorder.

6.6 Electronic integrator or other suitable method for peak area measurement.

6.7 Ultrasonic water bath.

6.8 Centrifuge.

6.9 Test tubes, 10-mL, screw-cap.

6.10 Pasteur pipets.

6.11 Volumetric flasks, 10-mL or appropriate sizes for preparing standard solutions.

6.12 Syringes, sizes appropriate for preparing standard solutions.

6.13 Pipets, 2-mL glass, delivery.

6.14 Tweezers.

6.15 Autosampler vials (if autosampler is used).

7. Reagents

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

7.1 Iso-octane, HPLC grade.

7.2 Methylene chloride, HPLC grade.

7.3 Toluene.

7.4 2,4,7-Trinitro-9-fluorenone.

8. Procedure

8.1 Cleaning of Equipment. Wash all glassware used for the laboratory analysis with detergent and rinse thoroughly with tap water and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter with a back-up pad in the three-piece cassette filter holder and close firmly. Secure the cassette together with tape or shrinkable band.

8.2.2 Remove the cassette plugs and attach the outlet of the filter cassette to the personal sampling pump inlet with flexible tubing. Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.3 Sample 500 L of air at a sampling rate of 2 L/min. Set the flow rate as accurately as possible using the manufacturer's directions. Since it is possible for a filter to become plugged by heavy particulate loading, the pump rotameter should be observed frequently and sampling should be terminated at any evidence of a problem.

8.2.4 Terminate sampling at the predetermined time and record sample flow rate, collection time and ambient temperature and pressure. If a pressure reading is not available, record the elevation. Also record the type of sampling pump used.

8.2.5 After sampling, disconnect the filter. Cap the inlet and outlet of the cassette with plugs. Label the cassette.

8.2.6 With each batch or partial batch of ten samples, submit a blank filter from the same lot of filters used for sample collection. This filter must be subjected to exactly the same handling as the samples, except that no air is drawn through it. Label this filter as a blank.

8.2.7 The samples should be shipped in a suitable container designed to prevent damage in transit. They should be shipped to the laboratory and analyzed as soon as possible.

8.3 Analysis of Samples

8.3.1 Remove the filter from the cassette holder and fold or roll it with the aid of tweezers such that it will slide into a 10-mL screw-cap test tube.

8.3.2 Add 2 mL of toluene to the filter. Slight crumpling of the filter in the bottom of the test tube with a slender spatula will enable this amount of solvent to completely cover the filter.

8.3.3 Suspend the sample in an ultrasonic bath and agitate for five minutes.

8.3.4 Centrifuge the sample at approximately 2500 rpm for 30 minutes to separate suspended particulates.

8.3.5 Transfer an aliquot to a clean autosampler vial. Alternatively, inject an aliquot directly into the HPLC.

8.3.6 Analyze the sample using the following HPLC conditions:

Column Temperature:	Ambient
Column Pressure:	500 psi
Flow Rate:	2 mL/min
Mobile Phase:	20% iso-octane, 80% methylene chloride
Detector:	UV at 280 nm
Injection Size:	100 µL
Capacity Ratio (k'):	2.7

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

8.4 Determination of Recovery

8.4.1 To correct for bias from the sample-work-up procedure, it is necessary to determine the recovery of the compound from the filter. The sample recovery determinations should cover the concentration range of interest.

8.4.2 Add a known amount of trinitrofluorenone in toluene to polytetrafluoroethylene filters and allow the toluene to evaporate. Prepare sets of filter samples containing trinitrofluorenone at three different levels covering the range of the field samples. Store these samples overnight and then analyze them along with blanks and standards according to the procedure outlined in Section 8.3. (Step 8.3.4 may be omitted in this case.) The sample recovery is calculated as the average amount found divided by the amount added. If the recovery is dependent on the amount of trinitrofluorenone collected on the filter, plot the

recovery versus weight of trinitrofluorenone found. Use this curve in Section 10.3 to correct for recovery losses.

9. Calibration and Standardization

A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same HPLC conditions and during the same time period as the unknown samples. A curve is established by plotting concentration in ng/mL versus peak area.

9.1 Prepare a 1.0 mg/mL stock solution in toluene. This solution is stable for two months, when stored in a refrigerator.

9.2 From the stock standard solution appropriate aliquots and dilutions are made in toluene. Prepare at least five standards to cover the range of interest. These dilute solutions will remain stable for one to two weeks, if stored under refrigeration.

9.3 Analyze these samples as per Section 8.3.

9.4 Prepare a calibration curve by plotting concentration of trinitrofluorenone in ng/mL versus peak area.

10. Calculations

10.1 Read the concentration of trinitrofluorenone (ng/mL) corresponding to the peak area from the calibration curve and calculate the weight in the sample as follows:

$$W_S = 2c$$

where: W_S = quantity on the filter sample (ng)
c = concentration read from standard curve (ng/mL)
2 = 2 mL, the volume of the sample solution.

10.2 Correct for the blank, if necessary

$$W_C = W_S - W_b$$

where: W_C = corrected weight (ng)
W_S = weight on sample filter (ng)
W_b = weight on blank filter (ng).

10.3 Read the recovery, R, from the recovery versus loading curve (Section 8.4) for the amount of trinitrofluorenone found on the filter and use it to correct for recovery losses by the following equation:

$$W_{rc} = \frac{W_c}{R}$$

where: W_{rc} = recovery-corrected weight
W_c = blank-corrected weight (ng)
R = recovery.

10.4 For personal sampling pumps with rotameters only, make the following volume correction:

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

where: V_c = corrected air volume (L)
f = sampling flow rate (L/min)
t = sampling time (min)
P_1 = atmospheric pressure during calibration of sampling pump (mm Hg)
P_2 = atmospheric pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K).

10.5 Calculate the concentration, C, of trinitrofluorenone in the air sampled using the appropriate equation.

$$C = \frac{W_c}{V_c} \quad \text{or} \quad C = \frac{W_{rc}}{V_c}$$

where: C = concentration in air ($\mu g/m^3$)
W_c = blank-corrected weight (ng)
W_{rc} = recovery-corrected weight (ng)
V_c = corrected air volume (L).

11. References

11.1 M. J. Seymour, "Determination of 2,4,7-Trinitro-9-fluorenone in Workplace Environmental Samples Using Liquid Chromatography," in preparation.

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VINYL BROMIDE

Methods Research Branch

Analytical Method

Analyte:	Vinyl bromide	Method No.:	P&CAM 349
Matrix:	Air	Range:	1.3 - 56 mg/m^3
Procedure:	Adsorption on activated charcoal, desorption with ethanol, GC/FID	Precision:	0.090 over the range 1.3 to 6.4 mg/m^3 0.063 over the range 6.4 to 56 mg/m^3
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

   1.1 A known volume of air is drawn through a coconut charcoal tube to adsorb the vinyl bromide vapor present.

   1.2 The charcoal in the tube is transferred to a small vial where the vinyl bromide is desorbed with 15 mL of absolute ethanol.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The height or area of the resulting peak for vinyl bromide is determined and compared with the peak heights or peak area obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The overall method was evaluated by collecting 6-L samples of test atmospheres containing vinyl bromide in the range of 1.32 to 56.5 mg/m^3 at 25 °C and a relative humidity of > 80%. The amounts of vinyl bromide collected ranged from 8.07 to 322 µg per 400-mg bed of charcoal.

   2.2 The slope of the analytical calibration curve was 0.804 mm peak height per ng of vinyl bromide for an attenuation of 1 x 32 with a Perkin-Elmer Sigma 2 gas chromatograph.

2.3 The lowest analytically quantifiable level for this method was determined to be abount 7.75 μg of vinyl bromide per sorbent sample extracted with 15 mL of absolute ethanol. This corresponds to a lower level of quantitation in air samples of 1.3 $\mu g/m^3$. The instrumental detection limit was about 0.25 μg/mL of vinyl bromide in ethanol for a 5-μL injection volume; the relative standard deviation of replicate determination of standards at this level was 10%.

2.4 The breakthrough volume of the sorbent tube was found to be approximately 10 L with a sampling rate of 0.2 L/min at a vinyl bromide concentration of about 130 mg/m^3, a sampling temperature of 40 °C, and a relative humidity of greater than 80%. The recommended sampling volume is 6 L to compensate for possible reduction of the capacity of the sorbent tube under potentially harsh field sampling conditions.

3. Interferences

3.1 The chromatographic operating conditions described below will separate vinyl bromide from ethylene, acetylene, and 1,2-dibromoethane, but not from bromine.

3.2 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of vinyl bromide.

3.3 Any substance that has the same retention time as vinyl bromide with the gas chromatograph operating conditions described in this method can interfere with the analysis. Therefore, retention time data cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, changing the separation conditions (column type, column temperature, carrier gas flow rate, etc.) may circumvent the problem.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for the replicate measurements was 9.0% over the range of 1.32 to 6.38 mg/m^3 and 6.3% over the range of 6.38 to 56.5 mg/m^3. The pooled RSD for the analytical method was 4.0% for 18 sorbent samples spiked with 7.75 to 335 μg of vinyl bromide and stored for 1 d.

4.2 The concentration of vinyl bromide in the test atmosphere was determined on the basis of the concentration and measured flow

rate of a certified gas mixture of vinyl bromide in nitrogen and the measured flow rate of dilution air (delivery rate calibration).

4.3 Samples of vinyl bromide on coconut charcoal were found to be stable at 25 °C for up to 14 d. The samples were stored in the dark.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the analytical procedure. The samples are analyzed by means of a quick instrumental method.

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

6. Apparatus

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

6.2 Sorbent tubes: SKC Catalog No. 226-09 (SKC, Inc., Eighty-Four, PA 15330) or equivalent. These sorbent tubes are 100 mm long by 8 mm o.d. glass tubes packed with a 400-mg sorbing section and a 200-mg backup section of coconut-based charcoal. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated by a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.1 in H_2O (0.3 kPa) at a sampling rate of 0.2 L/min.

6.3 Gas chromatograph with flame ionization detector.

6.4 A 6-m long by 2-mm i.d. nickel column packed with 10% FFAP on 80/100-mesh acid-washed DMCS Chromosorb W.

6.5 Glass serum vials, 15-mL, with crimp-on caps containing Teflon-lined silicone rubber septa.

6.6 Pipets and volumetric glassware of convenient sizes for making dilutions.

6.7 Ultrasonic bath.

6.8 Syringes, 10-μL.

7. Reagents

7.1 Vinyl bromide (liq.), 98% purity or better.

7.2 Ethanol, absolute.

8. Procedure

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

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break open the ends of the tube to provide openings that are at least 2 mm in diameter.

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

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

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

8.2.5 Sample the air at 0.05 to 0.2 L/min. (Although the lowest sampling rate used in the development of the method was 0.05 L/min, a lower rate such as 0.025 L/min may increase the possible sampling time.) Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 6 L.

8.2.6 Record the temperature and pressure of the air being sampled.

8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps.

8.2.8 To obtain a blank sample, process one unused charcoal tube in the same manner as the samples (break, seal,

and transport) but do not sample air through this tube. Submit one blank sample tube for every ten samples with a minimum of three blank tubes.

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

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

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Transfer the sorbing section and backup section to separate 15-mL vials. Discard the metal spring. Place the glass wool plug into the vial containing the sorbing section and the foam plugs into the vial with the backup section.

8.3.2 Desorption of Samples. After the two sections of a tube are transferred to small vials, pipet 15 mL of the solvent into each vial. Crimp a serum cap into place on each vial immediately after the solvent has been added. Extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature.

8.3.3 GC Conditions.

Carrier gas:	nitrogen, 25 mL/min.
FID air flow rate:	400 mL/min.
FID hydrogen flow rate:	30 mL/min.
Injection port temperature:	140 °C.
Column temperature:	isothermal at 50 °C for 3 min, programmed at 40 °C/min to 225 °C and maintained at 225 °C for 5 min.
Detector temperature:	240 °C.

Under these conditions, the analyte elutes in 3.0 min.

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

8.3.5 Quantitation of Response. Multiply the peak height by the attenuator setting necessary to keep the peak on scale. Read the results from a standard curve

prepared as discussed in Section 9. If the peak height indicates an apparent concentration above the linear range of the calibration, dilute the sample solution appropriately for reanalysis. (During the method development, the product of peak height and attenuator setting was found to be linear over the concentration range of about 0.25 to 50 µg/mL.)

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of charcoal. Also, for a given batch of charcoal the desorption efficiency may vary with the weight of contaminant adsorbed. The charcoal used for the study of this method gave an average desorption efficiency of 0.910 with a pooled RSD of 4.0% for loadings of 7.75 to 355 µg of vinyl bromide on 400-mg beds of sorbent material.

8.4.2 Procedure for Determining Desorption Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve vinyl bromide in ethanol to give stock solutions with concentrations such that 7.8 to 355 µg of vinyl bromide will be injected onto the sorbent in no more than 5 µL of a stock solution. Inject an aliquot of the appropriate solution into the front sorbing section of a sorbent tube while sampling 6 L of analyte-free air through the tube at 0.2 L/min. Cap the tube and store it overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 15 mL of absolute ethanol. Analyze the samples and standards as described in Section 8.3.

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

9. Calibration and Standardization

9.1 Prepare a concentrated stock solution of vinyl bromide in ethanol according to the following procedure:

9.1.1 Transfer several milliliters of absolute ethanol to a volumetric flask, and weigh the flask and its contents accurately on an electronic balance.

9.1.2 Chill the flask and its contents to near 0 °C in an ice-water bath.

9.1.3 Transfer a small volume of prechilled liquid vinyl bromide (at 0 °C) to the volumetric flask with a prechilled syringe.

9.1.4 Stopper the flask and allow it to warm up to room temperature.

9.1.5 Reweigh the flask on the electronic balance and determine the weight of vinyl bromide added from the difference in weights.

9.1.6 Fill the flask to the mark with absolute ethanol and thoroughly mix the solution in the flask by shaking.

9.2 Prepare a series of working standards, varying in concentration over the range of interest, by serial dilution of the stock solution with absolute ethanol. Prepare fresh working standards daily; the stock solution may be stable for several days if stored in an airtight container and refrigerated when not in use. However, no detailed stability data are available.

9.3 Analyze the five working standards under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve, plot the concentration of the standards in µg/mL versus peak area.

10. Calculations

10.1 Determine the sample concentration from the standard curve.

10.2 Determine the sample weight in micrograms by multiplying the sample concentration by the desorption volume.

10.3 Blank corrections are not expected to be necessary. If the analysis shows a blank correction is needed, make the correction as follows:

$$W_F = W_S - W_b$$

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

Follow a similar procedure for the backup section.

10.4 Make a correction for desorption efficiency as follows:

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

where: M_F = corrected amount (µg) in the front section
W_F = amount (µg) after blank correction
D = desorption efficiency corresponding to the weight, W_F.

10.5 Express the concentration, C, of vinyl bromide in the air sampled in mg/m^3, which is numerically equal to µg/L

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

where: M_F = corrected amount (µg) of vinyl bromide found on front section
M_B = corrected amount (µg) of vinyl bromide found on backup section
V = volume (L) of air sampled.

10.6 If desired, the results may be expressed in ppm by volume at 25 °C (298 K) and 760 torr

$$C(ppm) = C(\mu g/L) \times \frac{24.45}{106.96} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled
T = temperature (°C) of air sampled
24.45 = molecular volume (L/mol) at 25 °C and 760 torr
106.96 = molecular weight of vinyl bromide.

11. Reference

11.1 Spafford, R. B.; Dillon, H. K. "Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for Vinyl Bromide," NIOSH Contract No. 210-79-0100, Southern Research Institute: Birmingham, Alabama, May 1981.

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LEAD SULFIDE

Measurement Research Support Branch

Analytical Method

Analyte:	Lead Sulfide (Galena)	Method No.:	P&CAM 350
Matrix:	Air	Range:	0.06 to 4 mg/m^3
Procedure:	Filter collection, redeposition, X-ray diffraction	Precision:	0.047 (Analytical)
Date Issued:	8/31/81		
Date Revised:		Classification:	D (Operational)

1. Synopsis

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

   1.2 The filters are dissolved in tetrahydrofuran and then redeposited on silver membrane filters.

   1.3 The filter samples are scanned qualitatively by X-ray powder diffraction to determine the presence of lead sulfide and other phases, such as Pb_3O_4, which may cause matrix interference.

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

2. Working Range, Sensitivity, and Detection Limit

   2.1 The range of the method is from 0.06 to 4 mg/m^3 for a 500-L sample corresponding to 30-2000 µg per sample. The range of the method for samples containing lead sulfide is dependent on the amount of interfering compounds and X-ray absorbing substances present in the sample.

   2.2 The detection limit of lead sulfide using the secondary peak is 3 µg on a 25-mm silver filter; however, quantitative measurements cannot be made at this level.

3. Interferences

3.1 Using copper Kα X-ray radiation, lead oxide (PbO yellow-form), lead sulfate (anglesite) and copper iron sulfide ($CuFeS_2$ chalcopyrite), if present, will interfere with the primary lead sulfide peak. Lead oxide (Pb_3O_4 orange-form) and lead sulfate (anglesite), if present, will also interfere with the secondary lead sulfide peak. The oxides of lead do not occur naturally in appreciable amounts in galena mining but are formed when lead sulfide is heated at high temperatures (i.e., in smelting and roasting operations, see Section 11.2).

3.2 Dolomite, zinc sulfide (ZnS sphalerite) and chalcopyrite that are normally found in galena mining do not interfere with the secondary lead sulfide peak; for this reason the secondary lead sulfide peak was chosen as the analytical peak.

3.3 The tertiary lead sulfide peak interferes with the secondary silver peak.

3.4 If interferences are present, analytical measurements are made using a different lead sulfide peak with a commensurate decrease in sensitivity and precision.

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

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

4. Precision and Accuracy

4.1 The pooled relative standard deviation in the range of 30-2000 µg lead sulfide was 0.047.

4.2 The average recovery of lead sulfide from filters, after dissolution with tetrahydrofuran at the 30-, 60-, 100-, and 150- µg levels was 102.7% with 4.99% precision. Recovery studies by x-ray fluorescence spectrometry and inductively coupled plasma-atomic emission spectrometry techniques have independently verified the accuracy of these results.

5. Advantages and Disadvantages

5.1 The X-ray diffraction method is specific and can determine lead sulfide in the presence of other lead compounds, such as PbO using the secondary PbS peak. The method is non-destructive of the analyte.

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

5.3 If no interferences are present, the primary lead sulfide peak can be used as the analytical peak, resulting in improved sensitivity.

5.4 The equipment is relatively expensive.

6. Apparatus

6.1 Air Sampling Equipment

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

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

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

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

6.1.5 Thermometer, barometer, stopwatch.

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

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

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 Centrifuge tubes (wide-mouth), 40 mL.

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

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

6.10 Filter storage cassettes.

6.11 Forceps, applicator stick.

6.12 Polyethylene wash bottle.

6.13 Analytical balance to $\pm$ 0.01 mg, and weighing paper.

6.14 Ultrasonic bath.

6.15 Sieve, 10 µm pore size suitable for wet-sieving.

6.16 Assortment of pipettes, 2-25 mL.

6.17 X-ray diffraction filter holders.

6.18 Magnetic stirrer.

6.19 Test tube rack for the 40-mL centrifuge tubes.

7. Reagents

The analytical reagents should be ACS reagent grade or equivalent.

7.1 Lead sulfide, 10 µm particle size. Analyze qualitatively before use to determine purity.

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

7.3 Isopropanol.

7.4 Tetrahydrofuran (THF).

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

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

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

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

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

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

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

8.4 Analysis of Samples

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

	Peak Angles	
	2-Theta Primary	2-Theta Secondary
Lead Sulfide	30.10°	25.98°
Silver	38.12°	44.29°

8.4.2 THF Dissolution of Samples. Using forceps place filter samples in 40 mL wide-mouth centrifuge tubes with 10 mL of THF. The filter dissolves instantly upon contact with THF. Place the centrifuge tubes on the test tube rack and then position the rack containing the tubes in the ultrasonic bath for 10 minutes.

8.4.3 Place a silver filter in the filtration apparatus and attach the funnel. Pour the suspension from the centrifuge tube into the funnel.

8.4.4 Place a 5-mL aliquot of THF in the empty centrifuge tube and shake tube by hand or by a vortex mixer for a few seconds. Empty the THF in the same filtration funnel. Repeat this 5 mL THF rinsing for two more times collecting the THF in the same filtration funnel. Apply 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 silver filter with forceps.

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

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

	Lead Sulfide	Silver
Scanning range	25.20-26.30° 2θ	37.03-39.03° 2θ
Scanning time	10 sec./0.02° 2θ	0.5 sec./0.02° 2θ

Measure the background on each side of the peak for one half the time used for peak scanning, and add the counts from each side for a total (average) background. The position of the background must be determined for each set of samples. The net count of intensity for lead sulfide, I_S, 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 Section 8.4.6. Scan times should be consistent throughout the method.

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

$$\hat{I}_S = \frac{I_S}{I_r^\circ}$$

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

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}° (Section 8.4.7). Normalize the measured intensities (Section 8.4.8),

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

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

9. Calibration and Standardization

9.1 Preparation of Lead Sulfide Standards

9.1.1 Wet sieve the lead sulfide in isopropanol through a 10-µm sieve, or dry sieve using the sonic sifter with sieves ranging from 75 to 10 µm in pore size.

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

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

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

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

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

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

9.1.8 Mount a silver filter on the filtration apparatus. Place several mL of isopropanol in the filter funnel. Vigorously handshake the suspension and immediately withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet. Resume the procedure after shaking the suspension. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the suspension. As soon as the pipet has drained, apply the vacuum and rapidly filter the

suspension. Leave the vacuum on for sufficient time to dry the filter. Do not wash down the sides of the funnel after the deposit is in place, since this will affect the homogeneity of the dust surface. 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 Section 8.4.8, determine and record the normalized intensity, $\hat{I}_s$, for each peak measured.

10. Calculations

10.1 Calculate the exact weights of lead sulfide deposited on each standard filter from the concentrations of the standard suspensions and aliquot volumes. Record the weight, w, of each standard. Prepare a calibration curve by plotting $\hat{I}_s$ 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 (up to 400 µg) and curvature is expected above 400 µg due to X-ray absorption by the sample. The normalized intensities of the standards that show absorption effects should be multiplied by correction factors explained in Section 10.3 and 10.4 before the least-squares regression analysis is performed.

10.2 Determine the initial slope, m, of the linear calibration curve in counts/µg. The intercept, b, of the line with $\hat{I}_s$ axis should be approximately zero. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak. The weighting factor of $(1/\text{Std. deviation})^2$ is recommended to be used in the least-squares regression analysis, because it usually produces a smaller intercept.

10.3 Using the normalized intensities, $\hat{I}_{Ag}$, for the silver peaks of each sample (Section 8.4.8), and the $\hat{I}^{\circ}_{Ag}$ calculated for the clean side of the silver filter (Section 8.4.9), calculate the transmittance, T, of each sample as follows:

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

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

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

where $R = \frac{\sin\Theta_{Ag}}{\sin\Theta_S}$.

and Θ_{Ag} and Θ_S are the angles Θ (not 2Θ) of the silver and lead sulfide peaks. Table I lists f(T) values for T values from 0.5 to 1.0 for common $2\Theta_S$ and $2\Theta_{Ag}$ combinations.

10.5 Calculate the weight, w, in micrograms of the lead sulfide in each sample:

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

If the blank contains any lead sulfide, that amount should be subtracted from each field sample.

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

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

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

10.7 Calculate the airborne concentration, C, of lead sulfide in micrograms per cubic meter.

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

11. References

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

11.2 Snell, F. D. and L. S. Ettre, Encyclopedia of Industrial Chemical Analysis, 15: 161-169, Interscience Publishers, New York, 1972.

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Table 1

Matrix Absorption Correction Factors

for

Lead Sulfide/Silver Peaks, Degrees 2θ

Lead Sulfide		30.10	25.98		30.10	25.98
Silver		38.12	38.12		38.12	38.12
	T	f(T)	f(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2013	1.2346
	0.99	1.0063	1.0073	0.73	1.2109	1.2460
	0.98	1.0128	1.0147	0.72	1.2208	1.2575
	0.97	1.0193	1.0223	0.71	1.2308	1.2693
	0.96	1.0259	1.0299	0.70	1.2410	1.2814
	0.95	1.0326	1.0377	0.69	1.2514	1.2936
	0.94	1.0394	1.0456	0.68	1.2620	1.3062
	0.93	1.0463	1.0536	0.67	1.2729	1.3190
	0.92	1.0533	1.0618	0.66	1.2839	1.3320
	0.91	1.0605	1.0701	0.65	1.2952	1.3453
	0.90	1.0677	1.0785	0.64	1.3067	1.3590
	0.89	1.0751	1.0870	0.63	1.3185	1.3729
	0.88	1.0825	1.0957	0.62	1.3305	1.3871
	0.87	1.0901	1.1046	0.61	1.3428	1.4017
	0.86	1.0978	1.1136	0.60	1.3554	1.4165
	0.85	1.1057	1.1227	0.59	1.3682	1.4318
	0.84	1.1136	1.1320	0.58	1.3813	1.4473
	0.83	1.1217	1.1414	0.57	1.3948	1.4633
	0.82	1.1300	1.1511	0.56	1.4085	1.4796
	0.81	1.1383	1.1609	0.55	1.4226	1.4963
	0.80	1.1469	1.1708	0.54	1.4370	1.5135
	0.79	1.1555	1.1810	0.53	1.4518	1.5311
	0.78	1.1644	1.1913	0.52	1.4669	1.5491
	0.77	1.1733	1.2018	0.51	1.4825	1.5676
	0.76	1.1825	1.2126	0.50	1.4984	1.5866
	0.75	1.1918	1.2235	0.49	1.5148	1.6061

T = Sample transmittance (See Section 10.3)
f(T) = Sample correction factor (See Section 10.4)

TRACE ELEMENTS

Methods Research Branch

Analytical Method

Analyte:	Table 1	Method No.:	P&CAM 351
Matrix:	Air	Range:	5-2000 $\mu g/m^3$
Procedure:	Filter collection, acid digestion, ICP-AES analysis	Precision:	Varies with analyte (Table 1)
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 This procedure describes a general method for the filter collection, dissolution and determination of trace elements by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in industrial and ambient airborne material.

1.2 A known volume of air is drawn through a mixed cellulose ester filter. The filters are treated with a mixture of nitric and perchloric acids to ash the organic matrix and dissolve the elements.

1.3 Analysis of sample and standard solutions is accomplished by nebulization into an inductively coupled argon plasma and monitoring the emission spectra of the various elements.

2. Working Range, Sensitivity and Detection Limit

2.1 The working range is 5 to 2000 $\mu g/m^3$ (for each element) in a 500-L air sample. This corresponds to 2.5 to 1000 µg element/sample, dissolved in 10-mL. The samples may be diluted for higher element loadings.

2.2 The sensitivity and instrumental detection limits vary for the different elements and are given in Table 1. The sensitivity is defined as the slope of the calibration curve (intensity ratio vs. concentration) where the intensity ratio is the absolute intensity of a standard divided by the internal standard. The

internal standard is an electrical signal for balancing drifts or changes in the instrument electronics. The detection limit is defined as that concentration of a given element which produces a signal equivalent to two times the standard deviation of the blank signal for aqueous solutions. Values for the sensitivities and detection limits may vary from instrument to instrument.

3. Interferences

3.1 The high temperature of the plasma (5000 to 8000 °K) minimizes most chemical and matrix interferences. Interferences do exist, however, in ICP-AES and can be categorized as follows:

3.1.1 Physical interferences or nebulization and transport effects are the influences that determine the rate and form (i.e., particle size) in which analytes are delivered to the plasma. Changes in density and viscosity of different acids and acid concentrations affect the sample uptake rate. These effects are minimized by matching the acid concentrations of samples and standards and using a peristaltic pump to provide a uniform sample flow.

3.1.2 Chemical interferences are characterized by molecular compound formation, ionization effects and solute volatilization effects. These effects are not severe in ICP analysis and are minimized by careful selection of operating conditions (incident power, sample uptake rate and observation height). Matrix matching may also be used to minimize this type of interference.

3.1.3 Spectral interferences include: (a) unresolved overlap of molecular band spectra; (b) overlap of a spectral line from another element; (c) background from continuous or recombination phenomena; and (d) background from stray light. The first effect (overlap of molecular band spectra) should be minimized by judicious wavelength selection. The other types of spectral interference (spectral overlap and elevated background) are minimized by using interelement correction factors (programmed into the computer) and background correction (spectrum shifting).

3.2 This procedure describes a generalized method for analysis which is applicable to the majority of samples of interest (23 elements). There are, however, some elements which will not be quantitatively dissolved by the sample preparation procedure (Li, Mn, Mo, Sn, W and Zr) and some that require special

handling precautions (B and Si) because of their chemical form. For analysis of these elements, the digestion procedure should be modified according to the NIOSH method for that element listed in Table 1.

4. Precision and Accuracy

4.1 The analytical precision varies for the different elements (Table 1). Multielement spiked filters at 2.5 µg element/filter (up to seven elements per filter) ashed and analyzed by this procedure yielded a relative standard deviation (S_r) of approximately 5% while filters spiked at 1000 µg/filter yielded a relative standard deviation of approximately 3%.

4.2 Recoveries for spiked filters (at 2.5 and 1000 µg/filter) for the various elements are shown in Table 1. Quantitative recoveries were not observed for Li, Mn, Mo, Sn, W and Zr by this procedure. Also, Si and B require the use of labware other than glass.

5. Advantages and Disadvantages

5.1 The main advantage of the method is that analyte elements are determined simultaneously. This provides a very high analytical throughput compared to AAS, XRF, or colorimetry.

5.2 The method has a very large analytical range, compared to other elemental techniques. This makes the use of sample preconcentration, scale expansion and sample dilutions unnecessary in most cases.

5.3 The sensitivity is adequate for all elements in air samples provided an adequate volume of air is sampled.

5.4 One disadvantage is that all elements may not be completely solubilized by this technique.

5.5 ICP-AES systems are considerably more expensive than AAS systems and require large volumes of argon (~ 20 L/min) for operation.

6. Apparatus

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

6.1.1 The filter unit, consisting of the filter media (6.2) and appropriate cassette filter holder, either a two-

or three-piece filter cassette (Millipore Filter Corporation, Bedford, Massachusetts or equivalent).

6.1.2 A personal sampling pump of sufficient capacity to maintain a flowrate of 1.5 - 2.5 Lpm using a 37-mm filter. This pump must be calibrated so the volume of air sampled can be measured to an accuracy of ± 5%. The pump must be calibrated with a representative filter unit in the line.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors and belt for connecting sampling apparatus to worker being sampled.

6.2 Cellulose ester membrane filter, 0.8 µm pore size, 37-mm (Millipore Type AA or equivalent).

6.3 Glassware (borosilicate) and plasticware (PTFE).

6.3.1 125-mL Phillips or 50-mL Griffin beakers with watchglass covers.

6.3.2 15-mL graduated centrifuge tubes.

6.3.3 100-mL volumetric flasks.

6.3.4 125-mL polyethylene bottles.

6.4 Hotplate (suitable for operation at 120 °C and 160 °C).

6.5 Inductively coupled plasma-atomic emission spectrometer.

6.5.1 Computer-controlled emission spectrometer with background and spectral line overlap correction.

6.5.2 Radiofrequency generator.

6.5.3 Peristaltic pump for sample delivery to the nebulizer (~ 1.5 mL/min).

6.6 Supplies

6.6.1 Argon gas of a grade specified by the manufacturer of the instrument employed.

6.6.2 Water supply and drain for R.F. coil cooling.

6.6.3 Micropipettes, assorted sizes (Eppendorf or equivalent).

7. Reagents

7.1 ACS analytical reagent grade chemicals or equivalent shall be used in all tests. References to water shall be understood to mean double distilled water or equivalent. Care in selection of reagents and in following the listed precautions is essential if low blank values are to be obtained.

7.2 Concentrated nitric acid (68-71%), specific gravity 1.42.

7.3 Perchloric acid (70%).

7.4 Ashing acid (4:1 HNO_3:$HClO_4$).

7.5 Standard stock solutions (1000 µg/mL) for each element in Table 1, commercially prepared [ICP grade - SPEX (Metuchen, NJ) or equivalent] or prepared per instrument manufacturer's recommendations.

7.6 Mixed Calibration Standard Solutions

7.6.1 Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible contamination and spectral interferences. Care should be taken when preparing the mixed standards that the elements are compatible and stable.

7.6.2 Prepare standards by combining 1 mL of stock solution (for each element to be included in the standard) with 5 mL of 4:1 HNO_3:$HClO_4$ and diluting to 100 mL with distilled water. Transfer this 10 µg/mL standard to a 125-mL polyethylene bottle. Prepare fresh weekly.

7.6.3 Typical multielement standards should be prepared fresh weekly and are as follows:

1. Standard 1 - Acid Blank (4% HNO_3; 1% $HClO_4$;

2. Standard 2 - Ag, Ca, Co, Mn, Pb, V, Zn in 4% HNO_3; 1% $HClO_4$;

3. Standard 3 - Al, Be, Cd, Li, Ni, Tl in 4% HNO_3; 1% $HClO_4$;

4. Standard 4 - As, B, Mg, Mo, P, Sn in 4% HNO_3; 1% $HClO_4$;

5. Standard 5 - Cu, Fe, Na, Pt, Te, Y in 4% HNO_3; 1% $HClO_4$;

6. Standard 6 - Si, W in H_2O;

7. Standard 7 - Cr, Se, Ti, Zr in 4% HNO_3; 1% $HClO_4$.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before initial use, labware is cleaned with a sulfuric acid solution of Nochromix® (or equivalent) and then rinsed thoroughly with tap water, concentrated nitric acid, tap water and distilled water, in that order. Under no circumstances should chormic acid cleaning solutions (or other metal-based cleaning solutions) be used.

8.1.2 All labware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.1.3 For labware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the sulfuric acid cleaning solution.

8.2 Collection and Shipping of Samples

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

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

8.2.3 Take the sample at an accurately known flowrate in the range 1.5 to 2.5 Lpm. A sample size of 500 L is recommended. Check the pump during operation to assure proper functioning. Record the sampling time, flowrate, and ambient temperature and pressure.

8.2.4 After sample collection is complete, plug the openings of the cassette and submit the sampling unit to the laboratory. Overloading (> 2 mg total sample) of the filter must be avoided to prevent losses.

8.2.5 Filter samples should be sealed in individual plastic filter holders for storage and shipment.

8.3 Preparation of Samples

8.3.1 Most samples will be solubilized by this procedure, however, some species of Si, B, Li, Mn, Mo, Sn, W and Zr will not be completely solubilized. Alternative solubilization procedures for most of these elements are referenced in Table 1. The samples and blanks (minimum of one filter blank for every 10 filter samples) are transferred to clean 125-mL Phillips or 50-mL Griffin beakers and 5.0 mL of ashing acid (Section 7.4) is added. Each beaker is covered with a watchglass and heated on a hotplate (120 °C) in a fume hood until the sample dissolves and a slightly yellow solution is produced. Approximately four hours of heating will be sufficient for most air samples. However, subsequent additions of ashing acid may be needed to completely ash and destroy high concentrations of organic material and, under these conditions, longer ashing times will be needed. Once the ashing is complete, as indicated by a clear solution in the beaker, the watchglass is removed and rinsed into the sample beaker with distilled water. Increase the hotplate temperature to 160 °C and take the samples to near dryness (~ 0.5 mL acid remaining).

8.3.2 Quantitatively transfer the contents of the beaker to a graduated centrifuge tube or volumetric flask and dilute to 10 mL.

8.3.3 This 10-mL solution is analyzed directly for the elements of interest.

8.4 Analysis of Samples

8.4.1 Detailed operating instructions are not provided due to the differences between various makes and models of instruments. Start-up and operation should follow manufacturer's instructions. The precision, sensitivity, dynamic range and interferences (both elevated background and spectral line overlap) must be determined for each analytical line. Correction must be made for these interferences.

8.4.2 Blank filters must be carried through the entire procedure each time samples are analyzed.

8.4.3 "Spiked" filters (quality assurance samples - Section 9) must also be carried through the entire procedure.

8.4.4 Samples and standards should each be analyzed with a minimum of three four-second burns.

9. Calibration and Standardization

9.1 Calibration and standardization should follow the instrument manufacturer's instructions. Typically, a two-point standardization (blank and 10 µg/mL standard) is used. A suggested grouping for multielement standard solutions is given in Section 7.6.3. After standardization, sample analysis results are output in the concentration mode. Interelement correction factors (determined by instrument manufacturer's instructions) should be used throughout the analysis. For the 31 elements listed in Table 1, approximately 55 interelement correction factors were used.

9.2 A procedure similar to that described by Botto et. al (Reference 11.3) should be used to assure day-to-day reproducibility of correction factors for spectral line overlap. In this procedure, a 10 µg/mL solution of copper and manganese is analyzed prior to standardization and the intensity ratio for these elements determined. Prior to the analysis of samples, the intensity ratio is determined (a minimum of four times) and adjusted (if necessary) to fall within one standard deviation of the ten burns previously conducted. The nebulizer argon pressure is adjusted, if necessary, to make the intensity ratio fall within this range.

9.3 Several operational and performance parameters for some additional elements (Ba, Hf, Rh, Sb, Ta) are given in Table 2. The parameters are applicable to the variable wavelength channel found on several ICP systems.

9.4 To insure that the sample preparation procedure is being properly followed, clean membrane filters are spiked by adding appropriate amounts of the previously described standards. These spiked filters are then carried through the entire procedure beginning with Section 8.3. The amount of metal is determined and the percent recovery calculated. These tests will provide recovery and precision data for the procedure as it is carried out in the laboratory for the soluble compounds of the elements being determined.

10. Calculations

10.1 The corrected volume (V, m^3) collected by the filter is calculated by averaging the beginning (F_B, L/min) and ending (F_E, L/min) sample flowrates, converting to cubic meters, and multiplying by the sample collection time (t, min). The formula for this calculation is:

$$V = \frac{(F_B + F_E)t}{2000}$$

10.2 For personal sampling pumps with rotameters, the corrected air volume sampled (V_C) is determined by multiplying the sample flowrate (f, L/min) by the sampling time (t, min) and the square root of the pressure/temperature correction:

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

where: 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).

10.3 After any necessary correction for the blank (B, µg/mL) has been made, element concentrations (C_A, µg element/m^3) are calculated by multiplying the micrograms of metal per mL in the sample (C, µg/mL) by the sample volume after digestion (V_S, mL) and dividing by the volume of air sampled by the filter (V_A):

$$C_A = \frac{(C - B)V_S}{V_A}$$

11. References

11.1 "General Procedure for Metals," P&CAM 173, NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 5, U.S. Dept. of Health and Human Services, NIOSH Publ. No. 79-141.

11.2 Hull, R. D., "Multielement Analyses of Industrial Hygiene Samples" presented at the American Industrial Hygiene Conference, Portland, Oregon, May 1981.

11.3 Botto, R. I., "Interference Correction for Simultaneous Multielement Determinations by Inductively Coupled Plasma," to appear in "Developments in Atomic Plasma Spectrochemical Analysis, Proceedings of the International Winter Conference 1980," Heyden and Son Publishers, Philadelphia, Pennsylvania, 1981.

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Inorganic Methods Development Section

Table 1

Element	Wavelength (nm)	Instrumental Detection Limit (ng/mL)	Sensitivity intensity µg/mL	Recovery @ 2.5 µg/ filter* (%)	Precision[a] @ 2.5 µg/ filter (% S_r)	Recovery @ 1000 µg/ filter (%)	Precision[a] @ 1000 µg/ filter (% S_r)	Other[b] NIOSH Methods
Ag	328.3	26	0.65	111	2.0	91	7.5	
Al	308.2	14	0.23	93	8.2	100	2.3	
As	193.7	13	0.57	103	6.2	99	2.6	
B	249.7	1.0	0.33	(d)	(d)	(d)	(d)	
Be	313.0	1.5	1.29	107	4.0	90	3.4	
Ca	315.9	10	0.49	99	3.6	95	1.4	
Cd	226.5	1.6	0.83	107	3.2	99	2.0	
Co	231.2	7.4	0.38	101	4.0	95	0.5	
Cr	205.6	1.3	0.50	98	5.3	106	1.6	
Cu	324.8	2.1	0.72	98	3.6	99	2.2	
Fe	259.9	3.9	0.13	94	6.8	97	1.6	
Li	670.8	2.8	0.48	89	17.1	95	4.3	--
Mg	279.6	24	0.22	105	8.4	106	2.7	
Mn	257.6	0.4	0.74	84	6.2	93	3.5	S5
Mo	281.6	7.0	0.18	94	23.5	88	4.9	S376
Na	589.0	10	0.76	(c)	(c)	101	4.5	--
Ni	231.6	3.4	0.41	105	2.7	97	2.0	
P	214.9	22	0.17	(c)	(c)	91	5.6	
Pb	220.4	17	0.42	105	6.0	95	1.1	
Pt	203.7	15	0.69	106	4.1	91	7.5	
Se	196.0	21	0.28	105	6.8	97	4.9	
Si	288.2	16	0.54	(d)	(d)	(d)	(d)	--
Sn	190.0	64	0.49	74	33	67	16	S183
Te	214.3	29	0.41	102	5.0	94	6.3	
Ti	334.9	1.2	0.55	96	5.1	108	2.9	
Tl	190.9	17	0.22	103	4.3	99	1.7	
V	310.2	3.2	0.88	99	4.3	94	1.4	
W	207.9	13	2.58	35	53	23	60	271
Y	371.0	0.8	2.35	99	1.5	100	1.3	
Zn	213.9	0.6	0.60	101	1.3	94	1.3	
Zr	339.2	1.9	0.88	4.9	75	98	0.8	S185

*2.5 µg/filter corresponds to 5 µg/m³ for a 500-L air sample.
[a]N = 3.
[b]In addition to P&CAM 173.
[c]Blank levels too high to make accurate determinations.
[d]Contamination from glassware precluded accurate determinations.

Table 2

Variable Wavelength Channel

Element (Analyte)	λ (nm)	Slits Ent. (μm)	Slits Exit (μm)	Aperture (mm)	Dynode (gain)	Instrumental Detection Limit (μg/mL)	$\bar{S}_r$* @ 10 μg/mL (%)	Interferences**
Ba	455.4	10	20	6	1.0	~1	1.22	None
Hf	277.3	30	40	8	5.0	13	0.55	Fe, Pt, Zr: Elevated background
Rh	233.5	50	50	10	7.0	50	0.34	Fe, Mg: Elevated background
Sb	206.8	35	40	8	8.7	13	0.73	Co (Sb λ = 231.147)
Ta	226.2	30	40	8	7.0	23	0.44	Fe (Ta λ = 260.349); Ni, Se, W: Elevated background

*Pooled relative standard deviation (3 runs @ 5 burns/run).
**Elements which show a bias when the analyte is aspirated.

FORMALDEHYDE

Methods Research Branch

Analytical Method

Analyte:	3-Benzyloxazolidine	Method No.:	P&CAM 354
Matrix:	Air	Range:	0.55-4.71 mg/m^3 in a 12-L sample
Procedure:	Adsorption on coated Chromosorb 102®, desorption with isooctane, capillary gas chromatography-FID	Precision:	0.082
Date Issued:	8/31/81		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

1.1 Formaldehyde is absorbed by a sorbent tube containing Chromosorb 102® coated with N-benzylethanolamine. Formaldehyde is converted to 3-benzyloxazolidine by reaction with the N-benzylethanolamine.

1.2 The 3-benzyloxazolidine is desorbed from the sorbent with isooctane.

1.3 The resulting solution is analyzed for 3-benzyloxazolidine using capillary-column gas chromatography with flame ionization detection.

1.4 The area or height of the 3-benzyloxazolidine peak is determined and compared with a calibration curve obtained from injection of standard solutions.

2. Working Range, Sensitivity and Detection Limit

2.1 This method has been evaluated for a 12-L sample containing between 6.6 and 56.5 µg of formaldehyde. This corresponds to a concentration of 0.55 to 4.71 mg/m^3 of formaldehyde in air.

2.2 For a 1-μL injection of a 4-ng/μL standard, the peak height was 4 mm tall at an electrometer setting of 10^{-12} amp and an attenuation of 16.

2.3 The detection limit of the analytical system is at most 1.1 ng/μL of 3-benzyloxazolidine using splitless injection.

3. Interferences

3.1 Any compound having the same retention time as 3-benzyloxazolidine will present a positive interference.

3.2 The oxazolidines formed from acetaldehyde, propionaldehyde and n-butyraldehyde do not interfere. These compounds may be interferences if a packed column is used in the analysis.

4. Precision and Accuracy

4.1 The pooled relative standard deviation of the overall method was 8.2% in the range 6.6-56.5 μg formaldehyde per sample.

4.2 The overall recovery for laboratory generated samples was 99%. Samples can be stored for at least fourteen days at room temperature before analysis without loss.

5. Advantages and Disadvantages

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

5.2 Desorption and preparation of samples for analysis involve simple procedures and equipment. However, sample analysis by capillary column gas chromatography is a rather sophisticated technique.

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, causing the sample volume to be imprecise, since the pump is calibrated for one tube only. The use of pumps with distinct critical orfices or self-adjusting rates is recommended.

5.4 The method is specific for formaldehyde.

5.5 The method requires careful preparation of the coated sorbent.

6. Apparatus

6.1 A personal sampling pump calibrated at the recommended flow rate with a representative sampling device in line.

6.2 Sampling tube. The sorbent sampling tube consists of a glass tube, 10 cm x 4 mm i.d., containing a 120-mg front section and a 60-mg back-up section of the N-benzylethanolamine-coated Chromosorb 102®. The two sorbent sections are retained and separated by small plugs of glass wool. These tubes were found to have a pressure drop of 0.8 in. of water at a flow rate of 50 cm^3/min. Tube capacity was found to be 150 µg of formaldehyde at 80% humidity (8.6 mg/m^3 for a 16-L air sample) before significant breakthrough (>5%) occured.

Extract the Chromosorb 102® with a 50/50 mixture of acetone/methylene chloride in a soxhlet apparatus for 4 hours. Vacuum dry (<1 mm Hg) the sorbent overnight. Add 1 g of N-benzylethanolamine in 100 ml of toluene for each 10 g of extracted sorbent . Allow this mixture to stand for 1 hr with occasional swirling. Remove the solvent by rotary evaporation and dry with high vacuum (<1 mm Hg) at ambient temperature overnight. For each batch desorb several 100-mg portions of the coated sorbent with isooctane and analyze to determine the amount of background. If the background levels are found to be greater than 7 µg per 100 mg of coated sorbent, then discard the batch.

6.3 Ultrasonic bath.

6.4 Vials, 4-mL, with plastic screw caps.

6.5 Volumetric pipettes, 1-mL, 5-mL, 10-mL, and volumetric flasks, 10-mL, 1-L.

6.6 Burettes, 50-mL.

6.7 pH meter.

6.8 Gas chromatograph with split and splitless injection capability and equipped with a flame ionization detector and capillary column (Section 8.3.3).

6.9 Disposable pipettes.

7. Reagents

All reagents used should be of ACS Reagent Grade or better.

7.1 Distilled, deionized water.

7.2 Isooctane, distilled in glass grade.

7.3 37% formaldehyde solution.

7.4 0.02 N sulfuric acid solution.

7.5 0.01 N sodium hydroxide solution.

7.6 Sodium sulfite solution (1.13 M). Dissolve 14.3 g of sodium sulfite in enough distilled water to make 100 mL of solution. Reagent is stable for one week if kept refrigerated.

7.7 Toluene.

7.8 N-benzylethanolamine. Vacuum distilled before use (100-103 °C at 1 mm Hg) to remove gross impurities.

7.9 3-benzyloxazolidine. Add a solution of 1.51 g (10 mmole) of N-benzylethanolamine in 10 mL of toluene dropwise to a solution of 1 mL 37% formalin (0.37g formaldehyde, 12.3 mmole) in 25 mL of toluene. A 10% excess of formaldehyde is used to insure complete reaction of the N-benzylethanolamine. Stir the solution for 1 hr and remove the solvent by rotary evaporation. The product is a yellow viscous oil. Vacuum distillation at 58-62 °C at 1 mm Hg yields 3-benzyloxazolidine as a clear, colorless oil. This material is stable at room temperature for several months when stored in a closed vial.

7.10 Formaldehyde stock solution. Dilute 2.7 mL of 37% formaldehyde to 1 L with distilled, deionized water. This solution is stable for at least 3 months. Standardize this solution as described in Section 9.1.

8. Procedure

8.1 Cleaning of Equipment

Glassware should be washed in detergent and rinsed throughly with distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the caps from the sampling tube.

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

8.2.3 Orient the sampling tube in a vertical position during sampling in order to minimize channeling through the sorbent.

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

8.2.5 Measure the sampling time, volume and flow rate. The sample is taken at a flow rate of 50 cm^3/min. The total volume sampled should be no more than 12 L.

8.2.6 Record the temperature, pressure and relative humidity of the atmosphere being sampled.

8.2.7 To obtain a blank sample, handle a sorbent tube in exactly the same manner as a sample except draw no air through it. Submit at least three blank tubes for each batch of 10 samples. This large number of blank tubes is recommended due to the fact that a blank peak is expected, based on the previous analysis of the coated sorbent before packing (Section 6.2).

8.2.8 Cap the sorbent tubes with plastic caps immediately after sampling and ship to the laboratory for analysis.

8.3 Analysis of Samples

8.3.1 Preparation of Samples

Transfer the backup section and the glass wool plug following it to a 4-mL vial. Transfer the front section and the remaining two glass wool plugs to a separate 4-mL vial.

8.3.2 Desorption

Add isooctane (2 mL) to each vial and cap the vial. Place the samples in an ultrasonic bath for 45 min for desorption.

8.3.3 Analysis

Inject the sample into the capillary gas chromatograph via the splitless injection technique. If the amount of 3-benzyloxazolidine found in the sample is greater than 50 ng/μL, reanalyze the sample using the split injection technique. Typical operating conditions are:

Column:	Flexible fused silica Carbowax 20 M, 25 m long
Injector Temperature:	210 °C
Detector Temperature:	220 °C
Injection Volume:	1.0 µL
Column Head Pressure:	1 Kg/cm^2
Makeup Flow:	29 cm^3/min
Carrier gas:	Helium
Splitless Injection:	
Splitter Flow:	30 cm^3/min
Oven Program:	70 °C for 1 min; 10 °C/min for 13 min; hold at 200 °C
Retention Time:	11.5 min
Split Injection:	
Splitter Flow:	10 cm^3/min
Oven Program	150°C for 7 min; 10°C/min for 5 min; hold at 200°C
Retention Time	5.9 min.

8.3.4 Quantitation

Measure peak height or area by electronic integration and obtain the concentration from the standard curve.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of 3-benzyloxazolidine may vary from one laboratory to another and, also, from one batch of coated Chromosorb 102® to another. Thus it is necessary to determine the desorption efficiency for each batch of coated Chromosorb 102® used.

8.4.2 Using a 10-µL syringe and the standardized formaldehyde stock solution (Section 9.1), inject a packed sampling tube (Section 6.2) with a known amount of formaldehyde. Cap the tube and store overnight.

Prepare six tubes at each of three levels covering the range of interest in the above manner and store overnight to assure complete reaction of the formaldehyde with the N-benzylethanolamine. Treat several blank tubes in the same manner except add no formaldehyde to them. Desorb and analyze the sample and blank tubes in the manner described in Section 8.3.

The desorption efficiency (D) equals the average weight of 3-benzyloxazolidine in µg recovered from the tube (Q_r) times the conversion factor from µg 3-benzyloxazolidine to µg formaldehyde (0.184) and divided by the weight of formaldehyde in µg added to the tube (Q_a).

$$D = \frac{0.184 \times Q_r}{Q_a}$$

If D varies significantly with sample weight, plot D vs. Q_r and use the curve to correct for absorption losses in Section 10.3.

9. Calibration and Standards

9.1 Standardization of Formaldehyde Stock Solution

9.1.1 Place 5.0 mL of 1.13 M sodium sulfite solution in a beaker. Stir the solution using a magnetic stirrer. Measure the pH, which should be in the range between 7 and 9. Adjust to this range with base or acid if necessary. Record the pH value.

9.1.2 Pipette 10.0 mL of formaldehyde stock solution (Section 7.10) into the beaker. The pH should now be about 12.

9.1.3 Titrate the solution back to its original pH with 0.02 N H_2SO_4. Approximately 17 mL of acid will be needed.

9.1.4 One mL of 0.02 N H_2SO_4 is equivalent to 0.600 mg of formaldehyde. Thus:

$$C_s = \frac{30.0 \times [(N_a \times V_a) - (N_b \times V_b)]}{V_s}$$

where:
C_s = Concentration of the formaldehyde stock solution in g/L
30.0 = 30.0 g/equivalent of formaldehyde
N_a = Normality of sulfuric acid
V_a = Volume of acid used for titration
N_b = Normality of sodium hydroxide
V_b = Volume of base used for back titration if end pH was overrun
V_s = Volume of formaldehyde solution used in titration (10.0 mL).

9.2 Gas-chromatograph calibration procedure. With each set of samples analyzed, a complete calibration curve should be constructed using newly prepared standards.

9.2.1 Prepare standards covering the range of 1 to 400 µg/mL of 3-benzyloxazolidine in isooctane.

9.2.2 Analyze standards with the samples.

9.2.3 From the peak heights or areas, construct a standard curve plotting peak height or area vs. concentration (µg/mL).

10. Calculations

10.1 From the calibration curve, read the concentration of the front and back sections of each sample in µg/mL. Multiply by the volume in mL of desorbing solution to obtain the total weight in µg of 3-benzyloxazolidine per tube section.

10.2 Add the amounts found in the front and back sections of each tube and subtract out the amount found in the blank tube if any. If more than 25% of the total amount is found on the backup section, then the sample should be considered invalid because significant breakthrough has occured.

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

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

10.4 Convert the volume of air sampled (V) to the volume of air at standard conditions (V_S) of 760 mm of mercury and 25 °C, using the following correction formula:

$$V_S = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where: V_S = volume of air in liters at standard conditions
V = volume of air sampled in liters
P = barometric pressure in millimeters of mercury
T = temperature of sampled air in degrees Centigrade.

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

$$C_m = \frac{0.184 \times W_C}{V_S}$$

where: W_c = corrected weight of 3-benzyloxazolidine in µg in the air sample
V_s = volume of air sampled in liters

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

$$C = \frac{C_m \times 24.45}{30.0}$$

where: C_m = air concentration of formaldehyde (mg/m^3)
24.45 = molar volume of formaldehyde at standard conditions
30.0 = molecular weight of formaldehyde.

11. References

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11.2 Kennedy, E. R. and R. H. Hill, Jr. "Determination of Formaldehyde in Air as an Oxazolidine Derivative by Capillary Gas Chromatography," presented at the 1981 American Chemical Society Annual Meeting, New York, New York, August 1981.

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SCP METHODS

SELENIUM COMPOUNDS (as Se)

Analyte:	Selenium	Method No.:	S190
Matrix:	Air	Range:	0.10-0.50 mg/m^3
OSHA Standard:	0.2 mg/m^3	Precision:	0.090
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	8/29/75
		Revised:	3/25/81

1. Synopsis

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 The sample-containing filters are wet ashed with concentrated nitric acid to destroy the filter matrix followed by dissolution in hydrochloric acid to dissolve the selenium-containing residue. For selenium in steel dust, bulk samples should be tested to verify solubility and final solutions adjusted to contain at least 1% iron.

   1.3 The solutions of samples and standards are aspirated into the flame of an atomic absorption spectrometer (AAS). An electrodeless discharge lamp is used to provide a characteristic selenium line at 196.0 nm. The absorbance is proportional to the selenium concentration.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The working range for standard selenium solution using atomic absorption spectrometry as described (argon/hydrogen flame) is 0.5-40 µg/mL; it is 4-64 µg/mL using the air/acetylene flame. This method was validated with potassium selenite aerosol over the range 0.10-0.50 mg/m^3 at an atmospheric temperature and pressure of 19 °C and 762 mm Hg using a 360-L sample. The method was also tested with selenium metal fume over the range of 0.3-1.2 mg/m^3 using 90-L to 250-L samples. Under the conditions of typical sample size (360 L), the linear working range of the method is estimated to be 0.03-1.4 mg/m^3.

   2.2 The detection limit of this method using the 25 mL final volume is 5.9 µg/sample which corresponds to 0.016 mg/m^3 assuming a 360-L sample. The sensitivity is 0.6 µg/mL for 1% absorption. For selenium in steel dusts, the detection limit is 20 µg/mL, and the sensitivity is 1.2 µg/mL for 1% absorption. 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 times or by scale expansion to increase instrumental response.

3. Interferences

There is no known spectral line interference due to other elements. Selenium assay requires an instrument with a background corrector in order to compensate for potential interferences such as those caused by the presence of salts.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical sampling method in the range of 0.10–0.50 mg/m^3 was 0.090 for potassium selenite, and was 0.093 for 0.16–0.31 mg/m^3 selenium fume. This value corresponds to a 0.018 mg/m^3 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 effectively 100% for both potassium selenite aerosol and selenium fume was determined for the collection medium; thus, no bias was introduced in the sample collection step. Analytical recoveries less than 95% (Section 4.3) are accounted for by using the appropriate recovery factors (Sections 8.4 and 10.4). With these corrections made, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

4.3 Analytical recoveries for several selenium species are as follows: selenium metal, 91.8%; sodium selenate, 97.2%; selenium sulfide, 92.6%; selenium dioxide, 92.0%; potassium selenite, 92.3%; and selenium in steel (NBS SRM #339), 90.6%.

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 an instrumental method.

5.2 Standards must be treated in the same manner as test samples.

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, three-piece cassette filter holder.

6.1.2 Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. 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, 37-mm in diameter having 0.8 μm pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Å/mm in the ultraviolet region. The instrument must have the burner head for an argon-air/hydrogen flame and a background corrector.

6.3.1 Selenium electrodeless discharge lamp.

6.3.2 Oxidant: argon-entrained air.

6.3.3 Fuel: hydrogen.

6.3.4 Pressure regulators: two-stage for each compressed gas cylinder used.

6.4 Glassware, borosilicate.

6.4.1 125-mL Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated: 1-, 5-, 10-mL and other convenient sizes for making standards.

6.4.3 500-, 250-, 100-, 50-, 25-mL volumetric flasks.

6.5 Adjustable, thermostatically-controlled hot plate capable of reaching 140 °C.

7. Reagents

All reagents must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Concentrated hydrochloric acid.

7.4 Aqua regia, 1 volume concentrated nitric acid, 3 volumes concentrated hydrochloric acid.

7.5 Aqueous standard selenium stock solution, 1000 µg/mL, commercially available.

7.6 Selenium working standard solution, 100 µg/mL. Prepare fresh daily by appropriate dilution of the stock standard solution with 0.1 N nitric acid.

7.7 Iron solution, 1%. Dissolve 48.3 g ferric chloride, $FeCl_3 \cdot 6H_2O$ in sufficient distilled or deionized water to make 1 L of solution.

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, the glassware should be thoroughly rinsed with warm tap water, aqua regia, and then rinsed 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, aqua regia and water rinses are adequate.

8.2 Collection and Shipping of Samples

8.2.1 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.

8.2.2 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.

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

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 360-600 L is recommended. Sample at a flow rate of 1.5-2.0 Lpm. The flow rate should be known with an accuracy of ± 5%.

8.2.6 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.

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

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

8.2.9 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.

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

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of tweezers and transfer the filter to a 125-mL Phillips beaker.

8.3.2 Digestion of samples. Treat the filter in the beaker with 1 mL of concentrated nitric acid. Heat at 140 °C until the filter is just dissolved. Add 1 mL of concentrated hydrochloric acid and continue heating for one minute. Allow to cool.

8.3.3 Quantitatively transfer the flask contents into a 25-mL volumetric flask. Rinse the digestion flask at least twice with distilled water and make to volume with distilled water.

NOTE: For steel dust samples, use 1% iron solution instead of distilled water in this step.

8.3.4 Aspirate the solutions into an argon-air/hydrogen flame and record the absorbance at 196.0 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low selenium concentrations are found in the sample, scale expansion can be used to increase instrument response.

NOTE: The sensitivity in the argon-air/hydrogen flame may be suppressed 90% or more by high concentrations of iron. Therefore, in the case of small amounts of selenium in steel dust samples, use a lean air/acetylene flame.

NOTE: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.5 Appropriae 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. Use known amounts of the bulk sample for this determination. A known amount of the analyte, present in the bulk sample, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered and analyzed as described in Section 8.3. Determinations should agree within ± 5%.

For this study, amounts of analytes not exceeding 300 µg were deposited on six filters for each species. A parallel blank filter was also treated in

the same manner except no sample was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value over all species (Section 4.3) was found to be 93%.

$$\text{Recovery} = \frac{\text{Average weight } (\mu g) \text{ recovered}}{\text{Weight } (\mu g) \text{ added}}$$

9. Calibration and Standardization

9.1 From the selenium working standard solution, prepare at least six standards by adding 10-200 µg Se to separate 125-mL Phillips beakers containing blank filters. Digest these standards by the sample procedure used for samples beginning at Section 8.3.2.

9.1.1 Alternatively, a standard addition calibration procedure may be employed.

9.2 Proceed as in Section 8.3.3.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 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/25 mL.

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

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

where: µg sample = µg found in sample filter.
µg blank = µg found in blank filter.

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information such as flow rate in Lpm 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 as follows:

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

where: f = flow rate sampled.
t = sampling time.
P_1 = pressure during calibraton of sampling pump (mm Hg).
P_2 = pressure of air sampled (mm Hg).
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K).

10.5 The concentration of the analyte in the air sampled can be expressed in mg/m^3 ($\mu g/L = mg/m^3$).

$$mg/m^3 = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air volume sampled (L)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.2 Heavy Metal Aerosols: Collection and Dissolution Efficiencies, NIOSH Contract 210-79-0058, W. F. Gutknect, M. D. Ranade, P. M. Grohse, A. Damle, D. O'Neal, Research Triangle Institute, Research Triangle Park, North Carolina 27709, March, 1981.

PLATINUM AND INORGANIC PLATINUM COMPOUNDS

Analyte:	Platinum and inorganic platinum compounds	Method No.:	S191
		Range:	0.00079-0.0031 mg/m^3
Matrix:	Air	Precision:	0.062
OSHA Standard:	0.002 mg/m^3	Validation Date:	8/29/75
Procedure:	Filter collection, acid digestion, AA/high temperature graphite atomization	Revised:	3/25/81

1. Synopsis

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 The sample-containing filters are wet-ashed using nitric acid to dissolve the organic matrix; platinum and its compounds are then solubilized in either nitric-perchloric or nitric-hydrochloric acid solutions; platinum dioxide-containing samples are subjected to pre-ashing at 550 °C.

1.3 The solutions of samples and standards are analyzed by flameless atomic absorption spectroscopy using a heated graphite atomizer. A hollow cathode lamp is used to provide a characteristic platinum line at 265.9 nm.

1.4 The samples must be carefully interspersed with calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Working Range, Sensivity, and Detection Limit

2.1 The working range for standard platinum solution using atomic absorption spectrometry as described (electrothermal atomization) is 0.01-0.20 µg/mL. The method was validated with potassium hexachloroplatinate (K_2PtCl_6) over the range of 0.00079-0.0031 mg/m^3 at an atmospheric temperature and pressure of 24 °C and 767 mm Hg using a 720-L sample. Under the conditions of sample size (720 L), the linear working range of the method is estimated to be 0.0004-0.0060 mg/m^3 when the total sample collected is diluted to 25-mL and a 50-µL aliquot is analyzed.

2.2 The detection limit of the method using a 25-mL final solution volume is 0.10 µg platinum/sample, which corresponds to 0.00014 mg/m^3 assuming a 720-L sample. The sensitivity is 0.003 µg/mL for 1% absorption. 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 times, or by scale expansion to increase instrumental response.

3. Interferences

There are no known interferences to the platinum assay using the high-temperature graphite accessory.

4. Precision and Accuracy

4.1 Using potassium hexachloroplatinate, the coefficient of variation ($\overline{CV}_T$) for this method in the range of 0.00079-0.0031 mg/m^3 was 0.062. This value corresponds to a 0.00012 mg/m^3 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 99.7 ± 0.6% was determined for the collection medium; thus, no bias was introduced in the sample collection step. Analytical recoveries less than 95% (Section 4.3) are to be accounted for by using the appropriate recovery factors (Sections 8.4 and 10.3). With these corrections made, ($\overline{CV}_T$) is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

4.3 Analytical recoveries for the platinum species evaluated are as follows: platinum metal, 94% (8.3.2b); ammonium tetrachloroplatinate, 94% (8.3.2a); platinum dioxide, 98% (8.3.2c); potassium hexachloroplatinate, 97% (8.3.2a).

5. Advantages and Disadvantages

The method is tedious and requires a high degree of technical skill; however, it is the only one sensitive enough to analyze personal air samples.

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, three-piece cassette filter holder.

6.1.2 Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a 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, 37-mm diameter, 0.8 μm pore size.

6.3 Atomic absorption spectrophotometer having a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and deuterium background corrector accessory. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 265.9 nm wavelength.

6.4 The platinum radiation source used is a hollow cathode lamp; the line chosen for analysis is 265.9 nm.

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

6.6 Automatic or manual micropipettor for accurately injecting 50-μL sample aliquots into the graphite furnace tube.

6.7 Glassware, borosilicate.

6.7.1 125-mL Phillips beakers with watchglass covers.

6.7.2 Pipets, delivery or graduated: 1-, 5-, 10-mL.

6.7.3 25-mL volumetric flasks.

6.7.4 50-mL quartz crucibles with covers.

6.8 Adjustable, thermostatically-controlled hot plate capable of reaching 400 °C.

6.9 Oven or muffle furnace capable of reaching 550 °C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Perchloric acid.

7.4 Hydrochloric acid.

7.5 Nitric acid: perchloric acid mixture (2 parts HNO_3 + 1 part $HClO_4$).

7.6 Nitric acid: hydrochloric acid mixture (1 part HNO_3 + 1 part HCl).

7.7 Platinum standards.

7.7.1 Platinum standard stock solution, 1000 µg/mL, commercially available.

7.7.2 Dilute platinum stock solution, 1 µg/mL. Prepare by appropriate (preferably sequential) dilution of above solution. Prepare fresh daily in 0.01 M nitric acid.

7.7.3 Prepare a series of working standards by adding 0.5-3.0 µg of platinum to 25-mL volumetric flasks. Depending on the dissolution procedure used, either add: a) 0.5 mL concentrated nitric-perchloric acid and dilute to volume with distilled water (refer to Section 8.3.2a); or b) 2 mL nitric-hydrochloric acid mixture and dilute to volume with distilled water (refer to Section 8.3.2b). These standards should be prepared fresh daily.

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, the glassware should be thoroughly rinsed with warm tap water, aqua regia, tap water, and distilled water, in that order, and then dried.

8.1.3 For glassware which has been subjected to the entire cleaning procedure, aqua regia and water rinses will be adequate.

8.2 Collection and Shipping of Samples

8.2.1 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.

8.2.2 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.

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

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 720 L is recommended. Sample at a flow rate of 1.5-2.0 Lpm. The flow rate should be known with an accuracy of ± 5%.

8.2.6 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.

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

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

8.2.9 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.

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

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of tweezers and transfer the filter to a 125-mL Phillips beaker.

8.3.2 Wet ashing and digestion. If the sample is expected to contain platinum dioxide, proceed to (c) below; otherwise, destroy the organic filter matrix by treating the sample in each beaker with 2 mL of concentrated HNO_3. Cover each beaker with a watchglass and heat on a hot plate (140 °C) in a fume hood until all the filter is dissolved and the volume is reduced to about 0.5 mL. Repeat this process once more using 2 mL of HNO_3. Cool the beaker and contents.

a. If the platinum salts expected to be present are known to be readily soluble, for example, platinates, add 3 mL of HNO_3-$HClO_4$ mixture and continue evaporating to fumes to effectively complete digestion of the filter. Do not allow the solution to evaporate to dryness at any point. Platinum metal will not, however, be recovered (recovery < 5%) by this step.

b. For platinum metal or those platinum salts that are not solubilized employing the nitric acid-perchloric acid procedure, the following procedure should be employed. That is, after destruction of the organic filter matrix, add 2 mL of an equal volume mixture of concentrated nitric and hydrochloric acids and warm slightly for one minute. Then proceed to 8.3.3.

c. Place the filter in a 20-mL quartz crucible. Destroy the filter matrix with nitric acid as described above. Place a cover on each crucible and transfer the crucibles to a muffle furnace or oven capable of attaining 550 °C. Raise the temperature to 550 °C and maintain for eight hours or overnight. Allow each crucible to cool to room temperature. Dissolve the residue as described in (b) above.

8.3.3 Cool solutions and add 10 mL of distilled or deionized water to each one.

8.3.4 Quantitatively transfer the clear solutions into 25-mL volumetric flasks.

8.3.5 Rinse each beaker or crucible at least twice with 5-mL portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask and dilute to 25 mL.

8.3.6 Spectrophotometric measurements.

a. The instrumental parameters for source power, background corrector, and furnace alignment, as well as furnace parameters such as inert gas flow and time/temperature conditions for drying and atomization, should be established in accordance with the manufacturer's recommendations. Note, however, that in order to avoid premature loss of platinum the following drying and charring conditions should be observed:

Sample Cycle	Time in Seconds	Temperature (°C)
Sample drying	40	150
Sample charring	20	500
Sample atomization	10	2700

b. Inject a 50-µL aliquot of the sample solution into the graphite tube using a micropipet.

c. A minimum of two injections/sample should be done.

d. 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, reinject standard in duplicate, etc.

NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard (i.e., if the graphite tube gives erratic results and non-reproducible peak areas, it must be rejected and replaced because results so obtained are not reliable).

8.3.7 Measurement of area. The area of the absorption peak is measured by some suitable form of area measurement, such as a planimeter or an electronic integrator. Note that the peak height measurements will give somewhat poorer precision as peak shapes change with the aging of the graphite tube.

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 analyte. The analyte recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery of the analyte is less than 95%, the appropriate correction factor should be used to calculate the true value.

8.4.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the concentration expected in the sample, 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 ± 5%.

In the original validation study, an amount of K_2PtCl_6 equivalent to that present in a 720-L sample at the selected level was used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly. All filters were then digested and analyzed as described in Section 8.3.2a with a mean recovery of 97.2%.

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

$$\text{Recovery} = \frac{\text{Average weight (µg) recovered}}{\text{Weight (µg) added}}$$

9. Calibration and Standardization

9.1 Prepare a series of working standards containing 0.5-3.0 µg of platinum in 25 mL of dilute acid mixture. Refer to Section 7.7.3.

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 absorbance and peak width readings during any given day.

10. Calculations

10.1 Determine the weight in µg corresponding the absorbance area of the sample by using the appropriate response factor for the sample.

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

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

where: µg sample = µg found in sample filter.
µg blank = µg found in blank filter.

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information such as flow rate in Lpm multipled 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:

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

where: f = flow rate sampled.
t = sampling time.
P_1 = pressure during calibration of sampling pump (mm Hg).
P_2 = pressure of air sampled (mm Hg).
T_1 = temperature during calibration of sampling pump (°K).
T_2 = temperature of air sampled (°K).

10.5 The concentration of the analyte in the air sampled can be expressed in mg/m^3 ($\mu g/L = mg/m^3$).

$$mg/m^3 = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air volume sampled (L)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Heavy Metal Aerosols: Collection and Dissolution Efficiencies, NIOSH Contract 210-79-0058, W. F. Gutknect, M. H. Ranade, P. M. Grohse, A. Damle, D. O'Neal, Research Triangle Institute, Research Triangle Park, North Carolina 27709, March, 1981.

TELLURIUM

Analyte:	Tellurium	Method No.:	S204
Matrix:	Air	Range:	0.0495–0.24 mg/m^3
OSHA Standard:	0.1 mg/m^3	Precision:	0.055
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75
		Revised:	3/25/81

1. Synopsis

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 The sample-containing filters are wet-ashed using nitric acid to destroy the filter and other organic materials in the sample. The residue is then dissolved in dilute nitric acid solution.

1.3 The solutions of samples and standards are aspirated into the oxidizing air–acetylene flame of an atomic absorption spectrophotometer (AAS). An electrodeless discharge lamp is used to provide characteristic tellurium line at 214.3 nm.

2. Working Range, Sensitivity, and Detection Limit

2.1 The working range for standard tellurium solution using atomic absorption spectrometry, as described, is 1.0–40 µg/mL. This method was validated with tellurium hydroxide aerosol over the range of 0.0495–0.240 mg/m^3 using a 670-L sample at an atmospheric temperature and pressure of 22.5 °C and 746 mm Hg, respectively. The method was also tested with tellurium metal fume over the range of 0.2–1.6 mg/m^3 using 150-L to 200-L samples at an atmospheric temperature and pressure of 24 °C and 758 mm Hg, respectively. Under the conditions of typical sample size (600 L), the working range of the method is estimated to be 0.01–0.45 mg/m^3.

2.2 The detection limit of this method using the 5-mL final solution volume is 1.7 µg tellurium per sample, which corresponds to 0.003 mg/m^3 assuming a 600-L sample. The sensitivity is 0.5 µg/mL for 1% absorption. The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using smaller final solution volumes or by longer sampling times.

3. Interferences

There are no known interferences for the tellurium AAS assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling analytical method in the range of 0.0495-0.240 mg/m^3 is 0.055 for tellurium hydroxide aerosol. This value corresponds to a 0.006 mg/m^3 standard deviation at the OSHA standard level. $\overline{CV}_T$ for tellurium metal fume is 0.10 at about 0.2 mg/m^3 and 0.040 in the range of 1.1 to 2.5 mg/m^3. 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 effectively 100% was determined for the collection medium for both tellurium hydroxide aerosol and tellurium fume; thus, no bias was introduced in the sample collection step. There was also no apparent bias in the 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

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 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of tellurium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm, three-piece cassette filter holder.

6.1.2 Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Stopwatch.

6.2 Mixed cellulose ester membrane filter, 37 mm in diameter having 0.8 µm pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tellurium electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure regulators: Two-stage for each compressed gas cylinder used.

6.4 Glassware, borosilicate.

6.4.1 125-mL Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated: 1-, 3-, 5-, 10-mL.

6.4.3 100-mL volumetric flasks.

6.5 Adjustable, thermostatically-controlled hot plate capable of reaching 140 °C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute nitric acid (10 mL concentrated nitric acid diluted to 100 mL with distilled or deionized water).

7.4 Commercially prepared aqueous standard stock solutions; 1000 µg Te/mL.

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 followed by distilled water, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Collection and Shipping of Samples

8.2.1 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.

8.2.2 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.

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

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 600 L is recommended. Sample at a flow rate of 1.5 Lpm. The flow rate should be known with an accuracy of ± 5%.

8.2.6 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.

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

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

8.2.9 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.

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

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and backup pad with tweezers and transfer the filter to a clean 125-mL Phillips beaker.

8.3.2 Wet ashing. Treat the sample in each beaker with 5 mL of concentrated nitric acid to destroy the filter. 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. Add 2 mL concentrated nitric acid and heat to near-dryness at 140 °C. Using distilled water, rinse the material on the bottom of the watchglass into the beaker, rinse the sides of the beaker and allow the solution to evaporate to dryness.

8.3.3 At this point the tellurium residue is soluble in nitric acid and no special precaution is needed to solubilize this material. Cool each beaker and quantitatively add 5 mL of dilute nitric acid.

8.3.4 After the samples are dissolved, aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 214.3 nm. The absorbance is proportional to the tellurium concentration which 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.

8.3.5 Appropriate filter blanks must be analyzed in accordance with the total procedure.

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. Use known amounts of the bulk sample for this determination. A known amount of the analyte present in the bulk sample, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered and analyzed as described in Section 8.3. Determinations should agree within ± 5%.

For this validation study, quantities of elemental tellurium not exceeding 300 µg were deposited on six filters. A parallel blank filter was also treated in the same manner except no sample was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value was found to be 99%.

$$\text{Recovery} = \frac{\text{Average weight (µg) recovered}}{\text{Weight (µg) added}}$$

9. Calibration and Standardization

9.1 Prepare at least four working standards to cover the range from 20-400 µg/5 mL from the 1000 µg/mL stock tellurium standard solution. All standard solutions are made in dilute nitric acid and are prepared fresh daily.

9.2 Aspirate each of the standard solutions and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/5 mL. It is advisable to run standards 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 µg corresponding to the total absorbance from the standard curve. No volume corrections are needed because the standard curve is based on µg/5 mL.

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

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

where: μg sample = μg found in sample filter.
μg blank = μg found in blank filter.

10.3 Divide the total weight by the recovery to obtain the corrected μg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in Lpm 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:

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

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 ($^\circ$K).
T_2 = temperature of air sampled ($^\circ$K).

10.5 The concentration of the analyte in the air sampled can be expressed in mg/m^3 ($\mu g/L$ = mg/m^3).

$$\text{mg/m}^3 = \frac{\mu g \text{ (Section 10.3)}}{\text{Air volume sampled (L)}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Heavy Metal Aerosols: Collection and Dissolution Efficiencies, NIOSH Contract 210-79-0058, W. F. Gutknecht, M. B. Ranade, P. M. Grohse, A. Damle, D. O'Neal, Research Triangle Institute, Research Triangle Park, North Carolina, 27709, March, 1981.

LEAD AND INORGANIC LEAD COMPOUNDS

Analyte:	Lead and inorganic lead compounds	Method No.:	S341
		Range:	0.128–0.399 mg/m^3
Matrix:	Air	Precision:	0.072
Procedure:	Filter collection, nitric acid and hydrogen peroxide digestion, atomic absorption measurement	Validation Date:	10/24/75
		Revised:	3/25/81

1. Synopsis

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 The sample-containing filters are wet-ashed using nitric acid and hydrogen peroxide to destroy the organic matrix. The lead is then solubilized in nitric acid.

1.3 The solutions of samples and standards are analyzed by aspiration into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). An electrodeless discharge lamp is used to provide a characteristic lead line at 283.3 nm.

2. Working Range, Sensitivity and Detection Limit

2.1 The working range for standard lead solution using atomic absorption spectrometry as described is 0.6–40 µg/mL. This method was validated with lead nitrate aerosol over the range of 0.128–0.399 mg/m^3 using a 180-L sample at an atmospheric temperature and pressure of 22 °C and 761 mm Hg respectively. The method was also tested with lead fume over the range 0.15–1.67 mg/m^3 using 30-L to 180-L samples at an atmospheric temperature and pressure of 24 °C and 758 mm Hg, respectively. Under the conditions of a 600-L sample size, the working range of the method is estimated to be 0.01–0.66 mg/m^3.

2.2 The detection limit of the method using a 10-mL final solution volume is 2.6 µg lead per sample, which corresponds to 0.004 mg/m^3 assuming a 600-L sample. The sensitivity is 0.3 µg/mL for 1% absorption. 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 times, or by scale expansion to increase instrumental response.

3. Interferences

3.1 No cationic interferences have been observed; however, phosphate, carbonate, iodide, fluoride, and acetate suppress absorbance significantly at concentrations ten times greater than lead. Addition of EDTA to the solution so that the sample solutions are 0.1 M with respect to EDTA will overcome this interference.

3.2 At 217 nm, non-atomic species in the flame absorb strongly. When the sample has a high concentration of dissolved solids, it is necessary to correct for non-atomic absorption by using a hydrogen continuum lamp.

3.3 At 283.3 nm, non-atomic absorption is substantially weaker. In general, background correction is not necessary at this Pb line. In addition, although sensitivity at 283.3 nm is slightly poorer than that at 217 nm, the signal-to-noise ratio is significantly greater, allowing improved detection limits.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total sampling andanalytical method is 0.072 for lead nitrate aerosol in the range of 0.128-0.399 mg/m^3 and 0.068 for lead fume in the range 0.15-1.67 mg/m^3. These values correspond to 0.004 mg/m^3 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 effectively 100% for both lead nitrate aerosol and lead fume was determined for the collection medium; thus, no bias was introduced in the sample collection step. Analytical recoveries less than 95% (Section 4.3) are to be accounted for by using the appropriate recovery factors (Sections 8.4 and 10.3). With these corrections made, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

4.3 Analytical recoveries for several lead compounds are as follows (approximately 200 µg Pb taken):

Species	Digestion Method	Analytical Recoveries (%)
Lead metal	HNO_3 only	92 ± 4
Lead metal	With H_2O_2 addition	103 ± 3
Lead oxide (PbO)	HNO_3 only	93 ± 4
Lead sulfide (PbS)	HNO_3 only	93 ± 5
Lead dioxide (PbO_2)	With H_2O_2 addition	100 ± 1
Pb in paint (SRM #1579)	HNO_3 only	95 ± 6
Pb in paint (SRM #1579)	With H_2O_2 addition	95 ± 6

NOTE: For those analytical recoveries determined to be less than 95%, a correction factor is to be applied.

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 an instrumental method.

5.2 The method has been tested on a number of different lead compounds and found applicable to these.

6. Apparatus

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

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37 mm, three-piece cassette filter holder.

6.1.2 Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Thermometer.

6.1.4 Stopwatch.

6.2 Mixed cellulose ester membrane filter, 37 mm in diameter having 0.8 μm pore size.

6.3 Atomic absorption spectrophotometer. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Lead electrodeless discharge lamp or hollow cathode lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure regulators: Two-stage for each compressed gas cylinder used.

6.4 Glassware, borosilicate.

6.4.1 125-mL Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated: 1-, 3-, 5-, 7-, 10-mL.

6.4.3 1000-, 100-, and 10-mL volumetric flasks.

6.5 Nalgene bottles.

6.5.1 Five 100-mL capacity Nalgene bottles for storing dilute lead standards.

6.5.2 One 1000-mL capacity Nalgene bottle for storing 100 ppm lead stock solution.

6.6 Adjustable, thermostatically-controlled hot plate capable of reaching 400 °C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Hydrogen peroxide, 30%.

7.4 Dilute nitric acid (10 mL concentrated nitric acid diluted to 100 mL with distilled or deionized water used for dilute lead standards).

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 rinsed thoroughly with tap water followed by distilled water, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses will be adequate.

8.2 Collection and Shipping of Samples

8.2.1 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.

8.2.2 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.

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

8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.2.5 A sample size of 600 L is recommended. Sample at a flow rate of 1.5-2.0 Lpm. The flow rate should be known with an accuracy of ± 5%.

8.2.6 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.

8.2.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient

temperature and pressure. If pressure reading is not available, record the elevation.

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

8.2.9 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.

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

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and backup pad with tweezers and transfer the filter to a clean 125-mL Phillips beaker.

8.3.2 Wet ashing. Treat the sample in each beaker with 2-3 mL of concentrated nitric acid and 1 mL 30% hydrogen peroxide to destroy the organic filter matrix. Cover each beaker with a watchglass and heat on a hot plate (140 °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 sides of the beaker, and allow the solution to evaporate to dryness.

NOTE: If it can be safely assumed that there is no PbO_2 in the sample, then hydrogen peroxide can be omitted from the above procedure.

8.3.3 At this point, the lead residue is soluble in nitric acid; no special precaution is needed to solubilize this material. Cool each beaker and dissolve residues in 1 mL concentrated nitric acid.

8.3.4 Quantitatively transfer the clear solutions to 10-mL volumetric flasks.

8.3.5 Rinse each beaker at least three times with 2-3 mL portions of distilled or deionized water and quantitatively transfer each rinse to the solution in the volumetric flask. Dilute all samples to 10 mL with distilled or deionized water.

8.3.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 283 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 redissolved to some smaller volume such as 5 mL before aspiration. In such a case, use no more acid solution in Section 8.3.4 than is necessary to effect a quantitative transfer.

NOTE: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.3.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

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. Use known amounts of the bulk sample for this determination. A known amount of the analyte present in the bulk sample, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered and analyzed as described in Section 8.3. Determinations should agree within ± 5%.

For this study, amounts of analytes not exceeding 300 µg were deposited on six filters for each species. A parallel blank filter was also treated in the same manner except no sample was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value over all species was found to be 95% (Section 4.3).

$$\text{Recovery} = \frac{\text{Average weight (µg) recovered}}{\text{Weight (µg) added}}$$

9. Calibration and Standardization

9.1 Prepare a 100 ppm lead stock solution by dissolving 0.1 g lead metal in 100 mL concentrated nitric acid and dilute to 1 L with deionized or distilled water.

9.2 From the 100 µg/mL stock lead standard solution, prepare at least five working standards to cover the range from 5-20 µg/10 mL. Make all standard solutions in dilute nitric acid and store in 100-mL Nalgene bottle.

9.3 Aspirate each of the standard samples and record absorption.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/10 mL. It is advisable to run standards 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 µg corresponding to the total absorbance from the standard curve. No volume corrections are needed because the standard curve is based on µg/10 mL.

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

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

where: µg sample = µg found in sample filter.
µg blank = µg found in blank filter.

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 Determine the volume of air sampled at ambient conditions in liters based on appropriate information such as flow rate in Lpm 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 indicated flow rate. The expression for this correction is:

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

where: f = flow rate sampled.
t = sampling time.
P_1 = pressure during calibration of sampling pump (mm Hg).
P_2 = pressure of air sampled (mm Hg).
T_1 = temperature during calibration of sampling pump (°K).
T_2 = temperature of air sampled (°K).

10.5 The concentration of the analyte in the air sample can be expressed in mg/m^3 ($\mu g/L = mg/m^3$).

$$mg/m^3 = \frac{\text{Corrected } \mu g \text{ (Section 10.2)}}{\text{Air volume sampled}}$$

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Heavy Metal Aerosols: Collection and Dissolution Efficiencies, NIOSH Contract 210-79-0058, W. F. Gutknecht, M H. Ranade, P. M. Grohse, A. Damle, and D. O'Neal, Research Triangle Institute, Research Triangle Park, North Carolina 27709; March, 1981.

CUMULATIVE INDEX

Volume 1: Methods 102-262
Volume 2: Methods S1-S134
Volume 3: Methods S135-S391
Volumes 4-7: The volume is indicated in parentheses after the method number

Acetaldehyde ..... S345(5)
Acetic acid ..... S169(4)
Acetic anhydride S170
Acetone 127, S1
Acetone cyanohydrin ..... 340(7)
Acetonitrile (Methyl cyanide) S165
Acetylene dichloride (see 1,2-Dichloroethylene)
Acetylene tetrabromide (Tetrabromoethane) S117
Acid mists ..... 339(7)
Acrolein 118, 211
Acrylonitrile 202, S156
ALAD (δ-Aminolevulinic acid dehydratase) ..... 328(6)
Aldrin S275
Allyl alcohol S52
Allyl chloride S116
Allyl glycidyl ether ..... S346(4)
Aluminum ..... 173(5), 351(7)
Amines, aliphatic 211
Amines, aromatic 168
4-Aminobiphenyl ..... 269(4)
Aminoethanol compounds ..... 270(4)
bis(2-Aminoethyl)amine (see Diethylenetriamine)
δ-Aminolevulinic acid dehydratase ..... 328(6)
p-Aminophenylarsonic acid ..... 320(6)
2-Aminopyridine ..... S158(4)
Ammonia ..... 205, S347(5)
Ammonium sulfamate ..... S348(5)
Amorphous silica ..... 316(6)
n-Amyl acetate S51
sec-Amyl acetate (alpha-Methyl butyl acetate) S31
Aniline 168, S310
Anisidine ..... 168, S163(5)
Anthanthrene 183, 184, 206
Anthracene 206
Antimony ..... 107, 173, 189, 193, 197, 261(4), 351(7) S2
ANTU (δ-Naphthyl Thiourea) ..... S276(5)
Arsenic ..... 139, 140, 173(5), 180, 188, 192, 196, 286(5), 320(6), 346(7), 351(7), S309
Arsine ..... 265(4), S229
Asbestos ..... 239, 245, 309(5)

Azelaic acid 256
Aziridine ..... 300(5)
Azo dyes 234
Barium ..... 173(5), 351(7), S198
Benz(c)acridine 183
Benz(a)anthracene 183
Benz(a,h)anthracene 183, 184
Benz(a)anthrone 183
Benzene 127, S311
Benzenes, chlorinated ..... 343(7)
Benzene-solubles 217
Benzidine ..... 243, 315(5)
Benzidine-based dyes ..... 325(6)
Benzo Azurine G ..... 325(6)
Benzo(b)fluoranthene 183
Benzo(j)fluoranthene 183
Benzo(k)fluoranthene 183, 184
Benzo(g,h,i)perylene 183
Benzopurpurine 4B ..... 325(6)
Benzo(a)pyrene 183, 184, 186, 206, 251
Benzo(c)pyrene 183, 184
Benzoyl peroxide ..... S253(4)
Benzyl chloride S115
Beryllium ..... 121, 173(5), 279(4), 288(5), S351(7), S339
Bibenzyl 183
Biphenyl (see Diphenyl)
Biphenyl-phenyl ether mixture (see Phenyl ether-biphenyl vapor mixture)
Bis(chloromethyl)ether 213, 220
2,2-Bis[4-(2,3-epoxypropoxy)phenyl]propane ..... 333(6)
Bismuth ..... 173(5)
Bisphenol A ..... 333(6)
2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane (see DDT)
Boron carbide ..... 324(6)
Boron oxide .....351(7), S349
Bromoform S114
Butadiene (1,3-Butadiene) S91
1-Butanethiol (see n-Butyl mercaptan)
2-Butanone (Methyl ethyl ketone or MEK) 127, S3
2-Butoxy ethanol (Butyl cellosolve) S76
sec-Butyl acetate S46
tert-Butyl acetate S32
Butyl acetate (n-Butyl acetate) S47
sec-Butyl alcohol S53

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

tert-Butyl alcohol S63
Butyl alcohol (n-Butyl alcohol) S66
Butyl cellosolve (see 2-Butoxy ethanol)
n-Butyl glycidyl ether S81
n-Butyl mercaptan ..... S350(4)
n-Butylamine ..... 221, S138(4)
p-tert-Butyltoluene S22
Cadmium ..... 173(5), 191, 223, 224, 345(7), 351(7), S312, S313
Calcium ..... 173(5)
Calcium arsenate ..... 173(5)
Calcium oxide ..... 173(5), S205
Camphor S10
Carbaryl® (Sevin) S273
Carbon black S262
Carbon dioxide S249
Carbon disulfide 179, S248
Carbon monoxide ..... 112, 113, S340(4)
Carbon tetrachloride 127, S314
Carbonyl chloride (see Phosgene)
Chlordane ..... S278(6)
Chloride 115
Chlorinated camphene (Toxaphene) S67
Chlorinated diphenyl oxide S119
Chlorine 209
2-Chloro-1,3-butadiene (see Chloroprene)
1-Chloro-2,3-epoxypropane (see Epichlorohydrin)
1-Chloro-1-nitropropane ..... S211(5)
Chloroacetaldehyde ..... S11(5)
∝-Chloroacetophenone ..... 291(5)
Chlorobenzene (Monochlorobenzene) S133
o-Chlorobenzylidene malononitrile ..... 304(5)
Chlorobromomethane S113
Chlorodiphenyl (42% chlorine) ..... S120(4)
Chlorodiphenyl (54% chlorine) S121
2-Chloroethanol (see Ethylene chlorohydrin)
Chloroform 127, S351
Chloromethyl methyl ether 220
p-Chlorophenol ..... 337(7)
Chloroprene (2-Chloro-1,3-butadiene) S112
Chromic acid 152, 169, S317
Chromium ..... 152, 173(5), 182, 319(6), 351(7), S323, S352
Chromium fume ..... 345(7)
Chrysene 183, 184, 206

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Chrysotile ..... 245, 309(5)
Coal tar naphtha (see Naphtha, coal tar)
Coal tar pitch volatiles 183, 184, 217
Cobalt ..... 173(5), 351(7)
Cobalt, metal, dust, and fume ..... S203(4)
Congo Red ..... 325(6)
Copper ..... 173(5), 351(7)
Copper dust and mists ..... 173(5), S186
Copper fume ..... S354(4)
Crag herbicide I ..... S356(5)
Cresol, all isomers S167
Cristobalite ..... 109, 259(5), S315
Crotonaldehyde ..... 285(5)
Cumene S23
Cyanide 116, S250
Cyclohexane S28
Cyclohexanol S54
Cyclohexanone S19
Cyclohexene S82
Cyclohexylamine 221
Cyclopentadiene ..... 294(5)
DBPC 226
2,4 D ..... S279(5)
DDT (2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane) S274
DDVP 295
Demeton ..... S280(6)
Diacetone alcohol (4-Hydroxy-4-methyl-2-pentanone) S55
1,2-Diaminoethane (see Ethylenediamine)
o-Dianisidine-based dyes ..... 325(6)
Diazomethane S137
Diazonium salts 234
Diborane ..... 341(7)
1,2-Dibromoethane (see Ethylene dibromide)
2-Dibutylaminoethanol (see Aminoethanol compounds)
Dibutyl phosphate ..... 297(5)
Dibutylphthalate S33
1,1-Dichloro-1-nitroethane S213
o-Dichlorobenzene S135
p-Dichlorobenzene S281
3,3'-Dichlorobenzidine 246
Dichlorodifluoromethane (Refrigerant 12) S111
1,1-Dichloroethane (Ethylidene chloride) S123
1,2-Dichloroethane (see Ethylene dichloride)

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Dichloroethyl ether S357
1,2-Dichloroethylene (Acetylene dichloride) S110
Dichloromethane (see Methylene chloride)
Dichloromonofluoromethane (Refrigerant 21) S109
2,4-Dichlorophenoxyacetic acid and salts ..... S279(5)
1,2-Dichloropropane ..... 321(6)
Dichlorotetrafluoroethane (Refrigerant 114) S108
Dichloro-5-triazine-2,4,6-trione, sodium salt ..... 314(5)
Dichlorovos ..... 295(5)
Dieldrin S283
2-Diethylaminoethanol ..... 270(4), S140(5)
Diethylamine 221, S139
Diethylcarbamoyl chloride ..... 317(6)
Diethylene dioxide (see Dioxane)
Diethylenetriamine ..... 276(4)
Difluorodibromomethane S107
Difluorodichloromethane S111
Diglycidyl ether of Bisphenol A ..... 333(6)
Diisobutyl ketone (2,6-Dimethyl-4-heptanone) S358
Diisopropylamine ..... 221, S141(4)
Dimethoxymethane (see Methylal)
Dimethyl acetamide S254
Dimethyl benzene (see Xylene)
1,3-Dimethyl butyl acetate (see sec-Hexyl acetate)
Dimethyl formamide S255
2,6-Dimethyl-4-heptanone (see Diisobutyl ketone)
Dimethyl sulfate ..... 301(5)
N,N-Dimethyl-p-toluidine ..... 280(4)
Dimethylamine 221, S142
4-Dimethylaminoazobenzene..... 284(4)
2,4-Dimethylaminobenzene (see Xylidine)
N,N-Dimethylaniline 168, S164
Dimethylarsenic acid ..... 320(6)
1,1-Dimethylhydrazine 248, S143
Dimethylnitrosamine ..... 252, 299(5)
bis-(Dimethylthiocarbamoyl)disulfide ..... 228, S256(5)
Dinitrobenzene (all isomers) ..... S214(4)
Dinitro-o-cresol ..... S166(5)
Dinitrotoluene ..... S215(4)
Dioxane 127, S360
Diphenyl ..... S24(4)
4,4'-Methylenebis(phenyl isocyanate) (MDI) ..... 142, 347(7)
Dipropylene glycol methyl ether S69

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Direct Black 38 ..... 325(6)
Direct Blue 6 ..... 325(6)
Direct Blue 8 ..... 325(6)
Direct Brown 95 ..... 325(6)
Direct Red 2 ..... 325(6)
Direct Red 28 ..... 325(6)
2,6-Di-tert-butyl-p-cresol 226
Dowtherm A (see Phenyl ether-biphenyl vapor mixture)
Endrin ..... S284(6)
Epichlorohydrin (1-Chloro-2,3-epoxypropane) S118
EPN (O-Ethyl-O-p-nitrophenyl phenylphosphonothiolate) S285
2,3-Epoxy-1-propanol (see Glycidol)
1,2-Epoxypropane (see Propylene oxide)
2,2-bis[4-(2,3-Epoxypropoxy)-phenyl]propane ..... 333(6)
Ethanol (see Ethyl alcohol)
Ethanolamine (see Aminoethanol compounds)
Ether S80
2-Ethoxyethanol ..... S361(5)
2-Ethoxyethylacetate S41
Ethyl acetate S49
Ethyl acrylate S35
Ethyl alcohol (Ethanol) S56
Ethyl benzene S29
Ethyl bromide S106
Ethyl butyl ketone (3-Heptanone) S16
Ethyl chloride ..... S105(4)
Ethyl ether S80
Ethyl formate S36
Ethyl sec-amyl ketone (see 5-Methyl-3-heptanone)
Ethyl silicate S264
O-Ethyl-O-p-nitrophenyl phenylphosphonothiolate phosphonate (see EPN)
Ethylamine 221, S144
Ethylene chloride (see Ethylene dichloride)
Ethylene chlorohydrin (2-Chloroethanol) S103
Ethylenediamine ..... 276(4)
Ethylene dibromide (1,2-Dibromoethane) ..... 260(4), S104
Ethylene dichloride (1,2-Dichloroethane) 127, S122
Ethylene glycol ..... 338(7)
Ethylene glycol dinitrate 203, S216
Ethylene oxide S286
Ethylene thiourea ..... 281(4)
Ethylenimine ..... 300(5)
di-2-Ethylhexylphthalate (see di-sec-Octyl phthalate)
Ethylidene chloride (see 1,1-Dichloroethane)

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

N-Ethylmorpholine S146
Fluoranthene 183, 184
Fluoride 114, 117, 212
Fluoroacetate, sodium ..... S301(5)
Fluorotrichloromethane (Refrigerant 11) S102
Formaldehyde ..... 125, 235, 318(6), S327(4), 354(7)
Formic acid ..... 232, S173(5)
Furfural ..... S17(5)
Furfuryl alcohol ..... S365(4)
Galena ..... 350(7)
Gallium 177, 198
Glycidol (2,3-Epoxy-1-propanol) S70
Hafnium ..... 351(7), S194(5)
Heptachlor ..... S287(5)
Heptane S89
3-Heptanone (see Ethyl butyl ketone)
2-Heptanone (see Methyl (n-amyl) ketone)
Hexachlorobutadiene ..... 307(5)
Hexachlorocyclopentadiene ..... 308(5)
Hexachloroethane S101
Hexachloronaphthalene S100
Hexamethylenetetramine ..... 263(4)
Hexane S90
Hexavalent chromium ..... 319(6)
2-Hexanone (Methyl butyl ketone or MBK) S178
Hexone (Methyl isobutyl ketone or MIBK) S18
sec-Hexyl acetate (1,3-Dimethyl butyl acetate) S37
Hippuric acid ..... 327(6)
Hydrazine 248, S237
Hydrogen bromide .....339(7), S175
Hydrogen chloride ..... 310(5), 339(7), S246
Hydrogen cyanide ..... 116, S288(4)
Hydrogen fluoride 117, 212, S176
Hydrogen sulfide ..... 126, 296(6), S4
Hydroquinone S57
4-Hydroxy-4-methyl-2-pentanone (see Diacetone alcohol)
2-Imidazolidinethione (see Ethylene thiourea)
Indium ..... 173(5), 190, 194, 199
Iron ..... 173(5), 351(7)
Iron oxide fume .....345(7), S366(4)
Isoamyl acetate S45
Isoamyl alcohol S58
Isobutyl acetate S44
Isobutyl alcohol S64

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Isophorone S367
Isopropanol (see Isopropyl alcohol)
Isopropyl acetate S50
Isopropyl alcohol (Isopropanol) S65
Isopropyl benzene (see Cumeme)
Isopropyl glycidyl ether S77
Isopropylamine 221, S147
Isopropylether S368
4,4'-Isopropylidenediphenol ..... 333(6)
Kepone 225
Ketene S92
Lead ..... 102, 173(5), 191, 195, 200, 208, 214, 262, 351(7), S341
Lead Sulfide ..... 350(7)
Lindane S290
Liquified petroleum gas (see LPG)
Lithium ..... 173(5), 351(7)
LPG (Liquified petroleum gas) S93
MAPP (Methyl acetylene/propadiene) ..... S85(6)
Magnesium ..... 173(5), 351(7)
Magnesium oxide fume S369
Malathion S370
Maleic anhydride ..... 302(5)
Manganese ..... 173(5), 351(7), S5
Manganese fume ..... 345(7)
MBK (see 2-Hexanone)
MDI (see 4,4'-Methylenebis(phenyl isocyanate))
MEK (see 2-Butanone)
Mercury ..... 145, 165, 167, 175(5), S199(4), S342(6)
Mesityl oxide S12
Methanol (see Methyl alcohol)
2-Methoxyethanol (see Methyl cellosolve)
Methoxychlor ..... S371(4)
Methyl(n-amyl)ketone (2-Heptanone) S15
5-Methyl-3-heptanone S13
Methyl acetate S42
Methyl acetylene ..... S84(5)
Methyl acetylene-propadiene mixture ..... S85(6)
Methyl acrylate S38
Methyl alcohol (Methanol) 247, S59
Methyl bromide S372
alpha-Methyl butyl acetate (see sec-Amyl acetate)
Methyl butyl ketone (see 2-Hexanone)
Methyl cellosolve (2-Methoxyethanol) S79

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Methyl cellosolve acetate S39
Methyl chloride ..... 201, S99(4)
Methyl chloroform (1,1,1-Trichloroethane) 127, S328
Methyl cyanide (see Acetonitrile)
Methyl ethyl ketone (see 2-Butanone)
Methyl ethyl ketone peroxide ..... 331(6)
Methyl formate ..... S291(5)
Methyl iodide S98
Methyl isoamyl acetate S37
Methyl isobutyl carbinol S60
Methyl isobutyl ketone (see Hexone)
Methyl methacrylate ..... S43(6)
alpha-Methyl styrene S26
Methylal (Dimethoxymethane) S71
Methylamine ..... 221, 277(4), S148(6)
Methylcyclohexane S94
Methylcyclohexanol ..... S374(4)
Methylcyclohexanone ..... S375(4)
4,4'-Methylenebis(2-chloroaniline) ..... 236, 342(7)
4,4'-Methylenebis(phenyl isocyanate) (MDI) ..... 142, 347(7)
Methylene chloride (Dichloromethane) 127, S329
Methylhydrazine 248, S149
Mevinphos® ..... S296(6)
MIBK (see Hexone)
MOCA ..... 236, 342(7)
Molybdenum ..... 173(5), 351(7)
Molybdenum insoluble compounds S376
Molybdenum soluble compounds S193
Monochloroacetic acid ..... 332(6)
Monochlorobenzene (see Chlorobenzene)
Monomethyl aniline S153
Monomethyl hydrazine 248, S149
Monomethylarsonic acid ..... 320(6)
Morpholine S150
Naphtha, coal tar (Coal tar naphtha) S86
Naphthalene S292
Naphthylamines ..... 264(4)
∝-Naphthyl thiourea ..... S276(5)
Nickel ..... 173(5), 298(7), 351(7), S206
Nickel carbonyl ..... 344(7)
Nickel fume ..... 345(7)
Nicotine S293
Nitric acid .....339(7), S319(4)

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Nitric oxide ..... 231, S321(4)
p-Nitroaniline ..... 168, S7(5)
Nitrobenzene S217
4-Nitrobiphenyl ..... 273(4)
p-Nitrochlorobenzene S218
Nitroethane ..... S219(6)
2-Nitropropane ..... 272(4)
Nitrogen dioxide ..... 108, 231, S320(4)
Nitroglycerin 203, S216
Nitroglycol 203
Nitromethane ..... S220(6)
N-Nitrosodimethylamine ..... 252, 299(5)
Nitrotoluene S223
Octachloronaphthalene S97
Octane S378
di-sec-Octyl phthalate (di-2-Ethylhexylphthalate) S40
Oil mist ..... 159, 283(4), S272
Organic solvents 127
Organo(alkyl)mercury ..... 175, S342(6)
Organoarsenicals ..... 320(6)
Ozone 153, 154, S8
Palladium 173
Paraquat S294
Parathion 158, S295
PCBs ..... 244, 253, 329(6), S120(4), S121
Pentachlorobenzene ..... 343(7)
Pentachloroethane ..... 335(6)
Pentachloronaphthalene S96
Pentachlorophenol ..... 230, S297(4)
Pentane S379
2-Pentanone S20
Perchloroethylene (see Tetrachloroethylene)
Perylene 184, 206
Pétroleum distillates (Petroleum naphtha) S380
Petroleum naphtha (see Petroleum distillates)
Phenacylchloride ..... 291(5)
Phenanthene 206
Phenol ..... 330(6), S330
Phenyl ether S72
Phenyl ether-biphenyl vapor mixture (Dowtherm A) S73
Phenyl ethylene (see Styrene)
Phenyl glycidyl ether S74
Phenylhydrazine 248, S160

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Phenyloxirane ..... 303(5)
Phosdrin ..... S296(6)
Phosgene (Carbonyl chloride) 219
Phosphate 215
Phosphine S332
Phosphoric acid ..... 216, 339(7), S333
Phosphorus (white, yellow) ..... 242, 257, 351(7), S334(4)
Phosphorus pentachloride ..... S257(5)
Phosphorous trichloride 305
Phthalic anhydride S179
Picric acid ..... S228(4)
Platinum, soluble salts ..... 351(7), S191(7)
PNAs 183, 184, 186, 206
Polychlorinated biphenyls (PCBs) ..... 244, 253, 329(6), S121
Polymethylsiloxane 227
Polynuclear aromatic hydrocarbons (PNAs) 183, 184, 186, 206
Potassium ..... 173(5)
Propane S87
Propanol (see Propyl alcohol)
n-Propyl acetate S48
Propyl alcohol (Propanol) S62
n-Propyl nitrate S227
Propylene dichloride S95
Propylene oxide (1,2-Epoxypropane) S75
Propyne ..... S84(5)
Pyrene 183, 184
Pyrethrum ..... S298(6)
Pyridine S161
Quartz (see Silica, crystalline)
Quinone ..... S181(4)
Refrigerant 11 (see Fluorotrichloromethane)
Refrigerant 113 (see 1,1,2-trichloro-1,2,2-trichloroethane)
Refrigerant 114 (see Dichlorotetrafluoroethane)
Refrigerant 12 (see Dichlorodifluoromethane)
Refrigerant 21 (see Dichloromonofluoromethane)
Rhodium ..... 351(7)
Rhodium, metal fume and dust S188
Rhodium, soluble salts S189
Ronnel ..... S299(6)
Rotenone ..... S300(5)
Rubidium ..... 173(5)
Selenium ..... 124, 181, 351(7), S190(7)
Sevin (see Carbaryl)

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Silica, amorphous ..... 316(6)
Silica, crystalline ..... 106, 109, 110, 259(5), S315
Silicon ..... 173(5), 351(7)
Silver ..... 351(7)
Silver, metal and soluble compounds ..... 173(5), S182(5)
Sodium ..... 173(5), 351(7)
Sodium dichloroisocyanate dihydrate ..... 314(5)
Sodium fluoroacetate S301
Sodium-2,4-dichlorophenoxyethyl sulfate S356
Sodium hydroxide ..... 241, S381(4)
Stibine ..... S243(4)
Stoddard solvent S382
Strontium ..... 173(5)
Strychnine ..... S302(5)
Styrene (Vinyl benzene) 127, S30
Styrene oxide ..... 303(5)
Sulfate ..... 268(5)
Sulfite ..... 268(5)
Sulfur dioxide ..... 146, 160, 163, 204, 268(5), S308(4)
Sulfur hexafluoride ..... S244(5)
Sulfuric acid ..... 187, 267(5), 339(7), S174
Sulfuryl fluoride ..... S245(6)
Systox ..... S280(6)
2,4,5-T ..... S303(5)
TDI (see Toluene-2,4-diisocyanate)
Tantalum ..... 351(7), S201(5)
Tellurium ..... 173(5), 351(7), S204
Tellurium hexafluoride S187
TEPP ..... 336(6)
Terphenyl 183, S27
Tetrabromoethane (see Acetylene tetrabromide)
1,1,1,2-Tetrachloro-2,2-difluoroethane S131
1,1,2,2-Tetrachloro-1,2-difluoroethane (Refrigerant 112) S132
1,2,4,5-Tetrachlorobenzene ..... 343(7)
1,1,2,2-Tetrachloroethane S124
Tetrachloroethylene (Perchloroethylene) 127, S335
Tetrachloromethane (see Carbon tetrachloride)
Tetrachloronaphthalene S130
Tetraethyl lead ..... S383(4)
Tetraethyl pyrophosphate ..... 336(6)
Tetrahydrofuran S78
Tetramethyl lead (as Pb) ..... S384(4)
Tetramethyl succinonitrile 155

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Tetramethyl thiourea ..... 282(4)
Tetramethyl thiuram disulfide (see Thiram)
Tetranitromethane S224
Tetryl (2,4,6-Trinitrophenylmethylnitramine) S225
Thallium ..... 173(5), 351(7), S306
Thiophene 255
Thiram (Tetramethyl thiuram disulfide) ..... 228, S256(5)
Tin ..... 176, 351(7), S183
Tin, organic compounds 176
Tissue preparation 237
Titanium ..... 351(7)
Titanium diboride ..... 323(6)
Titanium dioxide S385
o-Tolidine-based dyes ..... 325(6)
Toluene 127, S343
Toluene-2,4-diisocyanate (TDI) ..... 141, 326(6)
o-Toluidine 168, S168
Toxaphene (see Chlorinated camphene)
Tributyl phosphate S208
1,1,2-Trichloro-1,2,2-trifluoroethane (Refrigerant 113) S129
1,2,4-Trichlorobenzene ..... 343(7)
1,1,1-Trichloroethane (see Methyl chloroform)
1,1,2-Trichloroethane 127, S134
Trichloroethylene 127, S336
Trichloroisocyanuric acid ..... S314(5)
Trichloromonofluoromethane (see Fluorotrichloromethane)
Trichloronaphthalene S128
2,4,5-Trichlorophenoxyacetic acid and salts ..... S303(5)
1,2,3-Trichloropropane S126
1,3,5-Trichloro-s-triazine-2,4,6-trione ..... S314(5)
Tridymite ..... 109, 259(5), S315
Triethylamine 221, S152
Trifluoromonobromomethane S125
Trimellitic anhydride ..... 322(6)
2,4,7-Trinitro-9-fluorenone ..... 348(7)
2,4,6-Trinitrophenylmethylnitramine (see Tetryl)
Triorthocresyl phosphate S209
Triphenyl phosphate S210
Tungsten ..... 271(4), 351(7)
Turpentine S88
Vanadium ..... 173(5), 290(5), 351(7),S391
Vanadium, V_2O_5 fume ..... S388(4)
Vinyl acetate ..... 278(4)

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

Vinyl benzene (see Styrene)
Vinyl bromide ..... 349(7)
Vinyl chloride 178
Vinyl toluene S25
Vinylidene chloride ..... 266(4)
Warfarin ..... 313(6)
Xylene (Xylol or Dimethyl benzene) 127, S318
Xylidine (2,4-Dimethylaminobenzene) 168, S162
Xylol (see Xylene)
Yttrium .....351(7), S200
Zinc ..... 173(5)
Zinc fume ..... 345(7)
Zinc oxide ..... 222, S316(4)
Zirconium compounds .....351(7), S185
Zirconium oxide ..... 250(4)

Volume 1: Methods 102 - 262
Volume 2: Methods 51 - S134
Volume 3: Methods S135 - S391

Volumes 4-7: The volume is indicated in parentheses after the method number

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